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Understanding the Interface between Polydopamine and Metal, Metal-oxide Nanoparticles toward Photocatalytic Applications

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List of Abbreviations

- A.A Ascorbic Acid
- Abs Absorbance
- Arb units Arbitrary units
- AFM Atomic Force Microscopy
- AO7 Acid Orange 7
- AuNPs Gold Nanoparticles
- AuNRs Gold Nanorods
- **BE** Binding Energy
- BQ p-benzoquinone
- CB Conduction Band
- CTABr Cetyltrimethylammonium Bromide
- DA Dopamine
- DAH Dopamine hydrochloride
- DHI 5,6 Dihydroxy Indole
- DHICA 5.6-dihydroxyindole-2-carboxylic acid
- DMF-Dymethyl formamide
- DOX-Doxorubic in
- DOS Density of States
- DOPA 3.4-dihydroxy-L-phenylalanine

e^{-}/h^{+} - electron-hole

- EDTA Ethylenediaminetetraacetic acid
- EDX Energy Dispersive X-ray Spectroscopy
- EELS Electron Energy Loss Spectroscopy
- ELB Electron-beam Lithography
- EM Electromagnetic Losses
- ER Evaporation Rage
- ESPT Intramolecular Excite-state Proton Transfer
- ETL Electron Transfer Layer
- $FIB-Focused\text{-}ion \;Beam$
- Fs-TAS Femtosecond Transient Absorption
- FTIR Fourier Transformed Infrared
- FTS Flame Transport Synthesis
- HA-Hyaluronic Acid

HPLC-MS – High-performance Liquid Chromatography Coupled with Mass Spectrometry Analysis

- HR-MS High-resolution Mass Spectrometry
- ICP-MS Inductively Coupled Plasma Mass Spectrometry
- IEF -- Internal Electric Field
- IPA Isopropyl Alcohol
- IR-Infrared

KE – Kinetic Energy

- L-H Langmuir-Hinshelwood
- LDAC Leucodopaminechrome
- LSP Localized Surface Plasmon
- LSPR Localized Surface Plasmon Resonance
- MB Methylene Blue
- Mn Average Molecular Weight
- MO Methyl Orange
- NIR Near Infrared
- NP-Nanoparticle
- NR-Nan or od
- PCL Polyca prolactone
- PDA Polydopamine
- PEG Poly(Ethylene Glycol) Methyl Ether Thiol (SH-PEG-CH₃)
- PVDF Poly(vinylidene)fluoride
- PVP Polyvinylpyrrolidone
- R123 Rhodamine 123
- Redox-Reduction-Oxidation
- Rh6G Rhodamine 6G
- RhB Rhodamine B

ROS - Reactive Oxygen Species

- SEM Scanning Electron Microscope
- SMFS AFM-assisted Single Molecule Force Spectroscopy
- SP Surface Plasmons
- SV Singular Value
- TA Transient Absorption
- TEM Transmission Electron Microscope
- TOC Total Organic Carbon
- UV-VIS-Ultraviolet-visible
- $VB-Valence \ Band$
- $XPS-X\text{-}ray\ Photoelectron\ Spectroscopy}$
- ZnOT ZnO tetrapods
- ZnOT/PDA ZnO Tetrapods/polydopamine
- χ_s Electron Affinity
- $\phi_m-\text{Work}$ Function of the Metal

Abstract

Polydopamine is a recently discovered biomimetic polymer with outstanding applications in surface engineering, biomedicine, and environmental remediation. It has been proven to create heterojunctions with several semiconductors, ameliorating their photocatalytic behavior by boosting charge separation and decreasing the recombination rate. Apart from semiconductors, it has also been combined with plasmonic materials to improve their characteristics. However, the mechanism leading to that behavior has not been deeply explored in the literature. Here, a semiconductor and a plasmonic material have been combined with polydopamine (PDA), and the interfaces have been studied for Rhodamine 6G (Rh6G) photodegradation.

In the first situation, several gold nanorods/polydopamine (AuNRs/PDA) nanocomposites with different characteristics were synthesized and the interface plasmonic material/PDA was studied. Initially, seed-mediated growth was carried out to obtain different gold nanorods (AuNRs) samples with varying sizes and localized surface plasmon resonance (LSPR) values. After selecting one of the samples, through self-polymerization of dopamine, a PDA layer surrounding the AuNRs was synthesized. Therefore, another 6 different AuNRs/PDA samples were obtained with AuNRs with the same characteristics but different PDA shell thicknesses going from ≈ 4 nm to ≈ 30 nm. Three of them were selected, and their photocatalytic response toward Rh6G was studied under Ultraviolet-Visible (UV-VIS) irradiation ($[Au] = 7.4 \mu g m L^{-1}$, $[Rh6G] = 2.5 \ \mu g \ mL^{-1}$). After identifying the sample with the better performance (AuNRs/PDA6), its consistency and reproducibility were studied. Hence, two additional cycles after recovering the nanocomposites, a reaction with the same catalyst-to-organic dye ratio, and reactions with the same catalyst concentration but different Rh6G concentrations were carried out. Additionally, the kinetics of the reaction were studied using the Langmuir-Hinshelwood (L-H) method. During the reactions, the temperature was followed up, unveiling a significant increase, so additional photocatalytic experiments with different power densities were performed to relate the degradation to the temperature increment. Besides, in these experiments, the influence of the source of irradiation was also studied by comparing the already-used UV-VIS lamp to a Near-Infrared (NIR) laser. After discarding the hypotheses of a thermal mechanism of photodegradation, the experimental results were compared with theoretical results calculated by using COMSOL Multiphysics, and the behavior of the hot electrons at the interface was studied by Femtosecond Transient Absorption Spectroscopy (fs-TAS). Finally, the Reactive Oxygen Species (ROS) production was measured by scavengers, unveiling their influence on the degradation mechanism. Here, it was demonstrated that the combination of the plasmonic properties of Au with the properties of PDA resulted in a strong photo-thermal effect where the PDA provides slow thermalization, enhancing the charge carrier transfer and reducing the recombination rate.

In the second situation, Zinc Oxide Tetrapods/polydopamine (ZnOT/PDA) composites were synthesized, and the interface semiconductor/PDA was studied. By inducing the selfpolymerization of PDA, two ZnOT/PDA samples were obtained differentiating by smooth and rough PDA layer. The photocatalytic behavior was studied towards Rh6G ($[Zn] = 2.5 \text{ mg mL}^-$ ¹, $[Rh6G] = 5.0 \ \mu g \ mL^{-1}$) under 1 sun irradiation. ZnOT/PDA1 (smooth PDA layer) depleted 97% of the initial concentration of Rh6G within 30 minutes of irradiation. Moreover, this photocatalytic yield was maintained for another 2 consecutive photodegradation cycles after recovering the photocatalysts. Additionally, varying concentrations of organic dye (2.5, 7.0, and 10.0 µg mL⁻¹) were tested to unveil the consistency of the degradation, and the kinetics of the reaction were studied by the L-H method. Finally, photo(sono)catalysis experiments were carried out at different output frequencies (10, 15, and 45 KHz) and output electrical powers (3 W and 30W) unveiling promising results. Bare Zinc Oxide tetrapods (ZnOT) were able to degrade the organic dye much faster than in the photocatalysis, however, that was not the scenario for the ZnOT/PDA1 composites. A complex situation where (at the used sonication power and frequency) the PDA layer blocks the effect of the sonication waves in the ZnOT unveils a new area of study where further steps must be taken.

Streszczenie

Polidopamina (PDA) jest niedawno odkrytym, wyjątkowym polimerem biomimetycznym, o zastosowaniach w inżynierii powierzchni, biomedycynie i ochronie środowiska. Udowodniono, że tworzy ona heterozłącza z niektórymi półprzewodnikami, poprawiając ich właściwości fotokatalityczne poprzez zwiększenie separacji nośników ładunków i tym samym-spowolnieniem procesu ich rekombinacji. Oprócz półprzewodników, została ona również połączona z materiałami plazmonicznymi w celu poprawy ich właściwości. Jednakże, odpowiedzialny za to mechanizm nie został jak dotąd dogłębnie zbadany i opisany w literaturze. W niniejszej pracy, półprzewodnik i materiał plazmoniczny zostały połączone z PDA, a powstałe w ten sposób interfejsy zostały zbadane pod kątem ich zdolności do fotodegradacji Rh6G.

W pierwszym przypadku, zsyntetyzowano kilka rodzajów nanokompozytów AuNR/PDA o różnych właściwościach i zbadano interfejs materiał plazmoniczny/PDA. Na początku, badano wzrost nanocząstek za pośrednictwem zarodków, w celu uzyskania różnych próbek AuNR, różniących się rozmiarem i wartościami zlokalizowanego rezonansu plazmonów powierzchniowych (LSPR). Po wyselekcjonowaniu jednej z grup próbek, zsyntetyzowano warstwe PDA otaczającą AuNR, poprzez autoutlenianie dopaminy. W wyniku tego, otrzymano kolejne 6 różnych grup próbek: AuNRs/PDA z AuNRs o tej samej charakterystyce, ale o różnych grubościach powłoki PDA od \approx 4 nm do \approx 30 nm. Następnie, wybrano trzy z nich i zbadano ich wydajność w fotokatalitycznej reakcji rozkładu Rh6G pod wpływem promieniowania UV-VIS ($[Au] = 7,4 \ \mu g \ mL^{-1}$, $[Rh6G] = 2,5 \ \mu g \ mL^{-1}$). Po zidentyfikowaniu, jaki rodzaj próbek charakteryzuje się najlepszą wydajnością (AuNRs/PDA6) zbadano ich stabilność i powtarzalność wydajności reakcji. W związku z tym przeprowadzono dwa dodatkowe cykle fotodegradacji, po odzyskaniu nanokompozytów z roztworu reakcyjnego. Przeprowadzono reakcję z tym samym stosunkiem katalizatora do barwnika organicznego oraz reakcje z tym samym stężeniem katalizatora, ale różnymi stężeniami Rh6G. Dodatkowo, kinetykę reakcji badano przy użyciu metody Langmuir-Hinshelwood (L-H). Podczas reakcji monitorowano temperaturę, co ujawniło jej znaczny wzrost. W związku z tym, przeprowadzono dodatkowe eksperymenty fotokatalityczne z różnymi gęstościami mocy lasera, aby powiązać proces degradacji ze wzrostem temperatury. Ponadto, w niniejszych eksperymentach, badano również wpływ źródła promieniowania, porównując stosowaną wcześniej lampę UV-VIS z laserem NIR. Po odrzuceniu hipotezy o termicznym mechanizmie fotodegradacji, wyniki eksperymentalne porównano z wynikami teoretycznymi obliczonymi za pomocą programu COMSOL Multiphysics, a wpływ gorących elektronów na interfejsie badano za pomocą ultraszybkiej spektroskopii laserowej (fs-TAS). Wreszcie, powstawanie reaktywnych form tlenu (ROS) zostało zbadane za pomocą zmiataczy (scavengers), wyjaśniając ich wpływ na mechanizm degradacji. Na skutek tego wykazano, że połączenie właściwości plazmonicznych Au z innymi właściwościami PDA skutkowało silnym efektem fototermicznym, w którym PDA zapewnia powolną termalizację, zwiększając transfer nośników ładunku i zmniejszając szybkość rekombinacji.

W ramach kolejnego eksperymentu, zsyntetyzowano kompozyty: tetrapody z tlenku cynku /polidopamina (ZnOT/PDA) i zbadano tak powstały interfejs półprzewodnik/PDA. Indukując polimeryzację PDA, otrzymano dwie próbki ZnOT/PDA różniące się chropowatością warstwy PDA. Wydajność fotokatalityczną badano w rekacji fotodegradacji Rh6G ([Zn] = 2,5 mg mL⁻ ¹, [Rh6G] = 5,0 μ g mL⁻¹) pod wpływem promieniowania imitującego promieniowanie słoneczne (1 sun). ZnOT/PDA1 (gładka warstwa PDA) doprowadził do fotodegradacji 97% Rh6G w porównaniu z początkowym stężeniem, w ciągu zaledwie 30 minut naświetlania. Co więcej, taka wydajność fotokatalityczna została utrzymana przez 2 kolejne cykle reakcji, po odzyskaniu fotokatalizatorów i ponownym ich wykorzystaniu. Dodatkowo przetestowano różne stężenia barwnika organicznego (2,5, 7,0 i 10,0 µg ml⁻¹), aby zbadać powtarzalność kinetyki degradacji, którą zbadano metodą L-H. Na koniec przeprowadzono eksperymenty foto(sono)katalizy przy różnych częstotliwościach procesu sonifikacji (10, 15 i 45 KHz) i wyjściowych mocach elektrycznych (3 W i 30 W), uzyskując obiecujące wyniki. Niemodyfikowane ZnOT były w stanie degradować barwnik organiczny znacznie szybciej niż w przypadku samej fotokatalizy, jednak inaczej było w przypadku kompozytów ZnOT/PDA1. Wyjaśnienie tego zjawiska jest złożone, przypuszcza się, że przy stosowanej mocy i częstotliwości sonikacji, warstwa PDA blokuje efekt fal sonicznych w ZnOT, co odkrywa zuepłnie nowy obszar badań, w którym należy podjąć dalsze kroki badawcze.

Résumé

La polydopamine est un polymère biomimétique récemment découvert qui a des applications remarquables dans l'ingénierie des surfaces, la biomédecine et la gestion durable de l'environnement. Il a été prouvé qu'il pouvait créer des hétérojonctions avec plusieurs semiconducteurs, améliorant ainsi leur comportement photocatalytique en stimulant la séparation des charges et en diminuant le taux de recombinaison. Outre les semi-conducteurs, il a également été combiné avec des matériaux plasmoniques afin d'améliorer leurs caractéristiques. Cependant, le mécanisme conducteur et un matériau plasmonique ont été combinés avec de la polydopamine (PDA), et les interfaces ont été étudiées pour la photodégradation de la rhodamine 6G (Rh6G).

Dans la première situation, plusieurs nanorods d'or/polydopamine (AuNRs/PDA) nanocomposites avec différentes caractéristiques ont été synthétisés et l'interface matériau plasmonique/PDA a été étudiée. Dans un premier temps, une croissance induite par des germes a été réalisée pour obtenir différents échantillons de nanorods d'or (AuNRs) de tailles et de valeurs de résonance plasmonique de surface localisée (LSPR) variables. Après avoir sélectionné l'un des échantillons, une couche de PDA entourant les AuNR a été synthétisée par auto-polymérisation de la dopamine. Par conséquent, 6 autres échantillons AuNRs/PDA différents ont été obtenus avec des AuNRs ayant les mêmes caractéristiques mais différentes épaisseurs de coquilles PDA allant de \approx 4 nm à \approx 30 nm. Trois d'entre eux ont été sélectionnés et leur réponse photocatalytique au Rh6G a été étudiée sous irradiation ultraviolette-visible (UV-VIS) ($[Au] = 7.4 \ \mu g \ mL^{-1}$, $[Rh6G] = 2.5 \ \mu g \ mL^{-1}$). Après avoir identifié l'échantillon le plus performant (AuNRs/PDA6), sa consistance et sa reproductibilité ont été étudiées. Ainsi, deux cycles supplémentaires après récupération des nanocomposites, une réaction avec le même rapport catalyseur/colorant organique, et des réactions avec la même concentration de catalyseur mais différentes concentrations de Rh6G ont été réalisés. En outre, la cinétique de la réaction a été étudiée à l'aide de la méthode Langmuir-Hinshelwood (L-H). Pendant les réactions, la température a été suivie, révélant une augmentation significative, de sorte que des expériences photocatalytiques supplémentaires avec différentes densités de puissance ont été réalisées pour relier la dégradation à l'augmentation de la température. En outre, dans ces expériences, l'influence de la source d'irradiation a également été étudiée en comparant la lampe UV-VIS déjà utilisée au laser proche infrarouge (NIR). Après avoir écarté l'hypothèse d'un mécanisme thermique de photodégradation, les résultats expérimentaux ont été comparés aux résultats théoriques calculés à l'aide de COMSOL Multiphysics, et le comportement des électrons chauds à l'interface a été étudié par spectroscopie d'absorption transitoire femtoseconde (fs-TAS). Enfin, la production d'espèces réactives de l'oxygène (ROS) a été mesurée par des piégeurs, dévoilant leur influence sur le mécanisme de dégradation. Ici, il a été démontré que la combinaison des propriétés plasmoniques de l'Au avec les propriétés du PDA résulte en un effet photo-thermique fort où le PDA fournit une thermalisation lente, améliorant le transfert de porteurs de charge et réduisant le taux de recombinaison. Dans la deuxième situation, des composites tétrapodes d'oxyde de zinc/polydopamine (ZnOT/PDA) ont été synthétisés et l'interface semi-conducteur/PDA a été étudiée. En induisant l'auto-polymérisation du PDA, deux échantillons ZnOT/PDA ont été obtenus en différenciant la couche lisse et la couche rugueuse du PDA. Le comportement photocatalytique a été étudié vis-à-vis du Rh6G $([Zn] = 2,5 \text{ mg mL}^{-1}, [Rh6G] = 5,0 \mu g \text{ mL}^{-1})$ sous une irradiation simulant la lumière solaire standard. ZnOT/PDA1 (couche lisse de PDA) a réduit 97% de la concentration initiale de Rh6G dans les 30 minutes d'irradiation. De plus, ce rendement photocatalytique a été maintenu pendant deux autres cycles consécutifs de photodégradation après récupération des photocatalyseurs. En outre, des concentrations variables de colorant organique (2,5, 7,0 et 10,0 µg mL⁻¹) ont été testées pour dévoiler la cohérence de la dégradation, et la cinétique de la réaction a été étudiée par la méthode L-H. Enfin, des expériences de photo(sono)catalyse ont été réalisées à différentes fréquences de sortie (10, 15 et 45 KHz) et puissances électriques de sortie (3 W et 30 W), dévoilant des résultats prometteurs. Les tétrapodes d'oxyde de zinc nus (ZnOT) ont été capables de dégrader le colorant organique beaucoup plus rapidement que dans la photocatalyse, mais ce n'était pas le cas pour les composites ZnOT/PDA1. Une situation complexe dans laquelle (à la puissance et à la fréquence de sonication utilisées) la couche de PDA bloque l'effet des ondes de sonication dans les ZnOT dévoile un nouveau domaine d'étude dans lequel d'autres mesures doivent être prises.

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Figure 1: Structure of a) L-DOPA. b) L-Lysine. c) Dopamine

Figure 2: Structure of a) DHICA. b) DHI.

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1. Introduction

Nanoscience refers to the study of molecules and structures within the nanometric scale, being a nanometer one thousand millionth of a meter. The prefix 'nano' comes from the Latin word 'nanus' and the Greek word 'vávoç', both meaning 'dwarf'. The practical application of this science is known as nanotechnology. In recent years, nanoscience and nanotechnology have gained a prominent place in actual society and research, generating a huge research area involving structures, systems, and devices with novel properties and applications.[8]

1.1. Polydopamine

Polydopamine (PDA) is a biomimetic polymer discovered and described in 2007.[9,10] It is the major pigment in natural melanin, and beyond biocompatibility, it shows appealing features, including outstanding adhesion and remarkable optical properties.[11,12] The characteristic functional groups of PDA are amine, imine, and catechol, which play an essential role in its chemical reactivity. These functional groups enable PDA to bind to transition metal ions or undergo covalent modification with molecules.



Figure 1: Structure of a) L-DOPA. b) L-Lysine. c) Dopamine.

PDA is closely related to mussels, whose adhesion properties have been primarily studied. It has been found that 3,4-dihydroxy-L-phenylalanine (DOPA) (**Figure 1a**) and lysine-enriched proteins (**Figure 1b**) are the reason behind these remarkable adhesion properties.[11]

Based on these findings, PDA with a structure similar to DOPA emerges as an important coating material. It is stable and can be deposited in almost all types of substrates with tunable thicknesses. PDA can be synthesized through a straightforward self-polymerization process from dopamine (DA) (**Figure 1c**) in an alkaline medium exposed to the air, creating uniform coatings on various substrates.[13]

Because of these characteristics, polydopamine has been recently applied in diverse fields, including chemical, medical, biological, material engineering, applied science engineering, and technology.[14] Nevertheless, to understand how PDA works, it is first necessary to take a look at its structure and polymerization process.

1.1.1. Polydopamine structure

To better understand what polydopamine is, it is necessary to first consider melanin.[15] Melanin refers to a diverse group of heterogeneous polymeric pigments largely present in the biology field. Allomelanin and pyomelanin are present in microorganisms and plants, whereas pheomelanin, eumelanin, and neuromelanin are primarily found in animal tissues[16]. Historically, because of their poor solubility in the most used solvents, high molecular weight, and high chemical complexity, the precise structure of these melanins has been challenging to determine.[4,15,17] Nevertheless, recent advances have significantly enhanced the synthesis and structure insights, particularly in the case of PDA.[1,18–21]

PDA is considered synthetic melanin, and recent studies suggest that it differs from natural eumelanins for three main reasons. First, in natural eumelanins, the 5,6-dihydroxyindole-2-carboxylic acid (DHICA) unit (**Figure 2a**) is predominant, constituting more than 50 % of the structural units.[22] In contrast, PDA-based eumelanin mainly contains 5,6 dihydroxy indole (DHI) (**Figure 2b**) subunits and this proportion even increases when Tris buffer is used to trigger the polymerization.[15]

Secondly, since PDA mainly contains DHI rather than DHICA, a reduction of -COOH units conforming oligomeric structures exists, leading to a more planar conformation. These pendant-COOH parts, with a larger presence in natural eumelanins, facilitate inter-unit bonding between neighboring moieties in DHICA and provide a higher rotation energy barrier.[23]

The third and final difference is that DHICA dimers can undergo an intramolecular excite-state proton transfer (ESPT) process, therefore granting a superior photoprotection, which is not presented in PDA-based materials since the majority unit found is DHI.[15,24]



Figure 2: Structure of a) DHICA. b) DHI.

PDA has been studied using different techniques, including mass and chemical spectrometry,[14] unveiling two main hypotheses about its structure. The first hypothesis proposes that PDA is a polymer formed from covalently bonded units from oxidized and cyclized dopamine monomers. Conversely, the second hypothesis claims that PDA is a supramolecular aggregate made by monomeric and/or oligomeric units such as dopamine, dopamine-quinone, DHI, or eumelanin-like derivatives. These units are joined together because of weak interactions, including hydrogen bonding, p-cation assembly, p-p stacking, and charge transfer.[3,4,25,26]

Nevertheless, recent research has shown that PDA might not be solely constructed by single indoline units just held together by hydrogen bonds. Therefore, the hypothesis that only weak interactions link these units is challenged.[1] Consequently, the idea of having C-C connections holding the monomers strongly arises. High-resolution mass spectrometry (HR-MS) demonstrated that PDA oligomers present varying degrees of saturation, revealing a higher prevalence of aminoethyl chains than five-membered N-heterocycles in the oligomer PDA chain. These results suggest a revised PDA possible structure featuring oligomers composed of indole units and open-chain dopamine units (**Figure 3**).[1]



Figure 3: PDA proposed final structure made by different units covalently bonded.[1]

AFM-assisted single molecule force spectroscopy (SMFS) has also been employed to investigate PDA potential covalent and non-covalent interactions at an intramolecular and single-molecule level. SMFS analysis determined that PDA films are made by high molecular weight polymer chains that interact through non-covalent weak and reversible interactions. However, it has also been demonstrated that these polymeric chains are indeed composed of covalently bonded units.[19]

Furthermore, it has been observed with time-dependent force spectroscopy that within the early stages of PDA coating formation, the film starts with the adsorption of small oligomeric species that can polymerize and eventually create these higher molecular weight PDA chains, thereby supporting the possible polymeric nature of PDA.[19] Despite the ongoing debate about its precise final structure, PDA presents many properties that make it suitable for surface engineering and photocatalytic applications.

1.1.2. Polydopamine polymerization

As previously mentioned, the PDA structure is still unknown, the same as its exact polymerization process. Consequently, several theories have been proposed, not only about its structure but also about its direct polymerization process[1]. Although a few different methods exist to polymerize and create PDA coatings, such as electrodeposition[27] or enzymatic

oxidation process,[11] direct polymerization is the most commonly used due to its simplicity and cost-effectiveness.

In an open-to-air alkaline medium (pH \approx 8.5), DA spontaneously self-polymerizes to PDA with oxygen serving as the oxidant without requiring the use of complex instruments, techniques, or harsh conditions. Typically, dopamine hydrochloride is used as a DA precursor, and the pH value is set with the action of buffers such as sodium periodate, sodium perchlorate, ammonium persulfate, tris buffer ((tris(hydroxymethyl)aminomethane), or metal ions.[11,28] Once the process starts the color gets darker, from colorless to dark black, and it is possible to cover different substrates or nanoparticles.[6,14,29] Besides, the PDA film/shell thickness can be tuned by controlling the polymerization time and/or the DA concentration.[6,28]

Even though the DA polymerization reaction itself is quite straightforward, the mechanism leading to the formation of PDA is still under research. DA polymerization involves the generation of several intermediates and complex redox processes, resulting in several proposed mechanisms.

It was initially thought to share important similarities with the melanin biosynthesis pathways where dopamine suffers an oxidative process into DHI to continue with other polymerization steps. Thus, a possible initial PDA structure composed of DHI dimers, trimers, or tetramers [30–32] covalently bonded arises.[9] In this mechanism (**Figure 4**), DA is oxidized to dopamine-quinone. Subsequently, through intramolecular cyclization, via 1,4 Michale-type addition, leucodopaminechrome (LDAC) is formed.[33] LDAC experiments oxidization and further rearrangement to finally form DHI that can also be further oxidized to 5,6-indolequinone. Both products, 5,6-dihydroxyindole and 5,6-indolequinone, can complete branching reactions at positions 2, 3, 4, and 7, creating multiple isomers of dimers and, finally, higher oligomers. These structures can self-assemble through the reverse dismutation reaction between catechol and o-quinone, forming the cross-linked polymer.[11] FTIR analysis showed changes in characteristic peaks, unveiling the formation of intramolecular cyclization and the formation of indole derivatives.[34] As a result, it is possible to unveil a possible highly cross-linked PDA final structure based on polymeric chains where covalent bonds bond the aryl parts of the monomers.



Figure 4: Melanine-like synthesis of PDA.[2]

Apart from the covalent bonds, another structure that is similar to a supramolecular synthetic or biological polymer can be proposed. It might be formed by an aggregate of cross-linked monomers through non-covalent forces such as hydrogen bonding, π - π stacking, and charge transfer. Moreover, the formation of cyclized nitrogenous species was further ratified by solid-state ¹⁵N nuclear magnetic resonance (NMR). Besides, an additional one-dimensional solid-state ¹³C NMR analysis revealed that these species were related more to indoline units than to indole units, creating the final possible structure (**Figure 5**).[3]



Figure 5: Polymerization of DA into PDA formed by intra and interchain noncovalent interactions, including charge transfer, π -stacking, and hydrogen bonding.[3]

In addition to both pathways, is possible to formulate a combined synthetic route where the covalent polymerization and the non-covalent self-assembly can co-exist. High-performance liquid chromatography coupled with mass spectrometry analysis (HPLC-MS) unveiled amounts of dopamine unable to polymerize, which can create a self-assembled complex with DHI at the first steps of the self-polymerization process. Thus, two molecules of PDA and one of DHI might interact by hydrogen bonds and π - π staking, creating a trimer. In parallel, the pathway shown in **Figure 4** can continue with the covalent bond creation. The key here is that these two paths are not contradictory, and both can co-exist in the self-polymerization of DA being part of the final structure where covalent bonds create a solid framework and non-covalent interactions contribute by adding stability and aggregation (**Figure 6**).[4]

Besides, by using ¹³C NMR, ¹⁵N NMR, and ultraviolet-visible (UV-VIS) spectra it has been found that the final structure may vary influenced by different conditions like the amount of DA and the buffer employed. It was possible to determine that quinone is generated slowly for low amounts of dopamine, showing a higher proportion of DHI units.



Figure 6: Two different pathways to the formation of PDA. Covalent bonds leading to oxidative polymerization and physical self-assembly of dopamine and DHI.[4]

However, when the DA concentration is higher, an increase in the amount of uncyclized elements is observed. Moreover, the buffer type also influences the final structure. When Tris buffer is used at low DA concentration, Tris molecules can be included within.[25]

In addition to the type of buffer used, the final pH value also contributes to the polymerization process.[35] For high values, oxidation-produced hydrogen protons are more likely to be neutralized by the medium, and the equilibrium shifts toward the product. Moreover, oxygen availability is also important since it triggers the initial oxidation of dopamine and transforms DHI into the corresponding quinone through hydrogen abstraction. Other oxidants such as sodium periodate, sodium perchlorate, ammonium persulfate, or metal ions can also be used.[11,28]

In the case of ammonium persulfate and copper ions used as oxidants, it is possible to obtain PDA films even in acidic conditions (pH = 4), a phenomenon which is not yet explained since the equilibrium would not be displaced toward the formation of the products.[36]

Regarding these findings, it seems that covalent-bond interaction is more important at the initial steps of the process; meanwhile, non-covalent bonds might be more important once the oligomerization reaction has taken place. As well as several structures and functional groups such as amino, catechol, quinone, carboxylic acid, and indolic/catecholic π -systems are integrated into polydopamine, it is possible to explain the PDA's strong adhesion capability to almost all kinds of surfaces. This, positionates polydopamine as a remarkable material for surface engineering and for covering structures such as semiconductors, plasmonic materials, or MXenes (**Annex I**).

1.2. Plasmonic materials

The materials' chemical, physical, and optical properties depend on the electrons' motion. When plasmonic materials such as gold, copper, or silver are downsized from the bulk to the nanoscale, their electrons suffer from spatial restrictions. This phenomenon, known as the confinement effect, influences the response of the material to incident light. When a plasmonic nanoparticle is exposed to light with a longer wavelength than the dimensions presented by the metallic material, the free electrons on the surface become asymmetrically distributed, leading to charge separation. This separation generates coulomb forces between the electrons and the nuclei, triggering the electron cloud's oscillations on the surface.[37,38]

These collective oscillations of electrons in the conduction band are called Localized Surface Plasmon (LSP), localized at the metal/dielectric interface.[39] When incident light matches the

LSP frequency, the plasmonic nanomaterial highly absorbs it, creating strongly localized and amplified electric fields in the vicinity of the particle surface. This phenomenon is called LSPR resonance (LSPR), where part of the light is scattered and another absorbed.[40,41] The properties of LSPR are highly dependent on the particle surface, size, shape surrounding medium, the density of electrons, and the dielectric properties of the metal.[37,38,40,42]

Once the light is absorbed and is highly energetic, LSP can decay radiatively or non-radiatively. The first decay generates the reemission of light[42] the second decay generates hot electrons.[43] Hot electrons are not in thermal equilibrium with the atoms in the material. In the case of noble-metal nanostructures, such as Au, the non-radiative decay can take place via intraband excitations inside the conduction band or interband excitations between the conduction band and other bands (eg. d-bands). For gold, the d-band energy level (2.4 eV) is below the Fermi energy; hence, interband excitations are more unlikely to occur than intraband excitations.[44] The rest of the photoexcited electrons are finally producing heat due to their relaxation process, which includes electron-phonon and electron-electron collisions.[45]

After non-radiative surface plasmon decay, electrons are excited above the Fermi energy level. In the case of Au, surface plasmons can transfer energies to hot electrons (**Figure 7a**). Around 1 to 4 eV, depending on the size and shape of the nanostructures and the carrier concentration. It is possible to create a structure with an appropriate semiconductor forming a Schottky barrier to capture these hot electrons, illustrated in **Figure 7b**. An n-type semiconductor with high density of states (DOS) in its conduction band ensures fast electron injection. Therefore, the generated hot electrons whose energies are higher than the Schottky barrier energy (φ_{sb}) can be injected into the semiconductor. Moreover, tunneling across the barrier can also occur but with a lower probability. In this system, the energy needed for hot electrons to overcome the energy barrier is found to be smaller than that of the semiconductor band gap (E_g).[46]



Figure 7: Plasmonic energy conversion. a) Electrons from the parabolic DOS in a conduction band of a plasmonic nanostructure being excited about the Fermi energy $(E_{f,m})$. b) Schottky barrier created by a plasmonic material and a n-type semiconductor. Hot electrons with energies above the Schottky barrier energy $(\phi_{sb} = \phi_m - \chi_s)$ are injected into the conduction band (E_c) of the semiconductor. χ_s is the electron affinity of the semiconductor and ϕ_m is the work function of the metal.[5]

In summary, plasmonic nanostructures arise as promising materials for photocatalytic applications since LSPR can be exploited to drive chemical reactions. The combination of hot electrons and thermal effects can improve the catalytic behavior. [47–49] Moreover, tuning the wavelength of the LSPR makes it possible to drive the catalytic reaction under VIS or IR light illumination. Furthermore, it is possible to develop photocatalytic nanoplatforms where all the carriers generated come from surface plasmons (SP) in metals instead of electron-hole in semiconductors.[48]

1.2.1. Au/PDA applications

Apart from being combined with semiconductors, polydopamine has also been integrated with plasmonic nanoparticles, creating hybrid nanostructures. PDA-based plasmonic nanostructures show significant potential in many plasmonic applications, including photocatalysis and
photothermal therapy. Au and PDA can play several roles in the different devices created with other materials.

Au/PDA nanocomposites have shown potential in environmental remediation by degrading several organic dyes in different conditions. For instance, methyl orange (MO) has been photodegraded and 4-nitrophenol has been reduced with NaBH₄ as a reducing agent by an Au/PDA composite on a glass substrate[49]. Additionally, 4-nitrophenol can also be depleted by a synthesized gold catalyst (PDA-g-C3N4/Au) where PDA acts as both a reductant and stabilizer for AuNPs. Furthermore, this composite achieves good catalytic performance targeting other nitroaromatics such as methyl orange, 2-nitrophenol, 2, 4-dinitrophenol, Erichrome Black T, and Congo red.[50] Moreover, under IR irradiation, 4-nitrophenol can be reduced by PTC Au@PDA nanoreactors with assembled block copolymers of polystyrene-b-poly(2-vinylpyridine). A synergistic effect exists between gold and PDA where the Au NPs preserve the higher surface temperature when irradiated by NIR laser due to the PDA layers. This triggers a notable acceleration of the reduction reaction[51].

Within nanomedicine, PDA and gold-based structures are employed in various applications with outstanding results, especially in civilization diseases such as cancer. Regarding its treatment, plasmonic properties of gold combined with PDA in layer-by-layer Au-PDA(core)@PDA(shell) sandwiches are used in photo-thermal cancer therapy.[52] Moreover, Au/PDA nanoplatforms can be loaded with several drugs and different tumor-targeting molecules to combine specificity with photothermal and drug delivery properties. For instance, Gold and PDA can create a nano complex with folic acid (PDA@Au@FA) that can be loaded with 5-Fluorouracil where folic acid binds with its receptor, which is remarkably overexpressed in breast cancer cells. Due to pH sensitivity, PDA acts as a gatekeeper and controls drug release; meanwhile, AuNPs act as a drug delivery platform and a source for photothermal effects.[53] Other tumor-targeting molecules and drugs such as hyaluronic acid (HA) and doxorubicin (DOX) can be loaded in gold and PDA devices. Their combination creates a PDA-Au@HA/DOX device that combines the photothermal performance of PDA and Au under NIR irradiation to destroy tumoral cells and release DOX.[54] Moreover, Au/PDA composites, aside from drug carriers, can also induce the production of reactive oxygen species (ROS) and hyperthermia.[55]

Beyond cancer treatment, Au/PDA nanostructures can also be used in NIR-II photothermal antibacterial treatment. Here, the red blood cell membranes are peeled and coated onto the

surface of the Au/PDA nanoparticles containing an aptamer. This enables the elimination of bacteria from infected blood and diminishes the level of bacteria in several organs.[56]

1.2.2. Gold nanorods (AuNRs)

As previously seen, nanostructured gold presents plasmonic properties that are useful in photocatalytic applications (among others). LSPR of gold nanoparticles is influenced by the particle size, shape, surrounding environment, and surface charge distribution [37,38,40,42]. Nowadays, there is the possibility of synthesizing many different nanostructures for gold nanoparticles, hexagons, octahedra, triangles, boxes, squares, spheres, and rods.[57] Among them, Au spheres are the gold nanoparticles that are most studied.[58] However, their spherical structure presents only one not very tunable LSPR mode confined within the visible range (**Figure 8a**).

Thus, AuNRs have gained important attention because of their tunable morphology, largely adjustable plasmon wavelength, and extraordinary anisotropic plasmonic properties.[37] This last characteristic, the anisotropy, provides two LSPR modes to the rod-shaped nanoparticle, transverse and longitudinal (**Figure 8b** and **8c**).

The longitudinal dipole plasmon wavelength of AuNRs experiments a linear increase from the VIS to the IR region when the length-to-diameter aspect ratio is increased. At this wavelength, extremely large extinction cross sections and high electromagnetic losses (EM) rise.[59] Besides, increasing the diameter of the nanoparticle increases their light scattering-to-absorption ratio.[58]



Figure 8: Plasmonic modes representation. a) AuNPs. b) AuNR longitudinal LSPR. c) AuNR transversal LSPR.

The properties of AuNRs are highly dependent on their shape, size, and the rest of the aforementioned characteristics. Therefore, to study and control the SP properties is necessary to design and develop effective synthetic methods to generate AuNRs with a narrow size distribution, high purity, and controlled morphology. AuNRs synthesis methods can be divided into two main categories. The first one is wet-chemical synthesis, including photochemical, electrochemical, seedless growth, and eventually, seed-mediated growth, which is the most used method. The second main category is physical preparation, which includes electron-beam lithography (ELB) and focused-ion beam (FIB).

In this research, seed-mediated growth has been carried out. This technique involves two main steps: the creation of gold "seeds" followed by the controlled growth of these seeds induced by the addition of the growth solution. Several factors, like the seed type, concentration of reagents, and environmental conditions, strongly influence the process.[6,60–62]

1.2.3. AuNRs/PDA nanocomposites

Among the possible structures of AuNRs/PDA nanocomposites, the most common include Janus nanostructures, core-satellite nanostructures, core-shell nanostructures, PDA films decorated with plasmonic gold nanoparticles and self-assembled nanostructures in multiple

dimensions[63]. In this project, a non-porous AuNRs/PDA core-shell structure was synthesized. This procedure involves a PDA shell formation by polymerization of DA at the plasmonic material surface.[6,64,65] The characteristics of the final PDA layer can be tuned by controlling the pH value, temperature, time of reaction, and/or DA concentration[66]. Besides, the coating can provide plasmonic NPs with structural stability[67], enhanced biocompatibility[68], and NIR absorption[69] without hindering the intrinsic plasmonic properties of the core.

Taking advantage of these combined properties, several studies unveil different applications where AuNRs/PDA structures can be used. Rhodamine 123 (R123) can be loaded at AuNRs/PDA nanocomposites and be functionalized for enhanced cellular uptake with folic acid.[70] The nanocomposite selectively accumulates in folate-positive HeLa cells but not in folate-negative HEK293 thus targeting cancer cells. Besides, near-infrared (NIR) light can activate the composite, resulting in phototherapy.[70,71] Moreover, hybrid nanosheets made by AuNRs embedded in PDA on PEGylated graphene oxide also have applications in photothermal therapy and as drug carriers.[72] Finally, AuNRs/PDA have been employed in the creation of fast-responsive light-driven liquid crystal elastomer actuators due to the enhanced photothermal effect that PDA provides to AuNRs.[73]

1.3. Semiconductors

Semiconductor (SC)-based photocatalysis offers outstanding potential to address challenges such as environmental remediation and energy-related applications facing them in an eco-friendly and sustainable way. Nevertheless, the application of this technology for large-scale purposes remains a challenge. The main limitation is their relatively low photocatalytic performance due to the high recombination rate of electron-hole (e^-/h^+) pairs. Moreover, other crucial aspects like the light absorption ability, redox capacity, and density of active sites also have a lot of room for improvement.

Typically, the photocatalytic process is constituted by different steps. Initially, charge carriers (electrons and holes) are photogenerated. Then, these charge carriers dissociate and migrate to the surface of the catalyst to finally undergo reduction-oxidation (redox) reactions at the mentioned surface.[74]

For a semiconductor to be effective in photocatalytic applications, it needs to produce the maximum possible flux of charge carriers enhanced by a broader range of absorbed wavelengths.[75] The band gap of the semiconductor gives the limit of this light absorption. Therefore, as band gap energy increases, the effectiveness of the light absorption decreases, making the semiconductor less suitable for photocatalysis. This light harvesting capacity is translated into photo-generated charge carriers, and once the e^-/h^+ pairs are photogenerated, they must travel from the bulk to the catalyst surface to carry out redox reactions.

The process proceeds as follows: the e^- located in the valence band (VB) gets promoted to the band gap of the catalyst and transit to the conduction band (CB); meanwhile, the h^+ remains in the VB. Generation of charge carriers takes from femtoseconds (fs) to picoseconds (ps), and then, the transition to the surface is in the range of nanoseconds (ns) to microseconds (μ s).[76]

During this whole process, charge carriers can be recombined with the bulk during their movement to/or at the surface of the semiconductor, releasing heat. The recombination rate of e^{-}/h^{+} is believed to be within psto ns, which is much faster than the transfer rate they undergo to the surface to be part of the redox reaction.[77] As the recombination withdraws the charge carriers from the possibility of undergoing redox reactions, several methods, such as heterojunctions, are designed to prevent it.

1.3.1. Heterojunctions in photocatalysis

Heterojunctions arise as an effective method to ameliorate the photocatalytic behavior of semiconductors by increasing the amount of photogenerated charge carriers and decreasing their recombination rate.[78,79] As mentioned before, a Schottky-type junction is created when a metal is combined with a semiconductor (**Figure 7b**). In contrast, when two semiconductors are involved, a heterojunction is formed.

Heterojunctions can be classified according to their constituent semiconductors (SCs) type. There are two types of SCs, p-type and n-type. In the first one, holes are the majority of charge carriers; in the second type, electrons are the majority of charge carriers. Regarding this classification, there are three possible combinations to form heterojunctions: p-p, n-n, and p-n type.

Moreover, heterojunctions can also be classified from the structural point of view. They can be constituted by layer-by-layer stacking of different 2-dimensional materials, making a van der Waals-type heterojunction. In addition, they can be constituted by different crystalline phases of the same chemical composition, resulting in facet-type heterojunction. Lastly, they can be formed by different crystal facets of a single semiconductor, known as a phase-heterojunction.[80,81]

The last possible classification is about the type of band alignment.[82] Three different types of band diagrams are possible: type I or straddling gap (**Figure 9a**), type II or staggered gap (**Figure 9b**), and type III or broken gap (**Figure 9c**). In a semiconductor/semiconductor heterojunction, electrons are believed to transport to the less negative CB and holes to the less positive VB. In type I alignment, excitons accumulate in the semiconductor with a smaller bandgap, in this situation, SC-2. Hence, there are more possibilities to recombine, not leading to a substantial photocatalytic performance. In the case of type II alignment, the situation changes; electrons and holes are split up in two semiconductors, so a better separation of charge carriers is reached. Nevertheless, in type III alignment, both electrons and holes cannot move to the other semiconductor staying in only one and being unable to create a heterojunction between them. The Fermi level gives the total chemical potential of the semiconductor electrons, and the value is normally different for different semiconductors. Hence, the flow of charge carriers is favored in one direction and hindered in the other, similar to a Schottky Junction where an internal electric field is created.



Figure 9: Heterojunction structure regarding the band alignment between them. a) Type I (straddling gap). b) Type II (staggered gap). c) Type III (broken gap).

Therefore, each type of heterojunction has its characteristics, so it is important to know how the semiconductors create the heterojunction, the type of band alignment, and the position of the band edges. These can unveil, for instance, the stronger reduction strength when the CB band is more negative or the most powerful oxidation ability when the VB is more positive.[82]

1.3.2. ZnO

Zinc Oxide is a n-type semiconductor with a wide band gap of $\approx 3.4 \text{ eV}$, a remarkable roomtemperature luminescence[83] and an absorption edge around 380 nm.[84] ZnO typically displays a wurtzite-type unit cell where oxygen and zinc atoms are tetrahedrally bonded (**Figure 10a**) moreover, the crystalline structure of ZnO can also be zinc blende (**Figure 10b**). This material presents a lack of symmetry center and a strong electromechanical coupling. When an external force is applied, the positive and negative charge centers can be displaced, unleashing lattice distortion and triggering piezoelectric properties along the [0001] direction (**Figure 10c**).[85,86]

Piezoelectricity is the ability to convert mechanical energy into electrical energy and vice versa. Among the II-VI compounds with the same wurtzite structure, the piezoelectric tensor offered by ZnO is at least two times higher than materials such as CdS, ZnS, or CdSe, making ZnO an appealing material for applications where piezoelectric properties are required such as piezoelectric sensor or mechanical actuators.[86] Besides, the piezoelectricity shown by ZnO has also been applied in catalysis. ZnO nanosheet microspheres have been proven to be photo and piezocatalytic active toward the degradation of MO, RhB, and AO7.[87] Moreover, ZnO NPs and ZnONRs have also been successfully used in the piezocatalytic degradation of MB.[88]

Particle size is crucial and greatly influences the UV and VIS maxima[89,90] presenting visible emission due to the transition of photo-generated electrons from the conduction band to a lower band.[89] or/and because there is a center recombination because of the oxygen vacancies allowing ZnO visible luminescence.[91,92]



Figure 10: a) Wurtzite-type unit cell structure. b) Zinc blende unit cell structure. c) Representation of how the structure is compressed by a mechanical force and expanded displaying piezoelectricity.

A large number of ZnO nanoparticles can be synthesized with several morphologies using different methods. It is possible to use electrodeposition, vapor deposition, or thermal evaporation, among others, to grow nanowires/nanorods,[93,94] nano-tetrapods,[95] and nanotubes.[96] Furthermore, other techniques like thermolysis or thermal decomposition can also be used to obtain ZnO nanobundles or nanospheres.[97] It has been compared with TiO₂ because of its optical similitudes. However, its absorption edge is broader, taking a part of the visible region, thereby offering a better performance under sunlight. [98,99]

Unfortunately, ZnO suffers from photo-corrosion and low stability; moreover, it also shows a quick recombination rate. To overcome these disadvantages, ZnO can be coupled with other semiconductors, doped with metals, or its surface can be functionalized with different organic polymers.[100]

1.3.3. ZnO tetrapods

A wide variety of different shapes and morphologies for ZnO nano and microstructures can be synthesized[101,102] by using different methods. Within these methods, wet chemical and biological have lost attention compared with physical synthesis since it does not need strong chemical reagents. However, the possible morphologies are limited.[103] Three-dimensional (3D) materials like tetrapods or multipods show different characteristics than the conventional

0D, 1D, and 2D nanostructures. ZnO structures present appropriate stability and high free volume very useful in varying applications.[104]

ZnO tetrapods' growth mechanism has been reported to start from the creation of octahedral seed nuclei[105] or zinc-blend core.[106] However, it is still not clear, and there is a lack of information in the literature.[104]

Classic synthesis methods have some drawbacks. In the case of wet chemistry, synthesis involves strong reagents that are hazardous for both humans and the environment. Strategies involving catalytic nanoparticles do not present a straightforward method for achieving a reduced synthetic yield. Besides, physical synthesis such as vapor-liquid-solid, microwave, or vapor deposition, even possibly a large-scale ZnO tetrapod production (microwave and combustion), has limitations because of its high economic costs and difficulty in controlling the size, shape, or quantity.

However, flame transport synthesis (FTS) can create micro and nanostructures of different metal oxides that are solvent-free and cost-effective, making large-scale production of micro and nanoscale ZnO tetrapods possible.[103,107,108] The FTS method is based on a further simplified version of the combustion method. Inside the muffle furnace, the metallic Zn microparticles, because of the action of the flame and high temperature, are directly converted into ZnO tetrapods through a solid-vapor-solid (SVS) growth process. Tetrapod size can be tailored from nano to micro and from low to high aspect ratio by changing the experimental condition in the FTS.[103] As no chemicals are used in this method, the tetrapod surface properties are not compromised and can be used in several applications.[103,108]

The tetrapod shape is made of four arms with a wurtzite phase connected by a central Zn blend core (**Figure 10b**)[109] at angles going from $\approx 105^{\circ}$ to 110° concerning each other. Because of the central core, ZnO tetrapods show significant differences in semiconducting, mechanical, and electrical features.[104,109,110] Moreover, the shape plays a pivotal role since the mechanical forces applied are transferred between the arms, leading to higher stability and offering good endurance in unpleasant conditions and harsh environments. Additionally, they can gather and build an interconnected structure with high porosity and a large surface area.

Regarding piezoelectricity, tetrapods mainly share characteristics with ZnO nanorods but with some changes. The highest and lowest piezoelectric potential occur in the central core when the

nanotetrapods are pulled or compressed (**Figure 10c**). Simulations have shown that thinner, taller, and more uniform nanotetrapods produce larger strains and potentials, unveiling that shape factors influence their piezoelectric behavior.[110]

ZnO tetrapods can be used for a large variety of sensing applications,[103,111,112] anti-viral infection and other diseases.[113,114] They can create highly porous materials with applicability in the fabrication of flexible ceramics[107,108] and be combined with polymers to create fibers for advanced biomedical applications.[115] Moreover, they can constitute sacrificial template-based strategies to develop new materials by combining metals and oxides with organic compounds.

1.3.4. ZnO/PDA composites

As explained before, polydopamine-based ZnO nanocomposites are a good option to overcome semiconductor drawbacks. PDA, as an organic semiconductor,[116] creates heterojunctions with ZnO. Moreover, it can act as a photosensitizer and protective material. ZnO/PDA composites exhibit similarities to other semiconductor/PDA hybrid materials like TiO₂/PDA.

The bandgap values of ZnO/PDA nanorods have been found to be directly influenced by dopamine concentration, leading to a decrease when the PDA concentration increases. It can move from 3.22 eV when [PDA] = 0.3 mg mL^{-1} to 3.18 eV when [PDA] = 0.5 mg mL^{-1} .[117] This behavior can be produced by the decrease of vacancies and charge transfer from ZnO toward PDA, and acceptor-doped ZnO nanostructures also observe similar effects with a Schottky-type junction.[118] PDA deposition in ZnO decreases oxygen vacancies from $1.5*10^{15} \text{ cm}^{-3}$ to $1.2*10^{14} \text{ cm}^{-3}$, triggering the photoluminescence quantum efficiency decrease from 0.28 to 0.12 respectively.[117] Moreover, the PDA coating can also alter the activation energy in ZnO/PDA by reducing the exciton binding energy, potentially due to the formation of an additional local electrical field between ZnO and PDA.[119]

Within catalysis, its efficiency is strongly influenced by photo-induced electron-hole pair recombination kinetics. A lower recombination rate ameliorates the photocatalytic behavior. When combined with ZnO, the catechol from the PDA can act as an electron trap because of its electron-withdrawing nature. This catechol is attached to the surface of ZnO by binding the

hydroxyl group, with the ZnO surface oxygen vacancies decreasing. This way, the composite's recombination rate and photocatalytic behavior are improved.[83]

These results enforce the idea of having a direct Z-scheme favoring charge separation and enlarging light harvesting.[120] Enhanced electron transfer can also be achieved by combining two factors: the strong adhesive properties of PDA and the strong chelating behavior toward metal ions. As a consequence, low-defect and homogeneous PDA films can be synthesized on ZnO and act as an electron transfer layer (ETL) as shown in polythieno[3,4-b]-thiophene/benzodithiophene:[6,6]-phenyl-C70-butyric acid methyl ester (PTB7:PC70BM) bulk heterojunction solar cells[121] and inverted non-fullerene organic (PBDT:ITIC) solar cells[122]. Hence, it shows an ameliorated photovoltaic performance when PDA is implemented in the composite.

Moreover, the processes that occur at the interface of the ZnO/PDA composites toward H_2O_2 production have been explored. Three-dimensional ZnO@PDA with inverse opal structures exhibited the presence of a built-in electric field pointing from PDA to ZnO because of the electron transfer after their contact. The internal electric field (IEF) drives the recombination of the photoinduced electrons of the ZnO CB with the holes placed at the PDA HOMO, drawing an S-scheme charge transfer. This type of heterojunction is responsible for enhanced light absorption, a higher lifetime, and strong redox ability in photogenerated carriers. Furthermore, the inverse opal structure, because of the supposed "slow photon" effect combined with the scattering and Bragg diffraction triggers light-harvesting. The S-scheme and the ameliorated light harvesting are responsible for better performance in photocatalytic H_2O_2 production if compared with bare PDA and ZnO.[123]

2. Objectives

2.1. AuNRs/PDA

The principal aim is to study the interface between a plasmonic material and an organic semiconductor toward an organic dye photodegradation. Gold is chosen as plasmonic material, while PDA is selected as the organic semiconductor and rhodamine 6G (Rh6G) as the organic dye. The progress assessment is organized as follows.

- Synthesis of AuNRs:
 - To produce AuNRs with controlled shape, size, stability, and reproducibility.
 - To self-polymerize DA on the AuNR surface to create a nanocomposite with a PDA shell.
- Control of AuNRs Characteristics:
 - To achieve AuNRs with a specific LSPR
 - To create comparable samples with varying PDA shell thicknesses.
- Study of Rh6G degradation:
 - To examine how different PDA shell thicknesses influence the ability to degrade Rh6G.
 - To measure temperature changes during degradation using a thermal camera.
 - To determine the ROS production with different scavengers.
- Kinetics and concentration measurement:
 - To use additional Rh6G to calculate reaction kinetics via the Langmuir-Hinshelwood method.
 - To Recover and measure the total organic carbon (TOC) concentration after the experiments.
- Experimental setup:
 - Conduct two sets of experiments:
 - First set: To utilize a xenon lamp (UV-VIS) as the energy source.
 - Second set: To use a NIR laser (808 nm) as the energy source.
- Additional studies and comparisons:
 - To study AuNRs/PDA with femtosecond transient absorption (fs-TAS) spectroscopy.

• To compare experimental results with theoretical calculations using COMSOL Multiphysics.

2.2. ZnO/PDA

Apart from gold, the other objective is to study the interface between PDA and a semiconductor. The elected semiconductor is ZnO in a tetrapod shape.

- Synthesis of PDA-Covered ZnO Tetrapods:
 - To create samples of ZnO tetrapods with varying roughness and thickness of the PDA layer.
- Photocatalytic Performance Evaluation:
 - To identify which PDA-covered ZnO composite offers the best photocatalytic performance under UV-VIS irradiation.
- Reusability and Stability Testing:
 - To measure the reusability and stability of the optimal composite over three consecutive photocatalytic rounds.
 - \circ To calculate the yield of the photocatalytic reaction.
- Kinetics of the Reaction:
 - To study reaction kinetics using the Langmuir-Hinshelwood method with different concentrations of Rh6G
- Piezoelectricity and Photocatalytic Performance:
 - To investigate whether the composite exhibits enhanced photocatalytic performance when its piezoelectricity is triggered.

3. Materials and methods

3.1. Chemical/Reagents/Materials

Dopamine Hydrochloride (DA) (98%), Poly(Ethylene Glycol) Methyl Ether Thiol (Mn = 6000)(SH-PEG-CH3) (PEG) and PEG (Mn 800). HAuCl4 (≥99.9%), = Cetyltrimethylammonium bromide (CTABr) (≥98%), AgNO3 (≥99.0%), Ascorbic Acid (A.A) (≥99%), Ethylenediaminetetraacetic acid (EDTA) (99.4-100.6%), p-benzoquinone (BQ) (synthesis graded), Rhodamine 6G (\approx 95%), Trizma® Base (99.9%), Poly(vinylidene)fluoride (PVDF), Polyvinylpyrrolidone (PVP), Polycaprolactone (PCL), Dymethylfomamide (DMF) (≥99%), Acetone (≥99.5%), Ethanol (≥99.9%), Acetic acid glacial (≥99.7%), Chlorform (≥99%), and Methanol (≥99.9%), were purchased from Sigma-Aldrich. NaBH₄ (99%) was purchased from Acros Organics. HCl (35-38%) and HNO₃ (65%) were purchased from P.P.H "Stanlab" Sp-z o.o Poland. Isopropyl alcohol (IPA) (≥99.7%) was purchased from Avantor Performance Materials Poland.

Different sizes and shapes ZnO tetrapods (ZnOT) were obtained in collaboration with the Smart Materials, Nano SYD, Mads Clausen Institute at the University of Southern Denmark (SDU). Sønderborg, Denmark.

3.2. Characterization methods and instruments

This chapter includes an overview of the instruments we have used to characterize and study our samples, how the different methods have been developed, and the information we have obtained.

3.2.1. Transmission Electron Microscope (TEM)

TEM was used to image the AuNRs and AuNRs/PDA nanocomposites. The analysis of the sample interaction with a beam of electrons obtains those images. The microscope is constituted by a vacuum chamber, an electron gun, electromagnetic lenses, a sample holder, and detectors. The electron gun generates an electron beam with energies between the 100-300 kV range. It is

focused by the lens system and directed toward the sample that is placed on a holder in a chamber. Inside the chamber, a high vacuum exists to ensure movement and prevent the air molecules from provoking electron scattering. After the beam interaction with the sample, the image is created. The interaction between the beam of electrons and the sample depends on the composition, density, and thickness. To generate a high-resolution image, contrasts generated by different processes are used.

The transmitted electrons generate the mass-thickness contrast. These electrons pass through the sample without a significant deflection, unveiling brighter areas for less dense parts of the sample. Moreover, electrons passing through the sample also suffer from phase shifts, resulting in interferences when the electron waves are recombined to generate phase contrast. Finally, depending on the crystallographic orientation, phase, or defects, electrons are elastically scattered, forming the diffraction contrast.

A high-resolution image is obtained by combining the results of these processes. Besides, other signals can be used in other techniques within the TEM mode to obtain more information about the sample. Inelastically scattered electrons are used in EELS to obtain information about the electronic structure, bonding structure, and chemical composition. X-rays are used in EDX for elemental analysis.[124–126]

TEM images were selected from several representative samples observed with a JEOL 1400 microscope operating at 120 KV. From the images, it was possible to unveil the morphology of the AuNRs, AuNRs/PDA, and PDA NPs therefore measuring their average longitudinal and transversal distance. The sample underwent drop-casting (dispersed in Mili-Q water) in a copper TEM grid (Formvar-/Carbon 200 mesh from Ted Pella) to be further dried in a vacuum desiccator.

3.2.2. Scanning Electron Spectroscopy (SEM)

In scanning Electron Microscopy, the work is similar to that in TEM, but the electron beam scans the surface instead of passing through the sample. TEM images arise from differences in the thickness, density, and atomic composition of the sample; in the case of SEM, images are primarily generated from variations in surface topography and elemental composition through signals like secondary electrons, characteristic X-rays, and backscattered electrons.

SEM is formed by an electron gun, condenser lens, scanning coils, sample chamber, detectors, and vacuum system. Similarly to TEM, a beam of electrons is generated (1-30 kV) and focused due to the condenser lens. Nevertheless, in SEM, the beam is not conducted to the sample but is directed by the scanning coils to scan the sample. The sample is placed in a chamber with conditions similar to TEM; however, different signals are used to produce the image.

Inelastic scattering of the incident electrons produces secondary electrons emitted from the surface of the sample. These provide high-resolution topographical information. Besides, the elastically scattered electrons (backscattered electrons) provide information about the compositional contrast. Here, the elements with higher atomic numbers unveil brighter areas in the image.

Finally, an energy-dispersive X-ray spectroscopy detector can detect characteristic X-rays, allowing for detailed elemental analysis and compositional mapping. They are produced when the electron beam ejects electrons from the inner shell levels of the sample, and electrons from higher energy levels occupy these vacancies, emitting X-rays. The collected signals are then converted into electrical signals, which will subsequently be processed to create a high-resolution image of the surface of the sample.[127]

ZnOT and ZnOT/PDA SEM images were selected from different representative samples observed with a JEOL JSM-7001F. A carbon double-sided tape attached samples to the adequate holder, and gold was sputtered on it to make it conductive.

3.2.3. Ultraviolet-visible (UV-VIS) spectroscopy

UV-VIS spectrometer was used to assess the Rh6G concentration evolution during the different reactions. Apart, it was also used to unveil the LSPR spectra of the different Au-based nanoparticles and nanocomposites.

The instrument is constituted by a light source, monochromator, cuvette holder, and detector.

The light is typically generated by the combination of a deuterium lamp (UV) and a tungstenhalogen lamp (VIS). Once generated, the light is dispersed by a monochromator therefore the operational wavelength or range of wavelengths can be selected. Subsequently, the light is directed toward the sample and the intensity of the transmitted light is collected by the detector. The difference between the initial and the transmitted intensity plots the final absorption spectrum. Finally, absorbance can be related to the concentration of the sample through the Beer-Lambert law (**Equation 1**).[128]

$$Abs = \varepsilon c l$$
 (1)

Where Abs is the absorbance, ε is the molar absorptivity, c is the concentration of the targeted sample, and l is the path length.

The samples were placed in a 1 cm² quartz Suprasil cuvette with a 10 mm light path (Hellma analytics 101-10-40), and results were obtained using a Lambda 950 (Perkin Elmer) spectrometer. An Ocean Optics QEPro high-performance spectrometer was also used in several experiments. In the case of Rh6G, its absorbance is around 530 nm, so a scan between 420 and 600 nm was carried out to unveil the peak, which shows its concentration, for AuNRs and AuNRs/PDA, a scan between 400 and 1100 nm was carried out to unveil the LSPR values. Moreover, longitudinal LSPR absorbance intensity was related to the concentration of gold in the samples since it was also analyzed by ICP- MS.

3.2.4. Inductively Coupled Plasma Mass (ICP-MS) Spectroscopy

The gold content in AuNRs and AuNRs/PDA and the zinc content in ZnOT and ZnOT/PDA composites were determined by ICP-MS spectrometry in collaboration with the Soft Matter Nanotechnology Centre for Cooperative Research in Biomaterials (CIC biomaGUNE) Basque Research and Technology Alliance (BRTA) in Donostia-San Sebastián, Spain.

ICP-MS is used to detect and quantify metals at trace levels. The instrument is constituted of different parts. The ion source (the ICP), a mass spectrometer (MS) composed of a quadrupole, a detector, a vacuum chamber where the MS works, a vacuum interface, and ion lenses to focus the ions through the system.

Initially, the sample is converted into an aerosol by a nebulizer and sprayed into the ICP, where the sample is ionized using high-temperature argon plasma. Subsequently, the ionized sample is introduced to the MS through the interface composed of two cones. The first cone is in contact with the plasma, called the sample cone, and the second cone is called the skimmer cone. Due to the cones, photons, neutral atoms, and molecules are banned from entering the mass analyzer. Finally, within the MS, typically a quadrupole mass filter, ions are separated regarding their mass-to-charge ratio and detected by an ion detector, normally an electron multiplier.[129]

In our case, AuNRs were previously digested using HNO_3 and HCl to dissolve all the samples fully and convert the gold into a measurable form. Gold was broken into its constituent ions, primarily in the Au³⁺ state. Subsequently, the sample was nebulized into an aerosol and introduced into a Perkin Elmer Analyst 800 ICP-MS. The gold underwent atomization and ionization due to the high-temperature plasma transforming it into Au⁺ ions. These ions were separated based on their mass-charge ratio at the mass spectrometer, and finally, a detector measured the ions and provided quantitative data on the gold content. ZnO-based composites followed the same procedure. Here, ZnO was broken into Zn²⁺ to further analyze the ions.

3.2.5. Fourier Transform Infrared (FTIR)

FTIR spectra were used to analyze the functional groups of PDA in AuNRs/PDA nanocomposites. By identifying them, it was possible to corroborate the correct DA polymerization on the surface of the PDA-containing composites. FTIR uses a broad-spectrum NIR light directed to an interferometer, split into two different beams that travel different paths. One beam travels through a fixed path, and the other undergoes a variable path to recombine them and create an interference pattern. This recombined light interacts with the sample, which absorbs specific wavelengths due to the different molecular bonds. The detector measures the non-absorbed light, unveiling an interferogram that Fourier will transform into the final infrared absorbance spectrum. Thus, the spectrum will show the peaks corresponding to specific wavelengths absorbed by the molecular bonds in the sample with the possibility of identifying functional groups.[130]

A single drop of synthesized nanocomposites was analyzed using an FT/IR 4700LE (Jasco) spectrometer in the transmittance mode within the range of 4000-400 cm⁻¹. AuNRs, PDA, and AuNRs/PDA nanoparticles were compared.

3.2.6. Thermal camera

The IR radiation emitted by objects is correlated with their temperature. Thermal cameras convert infrared (IR) radiation into electrical signals by using detectors capable of generating electrical signals with each pixel of the thermal image. The signals then can be processed by the camera to provide a visual representation where different temperatures are represented with varying intensities and colors.

Thermal images were taken with a thermal camera Sonel KT-650 placed 30 cm away from the cuvette during the irradiation experiments. Images were taken automatically every 3 minutes during the duration of the experiments.

3.2.7. Femtosecond Transient Absorption spectroscopy (fs-TAS)

With fs-TAS is possible to observe temporal changes in the absorbance properties of the materials hence studying the dynamics of excited states. This is achieved by using a probe pulse, this method excites the sample with an initial pump pulse to subsequently measure the absorbance at various time delays. So, analyzing absorbance changes over time makes it possible to shed some light on the lifetimes and pathways of excited states and intermediates.

A femtosecond laser generates ultra-short laser pulses, which will be split into a pump and a probe beam by a beam splitter. The pump pulse excites the sample while the probe pulse is sent through it with a small delay concerning the pump pulse. Once the sample interacts with the pulses, the difference between the absorptions is measured. For example, the difference between the excited sample and the sample in the ground state. By changing the time delay between the pulses, it is possible to shed some light on the dynamic processes that occur, such as electron and/or proton transfer processes, isomerization, excited state energy migration, and intersystem crossing.[131]

In our situation, when AuNRs are excited by the pump pulse, electrons can be promoted to higher energy levels and be transferred to PDA, which can act as an electron acceptor. The timeresolved spectra can provide information on the kinetics of the electron transfer, like the rate constant and the efficiency unveiling the interaction between gold and PDA. Hot electrons were investigated employing a Helios Spectrometer and a Spectra-Physics femtosecond laser system. The instrument had a response function of approximately 200 fs (full width at half-maximum), and transient absorption data were collected over a time range extending up to 3 ns. Samples were suspended in water and analyzed using a quartz cuvette with a thickness of 2 mm. A global analysis was performed over a broad spectral range of 430-830 nm to determine the characteristic time constants of the observed ultrafast processes. Singular value (SV) kinetic vectors were evaluated with Surface Explorer software (Ultrafast Systems). The primary SV kinetic vector was chosen for analysis, as other vectors were largely attributed to solvent artifacts and random noise. Due to the spectrometer's limitations, shorter gold nanorods ($\approx 75 \pm$ 2 nm in length and $\approx 20 \pm 3$ nm in width) were synthesized to ensure that their longitudinal plasmon resonance fell within the detectable range. These measurements were conducted in collaboration with Professor Marcin Ziółek from the Faculty of Physics, Adam Mickiewicz University, Poznań (Poland).

3.2.8. X-Ray Photoelectron Spectroscopy (XPS)

XPS was used to analyze the elemental composition of ZnOT and ZnOT/PDA composites. The aim was to determine the DA polymerization on the surface of the tetrapods, corroborating the correct formation of the PDA layer. Initially, the sample is placed in a vacuum chamber and irradiated with X-rays exciting the core-level electrons. When the X-ray energy is higher than the binding energy of these electrons, they are ejected from the sample surface as part of the photoelectric effect. Then, the kinetic energy of these emitted photoelectrons is measured by an electron energy analyzer, typically concentric hemispherical analyzers or cylindrical mirror analyzers. This kinetic energy (KE) can be related to the binding energy (BE). Therefore, the X-ray (hv) energy is equal to the BE plus the KE plus the spectrometer work function (φ_{spec}) as represented in **Equation 2**. Thus, the binding energy of the electron is calculated.

$$hv = BE + KE + \varphi_{spec} \quad (2)$$

Each element exhibits characteristic binding energies for its core electrons. Hence, the sample's elemental composition can be unveiled from the position of the peaks in the spectra. Moreover, small shifts can reveal information about the chemical state of the elements.[132]

ZnOT and ZnOT/PDA samples were analyzed in collaboration with dr Višnja Babačić from the Faculty of Chemistry of Adam Mickiewicz University, Poznań (Poland).

4. Experimental

4.1. Synthesis and functionalization protocols

4.1.1. AuNRs-based nanocomposites

Before the synthesis, glassware was treated with Aqua regia (HCl/HNO3 3:1 v/v). Ultrapure water (Milli-Q, 18.2 M Ω cm, 71.98 ± 0.01 mN m⁻¹) was used throughout the process.

4.1.1.1. Synthesis of AuNRs

AuNRs were synthesized by following a seed-mediated growth method. First, a seed solution was prepared at 37 °C by adding HAuCl₄ (0.01 M, 0.25 mL) to CTABr (0.1 M, 9.75 mL). This mixture was then combined with an ice-cold NaBH₄ solution (0.01 M, 0.60 mL) with vigorous stirring for a few seconds. Before use, it was kept at room temperature for 2 hours. Subsequently, the growth solution was prepared by mixing, in order, CTABr (0.1 M, 40 mL), HAuCl₄ (0.01 M, 2.0 mL), AgNO₃ (0.01 M, 0.40 mL), HCl (1.0 M, 0.80 mL), and ice-cold ascorbic acid (0.1 M, 0.32 mL). After mixing, 0.040 mL of the seed solution was added to the growth solution. The growth process occurred at 27–30 °C. The final mixture was stirred briefly, covered with aluminum foil, and left at room temperature for 24 hours. Additional AuNRs with different dimensions and LSPR values were synthesized by varying the seed solution and silver nitrate amount as shown in **Table 1**.

Sample	V (seed) (µL)	$V_{(AgNO3)}(\mu L)$	
AuNRs A	400	440	
AuNRs B	15	440	
AuNRs C	100	330	
AuNRs E	60	400	
AuNRs F	100	400	

Table 1: Synthesized AuNRs samples detailing the volumes of seed solution and silver nitrate used.

4.1.1.2. Synthesis of AuNRs/PEG

Before achieving the final structure, an intermediate nanocomposite was synthesized with PEG substituting the capping agent (CTABr). 40 mL of AuNRs was centrifuged twice at 12000 RPM for 12 minutes, and the obtained pellet was redispersed in 25 mL of an aqueous PEG solution (2 mg mL⁻¹, MW = 6000). Subsequently, it was vortexed for a few minutes and stirred for 20 hours to ensure a thorough coating. The resulting AuNRs/PEG were isolated by centrifugation (10000 RPM, 10 min, x2) and rinsed twice with Milli-q water. The whole process was repeated again to achieve a successful PEG coating. Additional synthesis using other molecular weight PEG (Mn = 800) was carried out to study the effect of the PEG in the final coating.

4.1.1.3. Synthesis of AuNRs/PDA

AuNRs/PEG were redispersed in Tris buffer (pH \approx 8.5) by sonication for 5 minutes. Subsequently, an aqueous solution of DA was added with varying concentrations (**Table 2**) to achieve different PDA shell thicknesses. The mixture was first vortexed and then sonicated for 30 minutes. Finally, the final product was collected by centrifugation (7000 RPM, 10 min, x2) and rinsed with Milli-Q water.

Table 2: Synthesized AuNRs/PDA nanocomposites detailing the concentration of DA in the initial aqueous solution and the concentration of DA in the final mixture.

AuNRs/PDA nanocomposite	[DA] _i (mg mL ⁻¹)	$[DA]_f (mg mL^{-1})$
AuNRs/PDA1	0.025	0.012
AuNRs/PDA2	0.100	0.050
AuNRs/PDA3	0.170	0.085
AuNRs/PDA4	0.250	0.125
AuNRs/PDA5	0.500	0.250
AuNRs/PDA6	1.000	0.500

4.1.1.4. Electrospinning fibers

Moreover, synthesized AuNRs were embedded in polymeric fibers by using the electrospinning technique. The possible electrospinning solution was prepared by dissolving the polymer in a mixture of solvents. Several polymers and solvents were used as displayed in **Table 3**. Different trials varying the final volume of the mixture and the concentration of the AuNRs were also carried out. Finally, the successful mixture was composed of 80 mg of PCL dissolved in 1 mL of chloroform/methanol (3:1). Subsequently, AuNRs with a final concentration of 100 μ g mL⁻¹ were dispersed in the final electrospinning solution.

Polymer	Solvent
Poly(vinylidene)fluoride (PVDF)	DMF/Acetone[133]
Polyvinylpyrrolidone (PVP)	Ethanol/Acetic acid[134]
Polycaprolactone (PCL)	Chloroform/Methanol[135]

Table 3: Polymers and solvents used in the preparation of the possible electrospinning solution.

The process was carried out in a homemade electrospinning instrument that was composed of a chamber where it can be found a lamp and a coil that rotates. Outside the chamber, there were a needle placed in a pump system and a high-voltage power supply system (**Figure 11**). The electrospinning solution was placed inside the needle, and by the pump action, the solution was introduced from the needle to the chamber with a constant flow rate of 0.5 mL h⁻¹. Between the needle and the rotating coil inside the chamber, a voltage of 20 kV was generated using a high-voltage power supply. Therefore, the polymeric fibers were created around the rotating coil which is wrapped in aluminum foil, to further collect the fibers by unwrapping the foil. Additionally, a high-temperature lamp is used to increase the temperature inside the chamber and help the solvents to evaporate.



Figure 11: Homemade electrospinning used to create the polymeric fibers. The chamber contains the rotating coil and the lamp. Outside the chamber and pointing to the coil through a hole in the chamber, it is possible to find the needle inserted in the pumping system. Finally, on the right is the high-voltage power supply system.

4.1.2. ZnO-based composites

Ultrapure water (Milli-Q, 18.2 M Ω cm, 71.98 ± 0.01 mN m⁻¹) was used throughout the process.

4.1.2.1. Synthesis of ZnOT/PDA

210 mg of ZnO tetrapods were dispersed in 50 mL of Tris buffer in a Petri dish, and continuously, 180 mg of DA hydrochloride was added. The mixture was gently shaken at 250 RPM without a magnetic dipole under UV light (λ =365 nm) during different reaction times (1 min, 5 min, and 15 min), obtaining several PDA layer thicknesses. Finally, the product was collected and rinsed with Milli-Q water at least 14 times before drying at 60 °C for 48 hours.

4.1.3. Synthesis of PDA NPs

200 mg of DA was dissolved in 100 mL of Milli-Q water. Subsequently, the solution was heated to 50 °C under magnetic stirring to add NaOH (1M, 0.07 mL). The final solution was stirred for 3 h and the PDA NPs were collected by centrifugation (22000 RPM, 20 min) and rinsed with water 3 times.

4.1.4. Synthesis of MXenes/PDA

To functionalize the surface of the MXenes with PDA, $Ti_3C_2T_x$ MXene (1 mg mL⁻¹, 1 mL) was dispersed in Tris buffer (0.01 M, 30 mL, pH \approx 8.5). The mixture was then sonicated for 10 minutes before adding 110 mg of DA. By varying the time of reaction to 1 and 2 hours, it was possible to synthesize final composites with different PDA coating thicknesses. The final products were collected by centrifugation (500 RPM, 8 min, x2) and rinsed with Milli-Q water.

4.2. Irradiation experiments

This chapter includes preparing and developing the experiments carried out under UV-VIS and NIR irradiation, either for composites made by ZnO, or AuNRs.

4.2.1. AuNRs-based nanocomposites

4.2.1.1. AuNRs/PDA photocatalysis, photothermal behavior, and photostability under UV-VIS irradiation

The experiments were conducted in a 1 cm² quartz Suprasil cuvette with a 10 mm light path (Hellma analytics 101-10-40) placed over a magnetic stirrer. The samples contained Rh6G as the targeted organic dye mixed with one of the synthesized particles as a potential catalyst. Samples were stirred with a magnetic dipole at 700 RPM to prevent precipitation and to have a homogeneous sample dispersion (total volume of 3 mL). The cuvette was irradiated with UV-VIS light using a Xenon Sciencetech lamp (LH-E300X) for 60 minutes, and the absorbance

spectrum was measured every 5 minutes using an Ocean Optics QE Pro high-performance spectrometer. Placed before the detector, a Thorlabs lens was used to prevent the saturation in the spectrometer (**Figure 12**). The parameters were settled down to have varying power densities over the sample (0.02, 0.45, 1.1, and 2.5 W cm⁻²). Moreover, the temperature was recorded every minute with a thermocouple and every 3 minutes with a thermal camera (Sonel KT-650) placed 30 cm away from the sample.



Figure 12: Light setup. Light is directed perpendicularly toward the cuvette which is placed above the magnetic stirrer with a dipole stirring the sample. The detector is immediately placed after the cuvette protected by a lens.

Preliminary experiments studied AuNRs/PDA with PDA shell thicknesses going from ≈ 4 nm to ≈ 30 nm, as potential catalysts toward Rh6G. The concentrations were $[Au]_f = 7.4 \ \mu g \ mL^{-1}$ and $[Rh6G]_f = 2.5 \ \mu g \ mL^{-1}$. Moreover, as control experiments, Rh6G, bare AuNRs, and PDA nanoparticles (average size of 90 ± 10 nm) were also tested under the same conditions and concentration. As a result, the nanocomposite with the biggest PDA shell (AuNRs/PDA6, an average PDA shell of ≈ 30 nm) offered the best yield under 2.5 W cm⁻² irradiation, hence the rest of the nanocomposites were excluded for further experiments.

Once AuNRs/PDA6 were selected, the photocatalytic yield, stability, and photothermal response were studied during the other two consecutive rounds. To complete the reproducibility results, a complementary 2 h photodegradation where the concentration of Rh6G and AuNRs/PDA6 was increased up to 3 times was carried out (same total volume of 3 mL).

Besides, additional Rh6G concentrations of 1.2, 2.5, and 7.5 μ g mL⁻¹ were tested to study the reaction kinetics through the Langmuir-Hinshelwood method.

4.2.1.2. AuNRs/PDA photocatalysis and photothermal behavior under NIR irradiation

The experiments were conducted in a 1 cm² quartz Suprasil cuvette with a 10 mm light path (Hellma Analytics 101-10-40) placed over a magnetic stirrer. The samples contained Rh6G as the targeted organic dye mixed with AuNRs/PDA6 as a catalyst. Samples were stirred with a magnetic dipole at 700 RPM to prevent precipitation and to have a homogeneous sample dispersion (total volume of 3 mL). The cuvette was irradiated with NIR 808 nm wavelength laser light (Changchun New Industries Optoelectronics Tech. Co., LTD., China) for 60 minutes, and the initial and final absorbance spectrum was measured by using a Lambda 950 (Perkin Elmer) instrument. The parameters were settled down to have varying power densities over the sample of 0.02, 0.45, and 2.5 W cm⁻². The temperature was recorded every 3 minutes with a thermal camera (Sonel KT-650) placed 30 cm away from the sample (**Figure 13**).



Figure 13: Laser setup. NIR laser is perpendicularly directed toward the cuvette, which is placed above the magnetic stirrer with a dipole that stirs the sample. The thermal camera is placed 30 cm away pointing to the sample to assess its temperature.

AuNRs/PDA6 photocatalytic yield and photothermal behavior toward Rh6G, under 2.5 W cm⁻² irradiation, with final concentrations of $[Au]_f = 7.4 \ \mu g \ mL^{-1}$ and $[Rh6G]_f = 2.5 \ \mu g \ mL^{-1}$ were

studied and compared with the control experiments (bare AuNRs and PDA NPS under the same conditions).

4.2.1.3. AuNRs/PDA photocatalytic ROS production

The experiments were conducted in a 1 cm² quartz Suprasil cuvette with a 10 mm light path (Hellma Analytics 101-10-40). The cuvette was placed over a magnetic stirrer. The samples contained Rh6G as the targeted organic dye mixed with AuNRs/PDA6 as a catalyst. Samples were stirred with a magnetic dipole at 700 RPM to prevent precipitation and to have a homogeneous sample dispersion (total volume of 3 mL). ROS production was studied using UV-VIS and NIR irradiation. For the UV-VIS irradiation, The cuvette was irradiated with UV-VIS light using a Xenon Sciencetech lamp (LH-E300X) for 60 minutes and the absorbance spectrum was measured at the end of the irradiation using a Lambda 950 (Perkin Elmer) instrument. The parameters were settled down to have a power density over the sample of 2.5 W cm⁻².

In the case of NIR irradiation, the cuvette was irradiated with NIR 808 nm wavelength laser light (Changchun New Industries Optoelectronics Tech. Co., LTD., China) for 60 minutes, and the absorbance spectrum was measured after 60 min of irradiation using a Lambda 950 (Perkin Elmer) instrument. The parameters were settled down to have a power density over the sample of 2.5 W cm^{-2} .

The selected ROS to assess were holes (h^+), hydroxyl radicals (\cdot OH), and superoxide (O_2^-) quenched by the scavengers, EDTA, IPA, and BQ, respectively. All the scavengers were added to the solution (10 mM), and their effect on the degradation of Rh6G was studied.

4.2.2. ZnOT-based composites

4.2.2.1. ZnOT/PDA photocatalysis and photostability under UV-VIS irradiation.

Photocatalytic and photostability experiments were conducted in a 1 cm² quartz Suprasil cuvette with a 10 mm light path (Hellma Analytics 101-10-40). The cuvette was attached to a rotor, and during the photocatalysis, it was rotated at 35 RPM to have a homogeneous dispersion of the ZnO/PDA composites (total volume of 4 mL). UV-Vis irradiation was carried out for 30 min with a Xenon lamp from Instytut Fotonowy Sp.Z.0.0, serial number IF-00107. The absorbance spectrum was measured every 5 minutes using a Lambda 950 (Perkin Elmer) instrument. The distance and parameters were settled down to have a power density of 1 sun (100 mW cm⁻²).

ZnOT, ZnOT/PDA1 and ZnO/PDA2 composites were tested in a final concentration of $[Zn] = 2.5 \text{ mg mL}^{-1}$ toward Rh6G photodegradation ([Rh6G] = 5.0 µg mL⁻¹). Moreover, additional Rh6G concentrations of 2.5, 7.5, and 10.0 µg mL⁻¹ were also tested to study the kinetics of the reaction.

4.2.2.2. ZnOT/PDA photo(sono)catalysis

Photosonocatalysis experiments were conducted in a 1 cm² quartz Suprasil cuvette with a 10 mm light path (Hellma Analytics 101-10-40). The cuvette was placed in several systems, which will be explained later. However, for all of them, UV-Vis irradiation was carried out for 30 min with a Xenon lamp from Instytut Fotonowy Sp.Z.0.0, serial number IF-00107, and the parameters were settled down to have a power density of 1 sun (100 mW cm⁻²). The absorbance spectrum was measured every 5 minutes using a Lambda 950 (Perkin Elmer) instrument. Besides, during the photocatalysis, varying output sonication frequencies and output electrical powers were applied to the sample. Two bone conductor speakers and an ultrasonic bath were used as ultrasonic sources. 3 sets of experiments were conducted where the sonic wave frequency and output electrical power were: 10 KHz and 3W, 15 KHz and 3W, and finally, 45 KHz and 30 W. ZnOT, and ZnO/PDA1 composites were tested in a final concentration of [Zn] = 2.5 mg mL⁻¹ toward Rh6G photodegradation ([Rh6G] = $5.0 \mu g mL^{-1}$).

5. Results and discussion

5.1. AuNRs-based nanocomposites

This chapter includes the work published in Advanced Functional Materials[6] and the extended research we carried out with gold and PDA.

5.1.1. Synthesis and functionalization

5.1.1.1. Synthesis of AuNRs

The synthesis of AuNRs involves a seed-mediated growth method where tiny Au nucleation centers are initially created to further grow them until the final NR shape (**Figure 14**). In the first step, the seed solution was prepared by mixing the gold precursor (HAuCl₄) with sodium borohydride (NaBH₄). Besides, cetyltrimethylammonium bromide (CTABr) was added as a capping agent. After mixing, the solution was heated up to 37 °C and maintained for 120 minutes. During the process, NaBH₄ reduces Au³⁺ ions into Au⁰, forming the aimed gold "seeds".



Figure 14: Seed-mediated growth method to synthesize AuNRs. Au⁺ is reduced by NaBH₄, creating the "seeds" to further grow the final AuNR structure by adding the growth solution.

In the second step, the growth solution was added to the seed solution, triggering the nanorodshaped growth. This solution contained more Au³⁺ ions, ascorbic acid, silver nitrate (AgNO₃), hydrochloric acid (HCl), and CTABr. Ascorbic acid slowly reduces Au^{3+} to Au^{0} , controlling anisotropic growth. Silver ions (Ag⁺) from AgNO₃, are adsorbed onto specific facets of the gold seeds, promoting the rod-like shape and banning the growth into other directions. Besides, the HCl was included to adjust the pH and the ionic strength of the solution, influencing the shape and size of the NRs. Finally, CTABr, as in the seed solution, acts as a capping agent, preventing agglomeration and ensuring the colloidal stability of the process and the final product.

Within this method, the amount of almost all the reagents used strongly influences the aspect ratio, shape, and size of the final AuNRs. Therefore, we conducted different experiments modifying the added volume of AgNO₃ and seed solution to obtain AuNRs with different dimensions, aspect ratios, and LSPR values. **Table 4** describes the amount used and the obtained sizes, LSPR, and aspect ratio.

AuNRs	V _(seed) (µL)	V _(AgNO3) (µL)	AuNRs diameter (nm)	AuNRs length (nm)	Transversal LSPR (nm)	Longitudinal LSPR (nm)	Aspect ratio
А	400	440	11.3 ± 2.6	59.4 ± 7.5	550	912	5.3
В	15	440	40.3 ± 8.3	110.9 ± 14.0	523	728	2.8
С	100	330	26.5 ± 4.8	76.5 ± 8.7	518	704	2.9
D	40	400	18.0 ± 2.4	81.6 ± 9.3	510	790	4.5
Е	60	400	17.2 ± 2.9	65.8 ± 10.8	514	803	3.8
F	100	400	21.7 ± 3.1	74.3 ± 7.9	511	842	3.4

Table 4: Samples characteristics (diameter, length, LSPR, and aspect ratio) and the volume of seed solution and silver nitrate used to synthesize them.

Firstly, AuNRs A and AuNRs B were synthesized by varying the amount of seed solution but keeping the same amount of AgNO₃ (440 μ L) for both syntheses. Consequently, the impact of the seed solution on the AuNR growth was studied.



Figure 15: TEM images of AuNRs A and histograms displaying the average length and diameter.

As revealed by the TEM images and the histograms in **Figure 15**, AuNRs A exhibited a very thin and short structure (diameter = 11.3 ± 2.6 nm, length = 59.4 ± 7.5 nm), resulting in a high aspect ratio (5.3). In contrast, obtained AuNRs B were larger and thicker (diameter = 40.3 ± 8.3 nm, length = 110.9 ± 14.0 nm) with a thick and elongated structure, resulting in a compact structure and an aspect ratio of 2.8 (**Figure 16**). Therefore, there were significant differences in size and shape between the two types of rods.

The observed morphology could be attributed to the number of nucleation centers present in the reaction, which is directly proportional to the added amount of seed solution. In the case of AuNRs A, because of the higher concentration of seed solution, more nucleation centers resulted in thinner and shorter rods due to the possibility of growing more NRs. Conversely, the number of nucleation centers decreased because of the lower seed solution concentration used in AuNRs B. Hence, larger and thicker rods were formed, and a decrease in the aspect ratio was observed.



Figure 16: TEM images of AuNRs B and histograms displaying the average length and diameter.

AuNRs A are significantly thinner and shorter than AuNRs A, with a higher aspect ratio. As a result, both the transverse and longitudinal LSPR values were highly redshifted compared with AuNRs B (**Figure 17**). Specifically, AuNRs A showed a transverse LSPR at 550 nm and a longitudinal LSPR at 912 nm, while AuNRs B exhibited a transverse LSPR at 523 nm and a longitudinal LSPR at 728 nm.

Theoretically, the transverse plasmon does not experiment with a significant change in the morphology of the NR. Conversely, it is strongly affected by the longitudinal plasmon.[136] A higher aspect ratio means that the longitudinal axis of the rod is significantly larger than the transverse axis within the proportions of the NR. Therefore, the field-induced charges are separated over a larger distance, resulting in a smaller restoring force and promoting the redshift.[137] The observed redshift in LSPR values for AuNRs A aligns with existing literature, which typically indicates that LSPR values redshift with increasing aspect ratio.[138]

Once the limits were established, the objective for AuNRs C was to synthesize AuNRs with dimensions and LSPR values intermediate between those of AuNRs A and AuNRs B. The volume of seed solution was adjusted to $100 \ \mu$ L aiming to create more nucleation centers than in AuNRs A synthesis, inducing the growth of longer rods.



Figure 17: LSPR values of AuNRs A and AuNRs B.

Nevertheless, the volume was kept lower than in the second synthesis to prevent AuNRs C from becoming as long as AuNRs B. Additionally, the added amount of silver nitrate was adjusted to 330 μ L. As can be noticed by the TEM images and histograms shown in **Figure 18**, AuNRs C meets the intended specifications with an average diameter of 26.5 ± 4.8 nm and an average length of 76.5 ± 8.7 nm. These dimensions are between those achieved with AuNRs A and AuNRs B.



Figure 18: TEM images of AuNRs C and histograms displaying the average length and diameter.



Figure 19: LSPR values of AuNRs C.
Regarding LSPR, a coherent behavior was expected when compared with the previous synthesized. However, the values obtained were 518 nm for the transverse and 704 nm for the longitudinal LPSR, as shown in **Figure 19**. These values are lower than the observed for the previous two nanocomposites, and despite having a similar aspect ratio (2.9) to AuNRs B (2.8), AuNRs C exhibit a blueshifted longitudinal LSPR. This discrepancy may be attributed to aggregation within the sample and/or the presence of other unintended morphologies, such as spheres or squares. These factors can contribute to the broadening or blueshift of the LSPR peak.



Figure 20: TEM images of AuNRs D and histograms displaying the average length and diameter.

Moving forward, it was decided to standardize the amount of silver nitrate at an intermediate value of 400 μ L. Subsequently, three additional syntheses were conducted with varying amounts of seed solution, narrowing the differences between the previous amounts used. At this stage, our goal was to produce reproducible gold nanorods for further experiments with a controlled LPSR and dimensions. The searched length and width were between 75 and 100 nm and within 15 and 25 nm, respectively, with a longitudinal LSPR around 800 nm. Apart from studying their properties, these desired characteristics were settled down to enlarge the possible applications of the nanocomposites. Not only for organic dye photodegradation but also for biomedical applications such as photothermal therapy and photodynamic therapy.[139]

Three different batches of AuNRs were synthesized. AuNRs D, E, and F were produced by using 40, 60, and 100 μ L of the seed solution, respectively. As a result, AuNRs with varying dimensions and LSPR were obtained. The average diameters of the AuNRs were: 18.0 ± 2.4 nm for AuNRs D (**Figure 20**), 17.2 ± 2.9 nm for AuNRs E (**Figure 21**), and 21.7 ± 3.1 nm for AuNRs F (**Figure 22**). Besides, the average lengths for AuNRs D, E, and F were: 81.6 ± 9.3 nm, 65.8 ± 10.8 nm, and 74.3 ± 7.9 nm, respectively.



Figure 21: TEM images of AuNRs E and histograms displaying the average length and diameter.

These dimensions along with the varying amount of seed solution, exhibited a behavior that agrees with the previously synthesized AuNRs A and B. However, with the fixed amount of silver nitrate in the current set of experiments, it is unveiled that the seed solution is the main influence on the diameter and length of the AuNRs. On the one hand, a lower volume of seed solution appears to favor the growth of longer nanorods, as observed with AuNRs D, which had the smallest seed amount of all three syntheses and the largest length. On the other hand, increasing the seed solution volume results in shorter nanorods, as shown in AuNRs E, possibly because the higher nucleation rate limits the growth phase, providing more nucleation centers to create more rods that are shorter and thinner.



Figure 22: TEM images of AuNRs F and histograms displaying the average length and diameter.

Interestingly, AuNRs F, synthesized with the largest volume of seed solution, exhibited an increase in both diameter and length if compared to AuNRs E. This, could be due to a more complex interplay between nucleation and growth processes.

Figure 23 shows the longitudinal LSPR values measured for each batch. The peaks appear at 790 nm for AuNRs D, 803 nm for AuNRs E, and 842 nm for AuNRs F. The longest nanorods (AuNRs D), with the higher aspect ratio, displayed the shortest LSPR value, whereas AuNRs F, with the lowest aspect ratio, exhibited the most significant redshift.

This behavior disagrees with the theoretical understanding that an increase in aspect ratio promotes the redshifting of LSPR. This can be due to several factors like the presence of undesired materials (squares, spheres...) added to the inhomogeneity of the AuNRs length. Although it is not significantly large, 10% for AuNRs D and F, and 16% for AuNRs E, it can slightly contribute to broadening and shifting the peaks.



Figure 23: LSPR values displayed by AuNRs D, E, and F.

For the subsequent experiments, which involve coating the AuNRs with PDA, which will induce a redshift, we selected AuNRs D with a longitudinal LSPR of 790 nm. Between the three samples, the lower longitudinal LSPR value, the narrow peak, and the lowest inhomogeneity were presented.

5.1.1.2. Synthesis of AuNRs/PEG

To finally achieve the hybrid nanocomposite (AuNRs/PDA) it was necessary to synthesize an intermediate compound where the PDA has been substituted by thiolated polyethylene glycol (PEG) as shown in **Figure 24**. CTABr, as a capping agent, stabilizes the AuNRs in the aqueous solution, creating a bilayer around them. The main property of PDA is its remarkable adhesion but, the electrostatic nature of CTABr can interfere with the formation of the PDA coating.

However, PEG is a nonionic surfactant[140] and can provide steric stabilization to the solution instead of electrostatic stabilization. Therefore, it can maintain the colloidal stability of the AuNRs without having issues with the ionic interactions, providing a better environment for the deposition of PDA at the AuNRs surface.



Figure 24: Substitution of CTABr by PEG.

In the AuNRs solution, the excess of CTABr tends to precipitate at room temperature. Prior to initiating the procedure, it is necessary to redissolve the CTABr by heating the solution to approximately 37°C. Subsequently, centrifugation carries out the separation, resulting in two different phases. The AuNRs precipitate at the bottom of the tube while the CTABr remains dissolved in the supernatant. The AuNRs are rinsed with water, and the procedure is repeated again. Then, the PEG is added, and the mixture is stirred for 24 hours. The whole process needs to be repeated another time.

PEG can exhibit different average molecular weight (Mn). Typically, PEG fluidity and viscosity vary with Mn, resulting in higher viscosity and lower fluidity at higher Mn values. Higher Mn can create a more robust and stable PEG layer, which is beneficial for surface modification. However, it can be more difficult to dissolve in water. In our case, using high Mn PEG can be beneficial since it is used in a competitive process with CTABr, which needs to be efficiently removed to avoid interferences in the PDA coating process.

Hence, we utilized two different molecular weights of PEG. Mn = 800 and Mn = 6000. In both instances, AuNRs were successfully coated with PDA. However, the coating process was more effective with Mn = 6000 (Figures 25a and 25b). In contrast, when Mn = 800 was used (Figures 25c and 25d), there was a higher degree of aggregation of AuNRs/PDA, and more DA

polymerized in the bulk rather than on the AuNR surface hence, PEG (Mn = 800) was discarded for further use.



Figure 25: TEM images of AuNRs/PDA. a) and b) when PEG (Mn = 6000) was used. c) and d) when PEG (Mn = 800) was used.

AuNRs/PEG (Mn = 6000) were also analyzed by TEM to study the thickness of the layer. Nevertheless, it was not thick enough to be measured (**Figure 26a**). Moreover, AuNRs/PEG (Mn = 6000) longitudinal LSPR value for AuNRs/PEG, experimented a small redshift with a broader peak (**Figure 26b**). However, this does not indicate that the PEG layer influences the LPSR values since the broadening and shifting of the peak is almost negligible. The reason for these slight changes might be external conditions like agglomeration or the use of another synthesized batch.



Figure 26: a) TEM image of AuNRs/PEG (Mn = 6000). b) Comparison between AuNRs and AuNRs/PEG LSPR values.

5.1.1.3. Synthesis of AuNRs/PDA

The final PDA coating was achieved by self-polymerizing DA on the AuNRs' surface, as illustrated in **Figure 27**. The previously synthesized AuNRs/PEG were dispersed in tris buffer (pH \approx 8.5), vortexed, and sonicated for 5 min before the addition of a DA aqueous solution. The mixed final solution was vortexed and sonicated for 30 min to collect the final product by centrifugation.



Figure 27: Final self-polymerization of DA at the surface of the AuNRs.

In this procedure, the final PDA shell thickness can be tuned by modifying the time of reaction or the dopamine hydrochloride concentration. Thus, it is also possible to tune the values of the LSPR since it depends on the surrounding media of the plasmonic material. The effect at the PDA layer and LSPR of different DA final concentrations was studied (**Table 5**).

Samula	[DA] _f (mg	PDA shell	Transversal	Longitudinal
Sample	mL ⁻¹)	thickness (nm)	LSPR (nm)	LSPR (nm)
AuNRs	-	-	510	790
AuNRs/PDA1	0.012	-	510	790
AuNRs/PDA2	0.050	4.7 ± 6.1	510	847
AuNRs/PDA3	DA3 0.085 4.1 ± 1.7		514	806
AuNRs/PDA4	0.125	12.2 ± 2.6	514	815
AuNRs/PDA5	0.250	18.2 ± 2.2	518	846
AuNRs/PDA6	0.500	30.4 ± 4.8	526	917

Table 5: Dopamine final concentration related to the PDA shell thickness and LSPR values.

The optimal thickness of PDA coatings, which creates a heterojunction with semiconductors to achieve the best performance, is believed to be a few nanometers.[141] In this study, the working material is not a semiconductor but a plasmonic material; however, since there was a lack of information about the optimal PDA coatings in plasmonic materials, the aim was to obtain a few nanometers of PDA layer to be comparable with the semiconductor case.

Small amounts of DA final concentration were used for the three initial sets of nanocomposites, AuNRs/PDA1, 2, and 3. In the first situation, AuNRs/PDA1, the final DA concentration was 0.012 mg mL⁻¹, obtaining a final composite where the PDA layer is negligible and almost invisible (**Figure 28**). Hence, the nanocomposite was discarded for further experiments.



Figure 28: AuNRs/PDA1 TEM images.

For AuNRs/PDA2, the final concentration of DA was increased to 0.050 mg mL⁻¹, showing a thicker PDA layer than AuNRs/PDA1. As illustrated in **Figure 29**, polymerization occurred but it was not favored in the faces of the AuNRs, creating a very inhomogeneous coating. Instead, DA polymerized in the bulk, causing the gathering of AuNRs around amorphous PDA aggregates. The PDA average shell thickness histogram indicates that, even though there was a large amount of small PDA layers, there was also a significant presence of bigger PDA amorphous agglomerates with a larger dispersity (4.7 ± 6.1 nm).



Figure 29: AuNRs/PDA2 TEM images and statistical PDA shell length distribution.

Finally, the DA final concentration for synthesizing AuNRs/PDA3 was increased up to 0.085 mg mL⁻¹. These nanocomposites exhibited a similar coating to AuNRs/PDA2. However, the AuNRs/PDA3 coating was homogeneous. As shown in TEM pictures and histogram (**Figure 30**), a uniform and single PDA layer coated all the nanorods, and the distribution at the histogram follows a Gaussian profile, with an average PDA shell thickness of 4.1 ± 1.7 nm.



Figure 30: AuNRs/PDA3 TEM images and statistical PDA shell length distribution.

It is evident from the three initial sets of nanocomposites that only AuNRs/PDA3 possess a proper PDA shell. This should influence the LSPR. **Figure 31**, shows the LSPR values of AuNRs/PDA1, 2, and 3 compared with bare AuNRs. The LSPR value of AuNRs/PDA1 does not differ from the value of the bare AuNRs. Since the PDA layer is negligible, its influence so it is, it might not provide a sufficient change in the dielectric environment to induce a noticeable redshift. The peak broadening observed may result from the aggregation of the rods, which is potentially promoted by the small PDA layer acting as a glue between the AuNRs. Conversely, AuNRs/PDA2 exhibited the three nanocomposites' largest redshift, up to 847 nm. Since the PDA coating is not uniform and incomplete, the dielectric environment near the AuNRs may not change consistently, provoking this irregular shift. Finally, despite AuNRs/PDA3 having the most homogeneous coating, they unexpectedly displayed the broadest and inconsistent peak. This phenomenon can be attributed to AuNRs/PDA aggregation leading to coupling effects between the nanorods, triggering shifts that not only depend on the coating.

Summarizing, AuNRs/PDA1 coating was negligible and AuNRs/PDA2 did not achieve a uniform and homogeneous coating, leading to a large redshift. However, AuNRs/PDA3 were successfully coated, but their peak was broad and unconsistant. Considering those results, another set of three nanocomposites was synthesized, but the amount of DA was increased trying to stabilize the coating of the nanocomposite and the LSPR.



Figure 31: LSPR values for AuNRs/PDA1 AuNRs/PDA2, and AuNRs/PDA3.

AuNRs/PDA4 were synthesized using a final DA concentration of 0.125 mg mL⁻¹. This concentration made it possible to homogeneously coat the AuNRs with a uniform PDA layer (**Figure 32**). The average 12.2 ± 2.6 nm thickness presented a thicker shell than the previously synthesized nanocomposites. Besides, the concentration was increased up to 0.250 mg mL⁻¹ in the synthesis of AuNRs/PDA5 leading to an increase in the PDA shell thickness of 6.0 nm up to an average value of 18.2 ± 2.2 nm (**Figure 33**). Moreover, both nanocomposites PDA shell thickness dispersion fit in a Gaussian bell as it is shown in their respective histograms.



Figure 32: AuNRs/PDA4 TEM images and statistical PDA shell length distribution.



Figure 33: AuNRs/PDA5 TEM images and statistical PDA shell length distribution.

Finally, AuNRs/PDA6 were synthesized using the largest amount of DA (0.5 mg mL⁻¹), showing the biggest PDA shell thickness. As shown in **Figure 34**, AuNRs were successfully coated with an individual PDA shell of 30.4 ± 4.8 nm. Taking into account the increment in thickness of AuNRs/PDA4, 5, and 6 compared between themselves, it is possible to unveil a relation between the added amount of DA and the final increment in thickness.

Starting from AuNRs/PDA4, in both cases (AuNRs/PDA5 and AuNRs/PDA6), the final dopamine hydrochloride concentration added was incremented 100% related to the previous nanocomposite. This, triggered PDA shell growth of about 66% more in AuNRs/PDA5, compared with AuNRs/PDA4, and 60% in AuNRs/PDA6, compared with AuNRs/PDA5. Hence, when the DA final concentration is doubled, a final increment of \approx 3/5 in the PDA shell is achieved.



Figure 34: AuNRs/PDA6 TEM images and statistical PDA shell length distribution.

This set of nanocomposites presented a PDA uniformly coated AuNRs with controlled sizes. Moreover, for all of the nanocomposites, both transversal and longitudinal LSPR redshift as the PDA layer becomes bigger, as shown in **Figure 35a**. This behavior can be attributed to different factors related to the dielectric environment surrounding the AuNRs, which can be altered by the PDA coating, leading, in this situation, to a reduction in LSPR energy, shifting the peak to longer wavelengths. The electronic interactions at the AuNRs surface can be affected by PDA's homogeneous and dense coating, which influences the resonance conditions. Starting from the longitudinal LSPR of 510 nm and a transverse LSPR of 790 nm for bare AuNRs, the redshift is minimal for AuNRs/PDA4 being 4 nm for the longitudinal mode (514 nm) and 25 nm for the transverse (815 nm). It was increased for AuNRs/PDA5 up to 8 nm for the longitudinal LSPR (518 nm) and 56 nm for the transverse LSPR (846 nm). Finally, AuNRs/PDA6 presented the largest redshift, reaching 16 nm for the transverse mode (526 nm) and 127 nm for the longitudinal mode (917 nm). It is noticeable that, even though the redshift was carried out in both plasmons, the increment of the transverse mode is almost negligible compared to the increment in the longitudinal mode. As it has been explained, this mode is more sensitive to the shape and size of the NR. Moreover, the strong interaction with the PDA shell contributes to the redshift.



Figure 35: a) LSPR values of AuNRs, AuNRs/PDA4, AuNRs/PDA5, and AuNRs/PDA6. b) FTIR spectra for AuNRs and AuNRs/PDA.

Besides, FTIR spectroscopy was employed to verify the successful polymerization of DA on the surface of AuNRs, resulting in a PDA shell. The FTIR spectrum, **Figure 35b**, of the AuNRs/PDA composites differs from the bare AuNRs spectrum by the exhibition of characteristical signals corresponding to organic group bonds presented by the PDA shell.

It is possible to observe -OH and N-H groups stretching vibrations indicated by the broad absorption band around 3200 cm⁻¹. In addition, the presence of C=N, C=C, and C=O bonds is

shown by the peaks observed in the region between approximately 1500 and 1630 cm⁻¹.[142] The obtention of these signals proved the successful PDA formation around the AuNRs.

5.1.2. Determination of Au concentration by ICP-MS

ICP-MS analyzed the concentration of Au in all the different samples in collaboration with Prof Sergio Moya's group at the CICBiomagune in San Sebastián (Spain).



Figure 36: a) Elemental Au concentration (mg L^{-1}) of AuNRs related to the absorbance. Linear fit equation in the inset. The blank signal was not included in the fit. b) Elemental Au concentration (mg L^{-1}) of AuNRs/PDA6 related to the absorbance. Linear fit equation in the inset.

The AuNRs, AuNRs/PDA3, AuNRs/PDA5, and AuNRs/PDA6 samples were dissolved by acids to first vaporize and then atomize the solution into its elemental components. Subsequently, these elemental components are ionized to further be determined by the mass spectrometer as PDA might intervene in the absorbance of the samples, bare AuNRs and AuNRs/PDA nanocomposites were analyzed separately.

In the case of bare AuNRs, three aliquots from three different synthesized batches were taken, and their maximum absorbance (at the longitudinal LSPR) was measured using UV-VIS spectra. Subsequently, these aliquots were analyzed by ICP-MS, unveiling the total Au concentration of each sample. **Figure 36a**, plots the absorbance of the sample versus the Au

concentration and shows the linear equation obtained, which relates the Au concentration of the final sample to its absorbance.

For the AuNRs/PDA, a similar procedure was carried out; however, in this case, two aliquots from two different batches were taken. Two batches of every synthesized nanocomposites (AuNRs/PDA3, AuNRs/PDA5, and AuNRs/PDA6) (**Figure 36b**). The results show consistent behavior among all the samples. As expected, Abs increases with AuNR concentration for both. With the calculated equation, it is possible to know the Au concentration in both bare AuNRs and the synthesized nanocomposite after measuring its absorbance.

5.1.3. Synthesis of PDA NPs

To correctly evaluate the photocatalytic behavior of the AuNRs/PDA nanocomposites, It was necessary to compare their efficiency with their components by themselves. Since uncovered AuNRs were already synthesized, PDA NPs were also synthesized. The procedure consisted of self-polymerizing DA by using NaOH to trigger the reaction.

Spherical PDA NPs (Figure 37a) were obtained with an average diameter of 95.0 ± 5.0 nm (Figure 37b). The size between the bare AuNRs and the PDA-covered AuNRs makes it possible to compare their behavior efficiently.



Figure 37: PDA NPs. a) TEM image. b) Diameter statistical distribution. PDA sphere at the inset. Reprinted with permission from ref.[6]

5.1.4. Irradiation experiments

Preliminary photocatalytic experiments were carried out on Rh6G using a xenon lamp as a light source with a power density of 2.5 W cm⁻², and the irradiation time was set to 1h. The first step was to identify the PDA shell thickness that offered the best performance. Hence, representative, reproducible, homogeneously-coated, and stable nanocomposites were selected. AuNRs/PDA3 presented the thinner homogeneous PDA layer, AuNRs/PDA6 presented the thicker, and AuNRs/PDA5 showed an intermediate value.

The photocatalytic performance of these nanocomposites was compared between themselves and their components alone. The used concentrations were 2.5 μ g mL⁻¹ for Rh6G and 7.4 μ g mL⁻¹ for the possible catalysts, AuNRs/PDA3, AuNRs/PDA5, AuNRs/PDA6, AuNRs and PDA NPs in 3 mL of total volume.



Figure 38: a) Rh6G degradation when AuNRs/PDA3, AuNRs/PDA5, and AuNRs/PDA6 are used and their components by themselves. b) Absorbance spectra of Rh6G every 5 minutes when AuNRs/PDA6 triggers degradation.

Figure 38a shows the photocatalytic results. The Rh6G degradation when PDA NPs were used as a possible catalyst and Rh6G tested alone was less than 5%. For bare AuNRs, it did not reach more than \approx 7%, almost the same degradation as when AuNRs/PDA3 were used. These findings reveal that the thinner PDA layer did not improve the photocatalytic behavior of the bare AuNRs.

However, as the PDA shell became bigger, the degradation also did. When AuNRs/PDA5 were used, degradation increased to almost 15%, and finally, for AuNRs/PDA6, with the biggest shell, a final degradation of more than 50 % of the initial concentration of Rh6G was achieved, as can be seen at the absorption spectra displayed in **Figure 38b**. Since the best performance was achieved by the composite with the biggest PDA shell, AuNRs/PDA6 were used for further experiments; hence the rest of the nanocomposites (AuNRs/PDA3 and AuNRs/PDA5) were discarded. These results unveiled that the larger PDA shell's larger thickness improves the nanocomposite's photocatalytic behavior.

5.1.4.1. Photoreproducibility, consistency TOC, and kinetics

The photocatalytic performance of AuNRs/PDA6 was further evaluated to assess the reproducibility and consistency of the degradation process. An additional 3h experiment was carried out in which the concentration for both the catalyst and the organic dye were increased up 3 times to 22.2 and 7.5 μ g mL⁻¹, respectively. The aim was to assess whether the behavior and trend of the photodegradation remained the same for larger amounts while preserving the same catalyst-to-organic-dye ratio.

In the absorbance spectra (**Figure 39a**), it is noticeable that the extended photodegradation follows a similar trend as the previous experiment (**Figure 38b**), unveiling more than half of the initial Rh6G concentration (59%) depleted within 1 h. Eventually, the photodegradation consistently moved forward, achieving 85% degradation after 2 h of irradiation, reaching 95% after 3 h.

Additionally, the total organic carbon (TOC) removal was also investigated after 1h, 2h, and 3h cycles, and the stability of the nanocomposites was evaluated by the observation of the nanocomposites through TEM (**Figure 39b**). Total organic carbon content decreased to 74 % after the first round, continued with the same trend, decreasing to 62 % after the second round, and finally, achieved a mineralization of 56% at the end of the three cycles. TEM images at the insets of **Figure 39b** show that AuNRs/PDA6 were stable after each cycle (1h, 2h, and 3h), and their structure remained undamaged.

Besides, once it was demonstrated that the AuNRs/PDA6 resist the photocatalytic cycles and that their structure remained unaltered, their performance toward different concentrations of Rh6G was also evaluated. The results will also be used to study the kinetics of the reaction.



Figure 39: a) Assessment of the photocatalytic activity of AuNRs/PDA6 ($[Au] = 22.2 \ \mu g \ mL^{-1}$) toward Rh6G ($[Rh6G] = 7.5 \ \mu g \ mL^{-1}$) during 3 h of irradiation. b) Total organic carbon removal percentage of three photocatalytic cycles of 1h, 2h, and 3h with AuNRs/PDA6 as a catalyst. TEM images of AuNRs/PDA6 after each run at the insets. b) Reprinted with permission from ref. [6]

Figure 40a shows the catalytic activity of AuNRs/PDA6 ($[Au] = 7.4 \,\mu g \,mL^{-1}$) for the additional Rh6G concentrations of 1.2, 5.0, and 7.5 $\mu g \,mL^{-1}$. The process was faster when the Rh6G initial concentration was reduced to 2.5 $\mu g \,mL^{-1}$, reaching 87% degradation in 60 minutes of irradiation. Conversely, higher Rh6G concentrations of 5.0 and 7.5 $\mu g \,mL^{-1}$ decreased the photocatalytic efficiency to 39% and 26%, respectively. These consistent results demonstrate that degradation occurs faster when the concentration of Rh6G diminishes.

To shed some light on this trend, the kinetics of the reaction were studied through the Langmuir-Hinshelwood model since it is the most used model for the degradation of Rh6G and many other organic dyes when irradiated by light.[143,144]

$$r_0 = -\frac{dC}{dt} = \frac{kK_{LH}C_0}{1+K_{LH}} = K_{app}C_0 \quad (3)$$

$$\frac{1}{K_{app}} = \frac{1}{kK_{LH}} + \frac{C_0}{k} \quad (4)$$

The L-H equations are illustrated in **Equation 3** and **Equation 4**.[143,144] In both equations, r_0 displays the initial degradation rate of the reactant (µg mL⁻¹ min⁻¹), c_0 shows its initial concentration (µg mL⁻¹), t refers to the reaction time (min), k is the reaction rate constant (µg mL⁻¹ min⁻¹), K_{HL} is the adsorption coefficient of the reactant (µg mL⁻¹), C shows the reactant concentration with regards to the time (t), and K_{app} is the apparent first-order rate constant (min⁻¹). In the case of the study, the low organic dye concentrations allow us to reduce **Equation 3** to an apparent pseudo-first-order kinetic model as displayed in **Equation 5**.

$$ln\left(\frac{c_0}{c}\right) = K_{app}t \quad (5)$$

The data obtained with the varying concentrations of Rh6G and the fixed concentration of AuNRs/PDA6 can be plotted in **Equation 5**, accomplishing a linear behavior that supports the pseudo-first-order model as illustrated in **Figure 40b**. Moreover, in the inset, the plotting 1/Kapp versus C₀ displays a linear behavior, unveiling the consistency of the photocatalytic process.

$$[Rh6G]_{1.2} \to ln\left(\frac{c_0}{c}\right) = (32.8 * 10^{-3} \pm 11.1 * 10^{-3}) t + (25.0 * 10^{-3} \pm 18.6 * 10^{-3})$$
(6)

$$[Rh6G]_{2.5} \to ln\left(\frac{c_0}{c}\right) = (12.1 * 10^{-3} \pm 5.5 * 10^{-4}) t + (11.4 * 10^{-3} \pm 11.1 * 10^{-3})$$
(7)

$$[Rh6G]_{5.0} \to ln\left(\frac{c_0}{c}\right) = (8.5 * 10^{-3} \pm 4.1 * 10^{-4}) t + (17.7 * 10^{-3} \pm 13.0 * 10^{-3})$$
(8)

$$[Rh6G]_{7.5} \to \ln\left(\frac{c_0}{c}\right) = (5.7 * 10^{-3} \pm 2.5 * 10^{-4}) t + (4.1 * 10^{-3} \pm 5.1 * 10^{-3})$$
(9)

The calculated linear correlation equations of **Figure 40b** are shown in **Equations 6**, **7**, **8**, and **9**. It is possible to observe a noticeable trend where K_{app} decreases as Rh6G concentration increases. This phenomenon unveils that since the catalyst concentration is the same for all the experiments, photodegradation occurs faster for lower concentrations of Rh6G.



Figure 40: a) Assessment of the photocatalytic activity of AuNRs/PDA6 ($[Au] = 7.4 \ \mu g \ mL^{-1}$) toward different concentrations of Rh6G (1.2, 2.5, 5.0, and 7.5 $\ \mu g \ mL^{-1}$). b) Langmuir-Hinshelwood equation and linear fit obtained with the results of the photocatalysis depicted in (a). Linear relation between $1/K_{app}$ and [Rh6G] is shown at the inset.

5.1.4.2. Photostability and photothermal response

AuNRs/PDA6 photocatalytic activity ($[Au] = 7.4 \ \mu g \ mL^{-1}$ and $[Rh6G] = 2.5 \ \mu g \ mL^{-1}$) was reproducible and consistent, proving that the nanocomposite was able to degrade the organic dye and resist the process. When scaled up 3 times, the trend of the degradation was maintained for 3 hours of irradiation until almost the total degradation (95%) of the organic dye. Besides, the consistency was maintained for different Rh6G concentrations. Stability tests were carried out to complete the reproducibility and consistency study of the composite.

After the main photocatalysis experiment ([Au] = 7.4 μ g mL⁻¹ and [Rh6G] = 2.5 μ g mL⁻¹, 1 h irradiation), the AuNRs/PDA6 nanocomposites were recovered by centrifugation (6.5 min, 7500 RPM, x2) and redispersed in fresh Rh6G solution to perform another two additional photocatalytic rounds.



Figure 41: a) Rh6G concentration for three consecutive photocatalysis cycles of 1h with the same reused sample of AuNRs/PDA6 as the catalyst. The evaporation rate of each cycle at the insets. b) Temperature increment during 1h of irradiation or AuNRs, PDA NPs, and Rh6G without catalysts. c) Temperature increment of the three consecutive photocatalysis cycles of 1h with the same sample of AuNRs/PDA6 reused as the catalyst. Data was measured with a thermocouple at the insets, and the maximum temperature reached each round was taken with a thermal camera snapshot.

Figure 41a shows the results where AuNRs/PDA6 remain stable for both additional cycles; however, the yield of the reaction decreases $\approx 41\%$ and $\approx 51\%$ for the second and third cycles, respectively. The cleaning process may not be straightforward under these yield decreasements. The next chapter will discuss a possible solution to this problem.

During the cycles, each cycle's weight loss and evaporation rate (ER) were also studied. During the first round, the weight loss was 2.63% with an ER of 888 μ g min⁻¹. Both values decreased for the second cycle, showing a 2.05% weight loss and an ER of 656 μ g min⁻¹ to, eventually, further decreasing to 1.91% weight loss with an ER of 643 μ g min⁻¹. These findings can be related to the thermal properties of the AunRs/PDA6 nanocomposite.[145,146]

The temperature increase during each photocatalytic cycle was followed up by using a thermocouple and a thermal camera to prove that the relatively high evaporation rate is due to the thermal properties of the Au/PDA nanocomposite.

Initially, a control experiment was carried out to settle down the temperature behavior in the absence of a catalyst and when the components of the nanocomposite act separately. The results plotted in **Figure 41b** show a temperature increment (Δ) of 4.5 °C when there is not any catalyst, 6°C for bare PDA NPs, and 7.5 °C for bare AuNRs.

However, when AuNRs/PDA6 was added as a catalyst, the temperature rose harshly for the first ≈ 17 minutes, reaching a maximum temperature before stabilizing for the rest of the photocatalysis. Results are shown in **Figure 41c** where this behavior is noticeable across all cycles. In the first cycle, the maximum temperature reached was 56.2 °C with an increment of $\Delta 32.4$ °C, in the second cycle the maximum temperature decreased to 48.3 °C with an increment of $\Delta 21.1$ °C, and finally, the maximum temperature in the last cycle decrease even more reaching 44.7 °C with an increment of $\Delta 13.7$ °C.

Even though the temperature increment diminishes during each new cycle, these values remain significantly higher than the temperature increment observed by PDA NPs and AuNRs. These results show that the temperature increment is attributable to a combination of Au and PDA properties. It is known that plasmons can drive photocatalytic processes [147,148] but typically, they might be combined with semiconductor materials[149,150] since plasmonic materials offer a relatively low catalysis performance.

In our study, the main hypothesis at this point was that the synergy between the properties of the two materials increased the bulk temperature, thereby triggering the Rh6G photodegradation. Hence, further experiments were carried out to validate this hypothesis.

5.1.4.3. Electrospinning fibers

As has been said before, the AuNRs/PDA6 cleaning process after each reaction is not straightforward. Due to the dispersion of the nanoparticles and the sticky nature of PDA, the loss of nanocatalysts during centrifugation could be caused by the decrease in the photocatalytic yield. At high centrifugation speeds, the nanocomposites attach at the bottom of the tube, whereas, at lower speeds, the force may be insufficient to have two separated and well-defined phases. We came across the idea of embedding our nanocomposites inside polymeric fibers synthesized by electrospinning as a possible solution. The aim was to immobilize the nanocomposites in a polymeric mesh to recover the whole amount of used nanoparticles after the photocatalysis.

Several polymers and solvents were used as represented in **Table 6** to create the fibers. Besides, several concentrations of AuNRs, AuNRs/PDA, and PDA NPs were mixed with them to include the nanocomposites in the final fibers.

Polymer	Solvent	Solvent proportion	
Poly(vinylidene)fluoride (PVDF)	DMF/Acetone[133]	3:2	
Polyvinylpyrrolidone (PVP)	Acetic acid/Ethanol[134]	3:1	
Polycaprolactone (PCL)	Chloroform/Methanol[135]	3:1	

Table 6: polymers used and solvent mixture with the proportion used.

Although all the nanocomposites were suspended when the solvents were added to the mixture, the PDA-containing mixtures turned into a solid paste when the polymer was added (**Figure 42a**). Conversely, the bare AuNRs were suspended in the final solution but, even for different concentrations of AuNRs and polymers, the solution did not work for obtaining polymeric fibers with embedded AuNRs when the polymers used were PVDF and PVP.

Finally, AuNRs ($[Au]_f = 100 \ \mu g \ mL^{-1}$), were suspended in 1 mL of chloroform/methanol (3:1), and 80 mg of PCL was added to the solution. Subsequently, the polymeric solution underwent electrospinning, obtaining uniform fibers with embedded AuNRs (**Figures 42b, 42c**, and **42d**). The concentration of AuNRs were much higher than that used in photocatalysis, and the process was successful. However, the loss of almost all the nanoparticles in the process and the incapability to determine the final concentration of nanoparticles, either AuNRs, AuNRs/PDA6, or PDA NPs, made this technique and results unuseful for our purpose.



Figure 42: a) AuNRs/PDA6 "dispersed" in chloroform/methanol (3:1). b) c) and d) TEM images of PCL fibers with AuNRs embedded.

5.1.4.4. Thermal response and degradation at different power densities

Hitherto, the degradation observed was likely attributed to the relatively high increase of the temperature as it has been proved that temperature can trigger organic dyes degradation.[151]

AuNRs/PDA6 exhibit longitudinal and transverse plasmon. Theoretically, under UV-VIS lamp irradiation, the excitation is predominantly targeted at the transverse plasmon which has less intensity than the longitudinal plasmon. The anisotropic shape of the AuNRs results in different oscillation modes of conduction for the electrons. Consequently, the oscillation of electrons along the rods' long axis (longitudinal) allows a larger dipole moment and a stronger interaction with the electromagnetic field, resulting in a stronger and more intense plasmonic behavior than in the short axis (transverse). Under NIR irradiation, we expected to target the longitudinal plasmon and study its influence on Rh6G degradation and temperature.

Experiments were carried out with the same conditions as the previous photodegradation ([Au] = 7.4 μ g mL⁻¹, [Rh6G] = 2.5 μ g mL⁻¹, 1 h, and 2.5 W cm⁻²) but under NIR irradiation instead

of Uv-VIS. As expected, the temperature increment was higher than that with the lamp, as can be seen in **Figure 43a**. Here, the maximum T achieved by AuNRs/PDA6 was 74.6 °C (Δ 49.5 °C) significantly exceeding that of bare AuNRs (58.6 °C, Δ 33.5 °C), and AuNRs/PDA6 under UV-VIS irradiation.



Figure 43: a) Temperature increment when laser and lamp irradiation for AuNRs and AuNRs/PDA6. The maximum temperature reached is shown on the insets (thermal camera). b) Normalized absorbance for Rh6G when lamp and laser irradiation.

Surprisingly, this increment in temperature did not correlate with the degradation rate. As shown in **Figure 43b**, Rh6G degradation reached 57% under UV-VIS irradiation but under NIR, the degradation only reached 25%. As can be noticed in **Figure 43b** and **Figure 39b** the achieved degradation when AuNRs/PDA6 were irradiated by light is 6% and 8% higher than in **Figure 38a**. Several photodegradation experiments ([Au] = 7.4 μ g mL⁻¹ and [Rh6G] = 2.5 μ g mL⁻¹, 1 h lamp irradiation), were carried out obtaining values between 51% and 59%. However, from here, we decided to be conservative and use a degradation of 51% to compare with further experiments.

Regarding those findings, a set of experiments was planned where the temperature increment and the organic dye degradation under UV-VIS and NIR irradiation were compared for several power densities (**table 7**). The aim of these experiments, apart from unveiling if the temperature increment is responsible for photodegradation, was also to collect more data to perform theoretical simulations further. By combining the experimental results and the theoretical simulations, it was hoped to shed some light on how the nanocomposite behaves at the interface, how the temperature is incremented, and corroborate if finally, the temperature is not the driving force behind the depletion of the organic dye.

	Final [Rh6G]%		ΔT (°C)	
Power density (W cm ⁻²)	Lamp	Laser	Lamp	Laser
0.02	91	88	1.6	5.9
0.45	82	88	5.4	13.2
1.1	83	-	8.1	-
2.5	51	25	32.4	49.5
Control*	96*	92*	56.2*	74.6*

Table 7: Relation between the power densities used and the final Rh6G degradation and temperature increment when the lamp or the laser reached the power density.

Figures 44a, 44b, and Table 7, present the obtained results. Initially, a power density of 0.02 W cm⁻² was chosen. It will further simulate how the single AuNR and AuNR/PDA6 behave under lamp and laser irradiation at this power density and calculate the EM losses. The results indicated that the final degradation achieved was 9% under lamp irradiation and 12 % under laser irradiation, with corresponding temperature increments of Δ 1.6 and Δ 5.9 °C, respectively.

When power density was increased up to 0.45 W cm⁻², degradation with the lamp doubled to 18 %, but it did not have any effect on the laser degradation, which was maintained at 12 %. The temperature rise under these conditions was $\Delta 5.4$ °C for the lamp and $\Delta 13.2$ °C with the laser.

Further increment of the power density up to 1.1 W cm⁻², showed a negligible change in the degradation under the lamp irradiation (17%) but the temperature continued rising, in this case, up to Δ 8.1 °C.

Finally, when the power density was set to the used power density of 2.5 W cm⁻², the final degradation was 51% for the lamp and 25 % with the laser, while the Δ T was Δ 32.4 °C and Δ 49.5 °C. Moreover, a control experiment was carried out to finally dismiss the hypothesis that temperature is the main force behind our degradation. The solution was heated up until the laser

and the lamp reached the maximum temperature at their maximum power density (2.5 W cm⁻²), and the concentration of Rh6G was measured after 1h. Degradation for the lamp temperature (56.2 °C) was 4 % and 8 %, with the maximum temperature reached with the laser (74.6 °C).



Figure 44: a) Rh6G final concentration in percentage after AuNRs/PDA6 photocatalysis ([Au] = 7.4 μ g mL⁻¹, [Rh6G] = 2.5 μ g mL⁻¹) under lamp and laser 1 h irradiation at different power densities. b) Temperature increment ΔT (°C) after AuNRs/PDA6 photocatalysis ([Au] = 7.4 μ g mL⁻¹, [Rh6G] = 2.5 μ g mL⁻¹) under lamp and laser 1 h irradiation at different power densities. *Control experiments, [Rh6G]% and ΔT (°C), T is set to the maximum temperature achieved in the previous experiments for 1 hour with no catalyst. † No data.

These findings clearly show that, while temperature plays a role in the degradation process under UV-VIS (lamp) and NIR (laser) irradiation, it is not the main force driving the photodegradation. Although a clear correlation exists between increasing the power density and the rise in temperature, particularly under laser irradiation, it is inexistent for degradation.

The depletion of Rh6G can not be attributed to a thermal effect, as it is evidenced by the control experiments, which induced minimal degradation. Higher rates of degradation were achieved by lamp irradiation, suggesting that the thermal mechanism is not the reason for this photodegradation.

5.1.4.5. Modelling of thermal behavior

Theoretical calculations were carried out in collaboration with dr Thomas Vasileiadis from the Faculty of Physics (Adam Mickiewicz University, Poznań, Poland). The modeling of thermal behavior aims to understand and correlate the macroscopic temperature behavior with the characteristics of the nanoparticles.

Initially, the extinction spectra were examined. The experimental value is similar to those expected from AuNRs with a length of 85 nm and a diameter of 24 nm (**Figure S1**). Nevertheless, the length of the synthesized AuNRs (**Figure 30**, **Figure 33**, and **Figure 34**) is slightly smaller than the one derived from the optical properties. This discrepancy might arise from the nonlinear increase in light-scattering efficiency as a function of nanoparticle size.

In the case of PDA's wavelength-dependent real and imaginary refractive indices, values from the literature were used, finding the best results from ref.[152] The calculated extinction cross-section spectra of the AuNRs/PDA nanocomposites are plotted in **Figure 45a**. As the PDA shell thickness becomes bigger, the LSPR redshifts agree with previous studies.[153] Besides, our experimental results agree with the calculations with less than a 5% error (**Figure 45a** and **Table S1**).

The mismatch between the theoretical and experimental results can be caused by aggregation between the nanoparticles. Aggregation can trigger the blueshift of longitudinal plasmons[154] and their asymmetric broadening to longer wavelengths (as it has occurred on several occasions in the chapters above). Next, the plasmonic enhancement was calculated as illustrated in **Figure 45b top**. The norm of the EM field relative to the incident field amplitude reaches a maximum value of ≈ 2 for a 30 nm PDA shell thickness, 520 nm laser wavelength, and transverse polarization (with the electric field perpendicular to the AuNRs long axis). Thus, at the Au/PDA interface, the EM field reaches the maximum, facilitating the charge transfer or direct interfacial optical transitions. Nevertheless, although the use of resonant light, the plasmonic enhancement remains limited.

Under the same conditions of wavelength and polarization, the EM losses, depicted in **Figure 45b down** are in the order of 10¹⁰ W m⁻³ for 20 mW power and 1 cm of focus diameter. These EM losses are primarily localized in the Au; however, the PDA shell also contributes to the absorption, especially at shorter wavelengths (Figure 45c, top) and off-resonant wavelengths (Figure 45c, down).

Simulations were repeated for both polarizations (with the incident electric field parallel to the AunRs long axis) in the 300 to 1100 nm range for all wavelengths. According to the spectrum and intensity of the lamp, the power distributed to each wavelength was calculated, and the total EM losses determined with this approach are shown in **Figure 45d**. The total absorption increases as the PDA layer becomes thicker, primarily due to the significant absorption of PDA near the peak of the lamp spectrum (≈ 550 nm, **Figure S2**).

EM losses can be used as heat sources for heat transfer calculations and thereby estimate the temperature rise.[155] Here, light intensities are insufficient to induce significant localized ultrafast heating in the AuNRs vicinity (**Figure S3**). Nevertheless, the complete action of NRs induces a noticeable global heating of the bulk solution in the 60 min irradiation. (**Figure S4**).



Figure 45: Plasmonic heating in aqueous AuNRs/PDA dispersion finite element method simulations. a) Results of the calculated extinction cross-section spectra of AuNRs/PDA nanocomposites with varying PDA coatings, 0, 4, 12, and 30 nm). b) Plasmonic enhancement (up) and EM losses (down) spatial distribution for an AuNR with 30 nm PDA thickness, 520 nm laser wavelength and transverse polarization, 20 mW power, and 1cm focus diameter. c) EM losses at 400 (up) and 800 nm (down) spatial distribution with transverse polarization. d) Total EM losses in pico-Watt per AuNR as a function of the PDA thickness. Lamp power 20 mW and 1 cm focus diameter. e) Final temperature increment of the AuNRs/PDA6 aqueous dispersion as a function of the irradiation power for the lamp and the NIR laser. Theoretical results are depicted as circles and experimental results as squares. The fitting line of the calculated data with an intercept at 0 K is also shown in the graph. Reprinted with permission from ref.[6]

With an Au concentration of 7 μ g ml⁻¹, it is possible to estimate that the concentration of NRs is around 40 * 10⁹ NRs mL⁻¹, allowing us to convert the EM losses per nanostructure to EM

losses per volume of the solution and being able to carry out simulations of the macroscopic heat flow, shown in **Figure 45e**. Here, it is observable that the experimental results (**Figure 44** and **Table 7**) are comparable with the calculated results (**Figure 45e**). Moreover, it can be induced that even when there is no nanoscale heating, AuNRs can produce measurable macroscopic heating.

Therefore, these results suggest that the main role of AuNRs during the photodegradation, considering the limited localized heating and plasmonic enhancement observed, is the transfer of electrons and holes to PDA. Hence, in the next chapter, we will use femtosecond transient absorption spectroscopy to shed some light on the dynamics and particularities of the charge transfer process.

5.1.4.6. Femtosecond Transient Absorption Spectroscopy (fs-TAS)

The results of the theoretical calculation suggest that, during photocatalysis, Au transfers electrons and holes to the PDA shell subsequently triggering Rh6G depletion. In this chapter, this hypothesis will be studied through fs-TAS spectroscopy. The experiments were performed in collaboration with prof Marcin Ziółek from the Faculty of Physics (Adam Mickiewicz University).

It is well established that the PDA can act in an electron-scavenging role.[156] Moreover, PDA can create S-scheme heterojunctions with semiconductors, facilitating the rapid electron transfer and storage in the PDA layer for subsequent chemical interactions.[157] To perform our experiments, we concluded that similar behavior is shown by the Au/PDA interface since there is a lack of information in the literature about this type of structure (metal/PDA).

Besides, the photodegradation improvement shown by our composites when PDA thickness increases is independent of electron tunneling effects. To investigate this, we conducted fs-TAS on both, bare AuNRs and AuNRs/PDA nanocomposites. The samples were dispersed in water and subjected to excitation at 400 and 800 nm wavelengths and pump pulse energies of 50 and 500 nJ. As expected, AuNRs' transient absorption spectra within the 430-830 nm range are primarily characterized by the photoinduced broadening of the plasmonic resonance bands at 525 nm (VIS region) and 780-900 nm (NIR region). This broadening is evident in TA as

characteristic bleach (negative amplitudes) at the centers of the resonance bands accompanied by positive amplitudes at the wings (**Figures 46a**, **46b**, and **Figure S5**).

Consequently, the decay of these signals shows the dominant thermalization processes that suffer the photogenerated hot electrons.[158–160] Moreover, the positive signal observed below 500 nm may partially arise from the modulation effect of the interband transition.[161] The results indicate that, when excited at 800 nm, bare AuNRs exhibit a minimal contribution to VIS bleaching.

In contrast, AuNRs/PDA show a significantly higher ratio of VIS/NIR bleach amplitudes, as can be seen in **Figure S6**. This suggests that the presence of PDA in the nanostructure enhances the coupling between the plasmonic resonances of the AuNRs for both longitudinal and transverse oscillations. Such enhanced coupling may be the reason for the improved photocatalytic behavior and the photothermal effects observed in the nanocomposites when NIR is irradiated.

In order to analyze the AuNRs dynamics, a two-exponential function was fitted to the first singular value (SV) kinetics, representing the most significant contribution to the TA evolution. The dominant fast component (τ 1) and the minor slow component (τ 2) correspond to thermalization processes driven by the electron-phonon and phonon-phonon interactions.[159,162]

Sample	AuN	NRs	AuNRs/PDA	
Excitation conditions	τ1 (ps)	τ2 (ps)	τ1 (ps)	τ2 (ps)
400 nm, 500 nJ	4.6	250	3.7	470
400 nm, 50 nJ	1.8	190	1.7	430
800 nm, 500 nJ	11	370	5.5	440
800 nm, 50 nJ	2.6	180	2.1	380

Table 8: TA global analysis (fast $\tau 1$ and slow $\tau 2$ components) time constants. Relative errors based on the same system repeated measurements are $\approx 10\%$.

The examples of the kinetics and fits are displayed in **Figures 46c**, and **46d** with **Table 8** summarizing the time-fitted constant. As it is noticeable, both time constants are consistently shorter at lower pump pulse energy (50 nJ vs 500 nJ), which is expected since fewer hot electrons are generated, leading to faster thermalization with phonons. At this same pump fluence for the same sample, $\tau 1$ is shorter at 400 nm excitation than at 800 nm due to the lower photon presence and reduced Au absorption at 400 nm, resulting in fewer generated electrons.



Figure 46: a) AuNRs/PDA TA color plots. b) AuNRs TA color plots. Comparison of AuNRs and AuNRs/PDA samples under 800 nm, 500 nJ of excitation, 1^{st} SV kinetics from TA global analysis and two-exponential fits for c) 400 nm and d) 800 nm excitation. Time zero is arbitrarily shifted to ≈ 1.5 ps to show the data clearly at the logarithmic scale. Reprinted with permission from ref.[6]

Conversely, the $\tau 2$ time constant is longer in AuNRs/PDA samples, typically indicating slower heat conduction or dissipation to the surrounding matrix (in our case, water). This suggests that

the semiconducting PDA layer can capture some charges or excitons that gradually diffuse back to the Au releasing heat and contributing to slower $\tau 2$.

Overall, PDA coating is able to slow down the phonon-phonon interaction in AuNRs, delaying heat diffusion into the water. Significant conclusions can be drawn from the variation observed in the dominant $\tau 1$ component between the AuNRs and AuNRs/PDA samples. Across all experimental conditions, with varying excitation wavelengths and fluence, $\tau 1$ is consistently faster in AuNRs coated with PDA compared to the bare AuNRs samples under the same conditions (**Table 8, Figure 46c**, and **46d**). A possible presence of an additional ultrafast electron transfer channel to PDA in the AuNRs/PDA samples can compete with the ultrafast thermalization; thus, an effective acceleration of the hot electron decay can be observed.

These findings can be related to results found on other coupled Au interfacial systems.[163–165] Hence, our hypothesis is confirmed. Electrons generated in Au are rapidly transferred to the PDA where they participate in reactions that drive the photodegradation.

5.1.4.7. Reactive oxygen species production

Hitherto, the experimental results unveiled that temperature increment is not the main driving force that leads to photodegradation. In addition, the hypothesis was confirmed by theoretical calculations and fs-TAS, which agreed that, during the photocatalysis at the Au/PDA interface, the quick transfer of electrons from Au to PDA is favored. Then, at the PDA surface, they are available to undergo chemical reactions. Therefore, the possible degradation of the organic dye could be caused by the production of ROS.[166]

Consequently, the ROS production was analyzed by using scavengers (10 mM). EDTA was selected to quench holes, IPA for quenching \cdot OH, and BQ to quench \cdot O₂⁻. [167,168] The results are illustrated in **Figure 47**.

Firstly, the degradation results achieved previously under VIS and NIR irradiation are shown. The degradation percentage depicted is not normalized, thus indicating the total degradation from the initial Rh6G concentration. Further experiments are normalized toward these values (which are the maximum possible degradation by using UV and NIR irradiation). The data show that AuNRs/PDA6 exhibit similar degradation under lamp irradiation for both IPA and EDTA

(20%) used as scavengers. Nevertheless, the degradation increases by up to 39% when BQ is used. In contrast, AuNRs/PDA6 show degradation rates of 20% for IPDA, 10% for EDTA, and 25% for BQ under laser irradiation.

To interpret the results, the Rh6G degradation is related and normalized (Δ) to the total possible degradation when no quencher is used. 51% for lamp and 25% for laser. Thus, in the case of EDTA, degradation rates are $\Delta = 40\%$ for both the lamp and laser, indicating that a similar number of holes are generated. Moreover, in the case of IPA, the degradation of the lamp is maintained at $\Delta = 40\%$ but increases to $\Delta = 80\%$ when irradiated with the laser, suggesting a higher production of hydroxyl radicals when the lamp is used. Finally, when BQ is added as a scavenger, the degradation reaches $\Delta = 76\%$ for the lamp and $\Delta = 100\%$ for the laser, unveiling that the superoxide production is the lowest ROS produced when the lamp is used and not produced when the laser is used.

AuNRs/PDA6 exhibited higher photodegradation when irradiated with UV-VIS light rather than with the laser. It is noticeable that in the case of holes, their production is similar for both sources of energy. Consequently, higher photodegradation achieved under UV-VIS irradiation is primarily triggered by a superior production of hydroxyl radicals and superoxide anions.


Figure 47: Rh6G concentration after 1 hour of lamp or laser irradiation with AuNRs/PDA6 as catalysts and different scavengers. IPA, quenching 'OH, EDTA quenching h⁺, and BQ quenching 'O₂⁻. Besides, Rh6G concentration is depicted when no catalyst has been used, but only the maximum temperature reached by lamp and laser is applied for 1 hour. Dashed bars illustrate the relative diminution of the degradation (Δ) having as a model the maximum degradation achieved without a scavenger as 100%.

According to the literature, Au NPs produce hot holes in the range of 2.6 to 2.8 eV and hot electrons between 1.30 and 1.65 eV[169] corresponding to the transversal and longitudinal plasmon values, respectively. Nevertheless, it has been demonstrated that a small number of hot holes are also generated below the intraband transition threshold at 600 nm and above it (more than 640 nm).[170]

These data agree with the role of hot holes in visible light; however, it raises questions about the presence of holes in NIR with no experimental evidence of the generation of OH species by AuNPs[171,172] if there is no ionizing radiation.[172] However, it has been proven that PDA can generate hydroxyl radicals under UV-VIS illumination, possibly explaining the higher rate

of them in VIS light, although this does not fully explain the presence of hydroxyl radicals under NIR irradiation.

5.1.5. Summary

A detailed synthesis plan was carried out and the influence of different parameters was analyzed on the final characteristics of the synthesized materials. Several AuNRs samples were initially synthesized by a seed-mediated growth in which the influence of seed solution and silver nitrate was studied. Thus, it was possible to obtain six different AuNRs samples with their own characteristics in terms of shape, size, and LSPR values. Here, it was discovered that a larger amount of seed solution supplied more nucleation centers to the reaction, triggering the formation of thinner and shorter AuNRs, probably due to the availability of more Au "seeds" to grow. After the synthesis process, CTABr was present in the AuNRs dispersion, adding stabilization. However, due to its electrostatic nature, it could be a drawback for the subsequent DA polymerization at the surface of the AuNR. Therefore, it was substituted by PEG, a nonionic surfactant that provided steric stabilization. Two different molecular weights PEG (Mn = 800, and Mn = 6000) were used, and their efficiency was compared, concluding in a better performance of PEG (Mn = 6000). Finally, the last step of the synthesis process consisted of inducing a self-polymerization of DA at the surface of the AuNR. It was controlled by adjusting the pH to ≈ 8.5 and varying the time of reaction to obtain different nanocomposites with varying PDA shell thicknesses going from ≈ 4 nm to ≈ 30 nm with longitudinal LSPR values ranging from 806 to 917 nm.

Once the synthesis process was finalized and controlled, the influence of the different PDA shell- thickness in photocatalysis, under UV-VIS irradiation, was studied ([Au] = $7.4 \,\mu g \,mL^{-1}$, [Rh6G] = $2.5 \,\mu g \,mL^{-1}$, $2.5 \,W \,cm^{-2}$, 1h). AuNRs/PDA3, 5, and 6 with average PDA shell thicknesses of 4.1 ± 1.7 , 18.2 ± 2.2 , and $30.4 \pm 4.8 \,nm$, and longitudinal LSPR values of 806, 846, and 917 nm respectively were compared. As a result, AuNRs/PDA6, with the largest PDA shell thickness and largest LSPR redshift offered the best photocatalytic behavior, degrading more than 50 % of the initial concentration of Rh6G. Subsequently, additional reactions were performed with varying concentrations of organic dye (1.2, 5.0, and 7.5 $\mu g \,mL^{-1}$) to study the consistency of the reaction and the kinetics (L-H method), unveiling a faster degradation for smaller Rh6G concentration. Moreover, another reaction was carried out where the irradiation

time was adjusted to 3 h and the concentration of the catalyst and the organic dye was increased 3 times, maintaining the same organic dye-to-catalyst ratio. This photodegradation also exhibited a consistent behavior, with more than 50% of Rh6G degraded within the first hour and ending with 95% degradation. Finally, the TOC content was analyzed after 1h, 2h, and 3h of irradiation, reaching a final mineralization after 3h of 56%. During these experiments, the AuNRs/PDA6 were analyzed by TEM after each cycle, and an undamaged structure was observed. Therefore, after these experiments, it was demonstrated that the AuNRs/PDA6 were stable, suitable for photocatalysis, and offered a consistent photodegradation toward different concentrations of Rh6G.

Since the AuNRs/PDA6 were stable and consistent, the photocatalytic yield and the ER after 3 consecutive cycles were studied while the temperature response was followed up. The yield of the reaction diminished $\approx 41\%$ after the second cycle and $\approx 51\%$ after the third last cycle. This noticeable decrease in the photocatalytic yield can be attributed to the non-straightforward recovery process of the nanocomposites. Hence, apart experiments were carried out to embed AuNRs/PDA6 inside polymeric fibers synthesized by electrospinning. The aim was to have the nanocomposites surrounded by a stable and resistant environment with the possibility of recovering the totality of the material after each degradation. However, only AuNRs were successfully embedded inside PCL fibers. Consequently, the idea was discarded after the impossibility of dispersing PDA-containing composites in the polymer and the massive loss of composites during the process, which triggered the impossibility of determining the final nanocomposite concentration within the fibers.

Returning to the reactions, the ER after the first cycle was 2.63% and decreased for the second and third cycles to 2.05% and 1.91%, respectively. Parallel, the temperature during the three cycles increased harshly for the first \approx 17 minutes to further stabilize for the rest of the reaction. The maximum final temperature after the first round was 56.2 °C (Δ 32.4 °C); after the second round, it was 48.3 °C (Δ 21.1 °C), and finally, 44.7 °C (Δ 13.7 °C) for the third round. Although the increment decreased after each cycle, all values remained much higher than bare AuNRs and PDA NPs even though the concentration diminished after each cycle due to the nanocomposite recovering process. The high-temperature increment was attributed to the already known thermal properties of plasmonic gold, and at this point, it explained the photocatalytic procedure since the temperature can trigger organic dye degradation. Therefore, the possibility of having a thermal mechanism is unveiled. To prove the hypothesis, further experiments were developed where the photodegradation and temperature increment were measured, varying the irradiation source's intensity and the wavelength. Two irradiation sources, the already used UV-VIS lamp, and NIR laser, were compared at power densities of 0.02, 0.45, 1.1, and 2.5 W cm⁻². Surprisingly, higher temperature increments were not directly related to higher photodegradation. When irradiated with the laser at 2.5 W cm⁻², temperature experimented with a massive increment of temperature (Δ 49.5 °C) that was not reflected in the degradation that was lesser than the achieved with the lamp (51%). Therefore, these findings clearly discarded the hypothesis of being under a thermal photocatalytic mechanism.

Hence, theoretical calculations were carried out to understand and correlate the macroscopic temperature behavior with the characteristics of our nanoparticles. Therefore, the calculated LSPR values of AuNRs covered by different PDA shell thicknesses unveiled a redshift when the PDA shell became thicker, as did the obtained experimental data. Moreover, EM losses were calculated according to the spectrum and intensity of the lamp and related to the PDA thickness of the nanocomposite. Subsequently, EM losses were used as heat sources for the heat transfer calculations, showing a complete action from the AuNRs/PDA to increase the temperature in the bulk. Finally, by the action of AuNRs/PDA6, the bulk temperature rise was calculated and related to the experimental results obtained at different power densities for both lamp and laser exhibiting a similar response. Therefore, due to the limited localized heating and plasmonic enhancement, the transfer of charge carriers from the Au to PDA appeared as a possible reason for the degradation of Rh6G.

To investigate that hypothesis, fs-TAS experiments were conducted on both composites, bare AuNRs, and AuNRs/PDA6 under excitations of 400 and 800 nm and pump pulse energies of 50 and 500 nJ. The results showed that a coupling exists between the plasmonic resonances of the AuNRs for both longitudinal and transverse oscillations in the AuNRs/PDA sample. Thus explaining the photothermal response and photocatalytic behavior when NIR is irradiated. Moreover, the AuNRs dynamics were analyzed, unveiling a possible ultrafast electron transfer channel to PDA that could compete with ultrafast thermalization. Therefore, the results show that electrons generated in Au are rapidly transferred to the PDA, where they can undergo several reactions that cause photodegradation of the organic dye.

Finally, since it was proved that the temperature increment was not the main driving force triggering the photodegradation, the production of ROS (h^+ , \cdot OH, and \cdot O₂⁻.) under UV-VIS and

NIR irradiation by using scavengers (EDTA, IPA, and BQ respectively) was studied. The higher photodegradation reached by AuNRs/PDA6 when illuminated by UV-VIS radiation was endorsed by the production of ROS. The production of holes was similar for both sources of energy. Nevertheless, the production of hydroxyl radicals and superoxide anions was significantly higher when the lamp was used.

Our study shed light on how the Au/PDA composites behave under NIR and UV-VIS irradiation toward the photodegradation of organic dyes. Moreover, their photothermal response was evaluated unveiling possible applications in photocatalysis and photodynamic/photothermal therapy.

5.2. ZnOT-based composites

This chapter will explain the research done with ZnO/PDA composites. Prof Yogendra Kumar Mishra provided ZnO tetrapods (ZnOT) from Southern Denmark University, and cubes were provided by Prof Rainer Adelung from Kiel University in Germany.

5.2.1. Preliminary ZnOT/PDA synthesis

5.2.1.1. ZnOT cubes

Considering the previous issue we had with the suspended catalysts, we managed to get macroscopic cubes with an average weight of 36.2 ± 3.1 mg and dimensions of 10×10 mm built by ZnOT (**Figure 48**). The purpose of the macroscopic cubes was to cover them with PDA, improving their photocatalytic properties.[123] The macroscopic cube dimensions allow for the complete recovery of the catalyst for its reuse in further photocatalytic cycles.

Since the porosity of the cubes is high (**Figure 48**), it seems possible to grow an individual PDA layer covering each tetrapod. Besides, the porosity enables the organic dye-containing solution to contact a larger surface area and be catalyzed. Moreover, the PDA layer can enhance the cubes' mechanical strength, making them more durable and stable for extended use.

The formation of the PDA layer was created by direct polymerization of DA at the surface of the ZnOT. In this process, 66 mL of Tris buffer was added to a petri dish with a magnetic stirrer in the center. Around the stirrer, 3 cubes were carefully placed in a triangular configuration, and 80 mg of DA was added. One of the cubes was removed after 6 h, another after 12 h, and the last cube was taken out after 24 h. Subsequently, the cubes were carefully rinsed with water for several times. The extended reaction time was chosen to ensure a homogeneous and uniform PDA coating on each tetrapod. The tangled structure and the impossibility of colliding or moving the cubes during the process required a longer reaction time. Moreover, previous studies involving the coating or macroscopic surfaces keep the polymerization times up to 24h.[9,173]



Figure 48: Picture of the macroscopic ZnOT cubes with dimensions of 10 x 10 mm. SEM images of the ZnOT building the cubes.

The polymerization of DA was visible since the solution and the cubes' color started to get darker. After 3 hours, the first cube was carefully taken off the solution and rinsed with water. Subsequently, the rest of the cubes were removed and rinsed at their respective times. As can be seen in **Figure 49a**, as the reaction took longer, the color of the cube turned darker, from smooth grey (6 h) to dark grey (12 h) and finally, dark black (24 h).

Cubes were analyzed by SEM (**Figure 49b**), and in all of the cases, a lot of PDA particles/aggregates were revealed. Although each tetrapod has been covered with a PDA layer, this is far from homogeneous. As the time of reaction increases, so does the inhomogeneity of the cover. DA was over-polymerized on each tetrapod for all polymerization times, making larger aggregates covering each part. Moreover, it is also noticeable that DA has polymerized within the bulk, creating PDA aggregates/particles trapped inside the cube's intricate structure.

These two factors, PDA aggregates on the surface of the ZnOT and PDA aggregates caged inside the cube, both increased with longer polymerization times.



Figure 49: a) Pictures of ZnOT cubes after 6, 12, and 24 h DA polymerization. SEM images of the ZnOT after 6 h (second line), 12 h (third line), and 24 h (fourth line) polymerization.

5.2.1.2. Dispersed ZnOT

Parallel to the ZnOT cubes synthesis, we carried out another study with dispersed ZnOT. The aim was the same as with the cubes: to induce DA self-polymerization on the ZnOT surface and cover them with a homogeneous PDA layer.

Therefore, a preliminary synthesis was carried out where 10 mg of ZnOT was dispersed in 10 mL of Tris buffer (pH ≈ 8.5) followed by the addition of 10 mg of DA, and the mixture was stirred for 1h. Once the reaction was finished, the sample was rinsed with Milli-Q water.

A similar experiment was performed with an increased DA concentration, using 15 mg under the same conditions. Besides, both processes were replicated with an extended reaction time of 2h to examine the effect of the concentration and time on the final thickness of the ZnO.

Figures 50a and **50b** show the TEM images after 1h reaction with a DA concentration of 1.0 mg mL⁻¹; meanwhile, in **Figure 50c**, the corresponding histogram is displayed. As can be seen, the tetrapods were coated with a thick layer of PDA of about 27.6 ± 10.3 nm. Nevertheless, the over-polymerization of DA triggered the formation of PDA aggregates within the bulk, which were not removed after the washing procedure. Besides, it was not possible to see any tetrapod preserving its structure after the polymerization process, likely due to mechanical stirring. However, the arms did not break into pieces, maintaining their structure.



Figure 50: TEM images of ZnOT/PDA after 1 hour of reaction. a) and b) TEM images when [DA] = 1 mg mL⁻¹. c) Histogram of the PDA layer thickness when [DA] = 1 mg mL⁻¹. d) and e) TEM images when [DA] = 1.5 mg mL⁻¹. f) Histogram of the PDA layer thickness when [DA] = 1.5 mg mL⁻¹.

When the initial concentration of DA was increased up to 1.5 mg mL⁻¹, the results were similar (**Figures 50d** and **50e**), but this time, the coating PDA layer increased its thickness up to 51.3 nm \pm 15.9 nm (**Figure 50f**). The increment of the initial DA amount leads to thicker layers, which, as can be noticed in the TEM images, start to detach slightly from the surface of the arms.

This phenomenon finally happened when the time of reaction increased to 2h. In the case of $[DA] = 1.0 \text{ mg mL}^{-1}$ (Figures 51a and 51b), PDA covers of $34.6 \pm 10.1 \text{ nm}$ (Figure 51c) were created but, probably due to the effect of the prolonged time of reaction, they were detached from the surface of the ZnOT arms as it can be seen in the TEM images. The PDA cover was torn off from the arm without losing its structure.



Figure 51: TEM images of ZnOT/PDA after 2 hours of reaction. a) and b) TEM images when $[DA] = 1 \text{ mg mL}^{-1}$. c) Histogram of the PDA layer thickness when $[DA] = 1 \text{ mg mL}^{-1}$. d) and e) TEM images when $[DA] = 1.5 \text{ mg mL}^{-1}$. f) Histogram of the PDA layer thickness when $[DA] = 1.5 \text{ mg mL}^{-1}$.

Finally, when $[DA] = 1.5 \text{ mg mL}^{-1}$ (2h of reaction) (**Figures 51d** and **51e**), the PDA cover increased to its maximum of $139.6 \pm 96.9 \text{ nm}$ (**Figure 51f**). The PDA cover was detached from the destroyed ZnOT arm as in the previous situation. These findings show that ZnOT do not resist mechanical stirring in any situation. Moreover, the added DA amount and the reaction time were responsible for generating a large number of PDA aggregates, which could not be eliminated. Even with the PDA formation at the surface of the arms, the big layers created were very rough in all the situations with attached PDA aggregates, and as the time of reaction increased, the PDA layers were more likely to detach the arm.

To address the problem of broken tetrapods, we came up with an alternative mixing idea that eliminated the need for a stirrer. We designed a setup where the tetrapods were placed in a round petri dish attached to a thermoshaker (later will be improved). The thermoshaker speed was set up to 250 RPM, enabling the petri dish to describe circular movements where the contained solution could be mixed without a stirrer. This method reduced collisions to only between the tetrapods, which were not enough to break their structure; hence, ZnO tetrapods were preserved.

Using this method, a second series of syntheses was conducted. In these experiments, 100 mg of ZnOT was mixed with 110 mg of DA in 40 mL of tris buffer, varying the reaction time to 1 h, 3 h, 6 h, 12 h, and 24 h. After the reaction, the product washing was improved and carefully rinsed up to 7 times. The reaction times were selected to replicate the same conditions as the previous cube synthesis to further compare their performance in photocatalysis. The samples were named according to the polymerization time, thus ZnOT/PDA1h, ZnOT/PDA3h, ZnOT/PDA6h, ZnOT/PDA12h, and ZnOT/PDA24h.

Figure 52, displays the SEM images of the obtained ZnO/PDA tetrapods, which were able to preserve their structure. There were still a lot of PDA aggregates/particles in the bulk even after the improved rinsing. However, as the tetrapods are dispersed, PDA aggregates/particles are significantly lower than in the previous synthesis with the cubes (**Figures 52a**, **52b**, **52c**, **52d**, **52e**, and **52f**). Besides, for all situations, the PDA layer is smoother. These findings unveiled that the tangled structure of the ZnOT promoted the PDA over-deposition on the ZnOT surface. Besides, it banned the bulk-created PDA aggregates/particles from being removed from the sample when rinsed with water trapped within the tangled structure.



Figure 52: SEM images ZnOT/PDA after different DA polymerization times. a) 1 h. b) 3 h. c) 6 h. d) 12 h. e) 24 h. f) Detail of the PDA layer formed in the arm of one of the ZnOT after 24 h of DA polymerization.

5.2.1.3. Band gap calculations

Before its use in photocatalytic applications, their band gap was calculated using the Tauc plot method. The aim was to unveil how the PDA modifies the band gap values and to predict which composites will offer better photocatalytic behavior.

Firstly, the absorbance of ZnOT, ZnOT/PDA1h, ZnOT/PDA3h, ZnOT/PDA6h, ZnOT/PDA1h, and ZnOT/PDA12h, was measured (**Figure 53a**). As can be noticed, bare ZnOT presents a peak at 385 nm, which slightly broadens as the polymerization time becomes bigger (thicker PDA layer). However, the peak is no longer visible when the polymerization time reaches 6h. Finally, the Tauc plot method was followed to calculate the band gap. It is based on **Equation 10** where α is the energy-dependent absorption coefficient, h is the Planck constant, v is the frequency of the photon, E_g is the band gap energy, and B is a material-dependent constant. Finally, the factor γ is dependent on the electron transition nature; therefore, for a direct transition band gap, $\gamma = \frac{1}{2}$, while for the indirect transition band gap $\gamma = 2.[174]$

$$(\alpha h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g) \quad (10)$$

In the case of ZnO, $\gamma = \frac{1}{2}$ due to the direct transition band gap.[175] The energy of the photon, in eV, can be calculated by **Equation 11**. Moreover, the absorption coefficient can be related to the absorbance ($\alpha \approx Abs$). Hence, **Equation 10** can be rearranged to **Equation 12**.

$$E = h\nu = \frac{1240}{\lambda} \quad (11)$$
$$(Abs E)^2 = B(E - E_g) \quad (12)$$

By plotting $(Abs E)^2$ versus E, the Tauc plot is obtained. When a linear relationship exists, the electrons have enough energy to be excited across the band gap. Consequently, when $(Abs E)^2$ is equal to 0 at that linear behavior, it means that the material does not absorb any photons. Therefore, by extrapolating the linear range to the x-axis, it is possible to know the energy where the material begins to absorb photons, triggering the electron transition; hence, it is possible to unveil the band gap energy.

For our samples, and due to the wide absorption (**Figure 53a**), it was not possible to obtain the Tauc plot of ZnOT/PDA6h and ZnOT/PDA12h. Conversely, narrow peaks of bare ZnOT, ZnOT/PDA1h, and ZnOT/PDA3h allowed the calculation of the band gap energy (**Figure 53b**). Bare ZnO showed a band gap energy value of 3.11 eV. It decreased to 3.00 eV for ZnOT/PDA1h and experimented with a final decrease to 2.83 eV for the composite with the large time of polymerization (ZnOT/PDA3h).



Figure 53: a) Absorbance spectra for bare ZnOT and the obtained ZnOT/PDA samples with different PDA polymerization times. b) Tauc Plot of bare ZnOT, ZnOT/PDA1h, and ZnOT/PDA3h with the intersection with the x axis displayed.

This observed behavior can be related to the PDA layer. As the PDA layer becomes thicker, the energy decreases. The formation of point defects and charge transfer from ZnO to the PDA can explain the results.[176] Moreover, similar effects have been reported in Schottky-type junctions and acceptor-doped ZnO nanostructures; the electron transfer occurs from the ZnO to the layer or the doping agent[117] agreeing with the observed behavior.

5.2.2. Preliminary photocatalytic setup

During the synthesis process, it was clear that the ZnOT were too fragile to be placed in a cuvette and magnetically stirred. Thus, a holder was designed and printed using a 3D printer to overcome that issue. **Figure 54a** shows the holder placed inside the cuvette. It can be noticed that the holder has a mesh on which to place the ZnOT and does not reach the bottom of the cuvette, leaving some room for the magnetic stirrer to stir the solution. Since the holder blocked the incident light, and the ZnOT were placed flat on the surface of the mesh, the irradiation was redirected from above by using a parabolic mirror (Thorlabs) as can be seen in **Figures 54b** and **54c**.



Figure 54: a) Holder and its position inside the quartz cuvette. b) The cuvette with the holder is illuminated from above by reflecting the light in the mirror. c) Experiment in progress. ZnOT on the holder in a Rh6G solution is illuminated from above through the parabolic mirror.

A xenon lamp was used as an irradiation source (UV-VIS), and the parameters were settled to have an irradiation power density of 1 sun illumination (100 mW cm⁻²). As the average weight of the cubes is 36.2 ± 3.1 mg, further experiments included in this chapter were performed with 36.2 mg of sample to compare the results.

5.2.2.1. Temperature behavior

Their thermal response to light was investigated before studying the photocatalytic behavior of the ZnOT and ZnO cubes. Samples were placed in the holder and illuminated from above with 1 sun irradiation. The cuvette was filled with 3 mL of Milli-Q water, and the solution was gently stirred to simulate the photodegradation conditions. Due to the presence of numerous PDA aggregates/particles in the synthesized cubes/PDA, an additional synthesis was carried out, decreasing the polymerization time to 1h to avoid over-polymerization. Samples obtained after 1h and 12h of polymerization were used. The aim of selecting that range for both cubes and dispersed ZnOT, was to unveil if there was any difference between both extremes.

Thermal pictures of ZnOT/PDA 1h, ZnOT/PDA 12 h, and ZnOT were taken. **Figure 55a** shows the temperature increment in the case of ZnOT, **Figure 55b** for ZnOT/PDA 1h, and **Figure 55c** for ZnOT/PDA 12h. As can be seen, the temperature increment differences between them were almost negligible. The same behavior was observed for the cubes (**Figures 55d**, **55e**, and **55f**).

It is noticeable that the temperature increment was slightly higher for the PDA-covered samples. However, in both cases, this small increment can not be assigned directly to the PDA cover since the data is not reliable. The plots' variation and behavior in **Figure 55** unveil a non-orderer trend where the data hardly oscillates.



Figure 55: Temperature increment under 1 sun illumination. a) ZnOT. b) ZnOTPDA1h. c) ZnOT/PDA12h. d) ZnOT cube. e) ZnOT/PDA cube 1h. f) ZnOT/PDA cube 12 h.

Although the holder was used to place the samples, it did not improve the results' reliability and reproducibility. In the case of the cubes, when placed on the holder, the light only irradiates directly on one of the faces. Their faces did not have the same shape and size and neither did the same PDA polymerization grade. Additionally, in the case of dispersed ZnOT, most of them fell from the holder due to the movement of the stirrer. Moreover, the specific surface irradiated with the light is never the same, even if the tetrapods would not fall. These issues make the results untrustable and non-reproducible; however, since there is not any high increment of temperature for the PDA-covered samples, it clarifies that PDA does not have an impact on the temperature behavior of the samples.

5.2.2.2. Preliminary photocatalysis

Although the mentioned problems, a preliminary photocatalysis study was conducted. The objective was to unveil the PDA cover, which offered the best results. Consequently, the polymerization process will be improved later to obtain a more reproducible composite without PDA aggregates and with a smoother and homogeneous surface.

Initially, the photodegradation of the cubes was studied. ZnOT bare cubes and ZnOT/PDA after 3 h and 12 h of polymerization were compared during 2h of 1 sun irradiation (**Figure 56a**). Degradation was more effective for bare ZnOT cubes, reaching 70 %, than with the 3 h coated cubes (32 %) and 12 h coated cubes (45 %). After these results and due to the non-reliability and non-reproducibility method, it was decided to move forward with the dispersed ZnOT and discard the cubes.

Aiming ZnOT with less PDA aggregates and a smoother surface, a new synthesis of 0.5 h was carried out ($[DA] = 1.0 \text{ mg mL}^{-1}$). The photocatalytic behavior of these new ZnOT/PDA, ZnOT/PDA after 1h of polymerization, and bare ZnOT was tested in **Figure 56b**. No holder was used, so all the tetrapods were broken when they were placed in the cuvette and mechanically stirred. Bare ZnOT were able to degrade all the organic dye after 120 minutes meanwhile, the covered ZnOT/PDA offered a worse performance, 90 % of degradation when covered for 1h and 30 % when covered for 0.5h. Even though the degradation is higher, the trustability of the method is still questionable. ZnOT are too heavy and by gravity, they place themselves at the bottom of the cuvette. The magnetic stirrer, apart from breaking them, lifts the tetrapods in different ways and very poorly. Moreover, depending on the weight of the sample and the amount of undesired PDA aggregates the surface area that receives the incident light was variable and unpredictable.

Although the tetrapods fell from the holder, at this point, it was the only solution we had to fix the broken and inhomogeneous stir of the sample. To continue reducing the amount of PDA aggregates, another sample of ZnOT/PDA was synthesized ($[DA] = 1.0 \text{ mg mL}^{-1}$) (15 min).



Figure 56: Photodegradation experiments under 1 sun illumination. Assessment of Rh6G concentration in percentage. a) ZnOT cubes, ZnOT/PDA cubes after 6 and 12 h polymerization. Placed on the holder b) Dispersed ZnOT, ZnOT/PDA after 0.5 and 1 h polymerization. c) Holder, Rh6G, ZnOT, and ZnOT/PDA after 15 min polymerization. Placed, both ZnOT and ZnOT/PDA, on the holder. d) Comparison between ZnOT/PDA after 1, 5, 15, and 60 min of polymerization.

Surprisingly, in photocatalysis, results were similar to those of the uncovered ZnOT were obtained (**Figure 56c**). Consequently, additional syntheses of 1 and 5 min ($[DA] = 1.0 \text{ mg mL}^{-1}$) were conducted.

Subsequently, their photocatalytic response after 1 h of 1 sun illumination, using a holder, was compared to the already synthesized ZnOT/PDA of 15 and 60 min. **Figure 56d** shows that the best degradation was achieved by the 5-minute composite (50%), followed by the 1-minute composite (55%). Finally, the 15 and 60 minutes displayed a worse degradation than the bare ZnOT.

These results showed that the thinner layers were able to improve ZnOT's photocatalytic behavior. Nevertheless, the reduced time of synthesis does not guarantee the decrease of PDA undesired particles and aggregates presented in the sample. In fact, it does create a big issue. The compared weight for all of the samples in this chapter is the same (36.2 mg). However, except for bare ZnOT, the same amount of pure ZnO is not being compared since the PDA layer increases the weight and also does the PDA aggregates and dispersed PDA particles.

Although the obtained results are not representative nor reliable, several main points are clear to us. The best performance is probably achieved when the PDA layer is thin. Therefore, it is urgent to develop a synthesis procedure to obtain a thin, homogeneous, and smooth PDA layer, getting rid of all the PDA undesired aggregates and particles. In addition, it is also necessary to calculate the exact amount of ZnO in each sample to be able to compare the results in catalysis with the trustability of having the same amount of semiconductor. Finally, we need to design a photocatalytic setup where all the samples tested have the same conditions, and the structure of the tetrapods is preserved.

5.2.2.3. Preliminary piezoelectricity

Additionally, since ZnOT/PDA after 5 minutes of polymerization (ZnOT/PDA5min) achieved the best photocatalytic yield, it was studied if they could also degrade some organic dye in darkness. Most of our tetrapods in the sample are within the microscale. Hence, they have large, thin arms that could generate piezoelectricity when mechanically shaken.

A preliminary attempt was carried out for 36.2 mg of tetrapods placed on the holders. The solution was stirred to induce the movement of the ZnOT arms, thereby triggering piezoelectricity. The bare ZnOT and ZnOT/PDA5min performance were compared in dark conditions for varying stirring rates (0, 250, and 750 RPM) after 2 h (**Figure 57**). As can be seen, for both composites at all different stirring rates, the photodegradation remained below 20%. There is no substantial change between the different RPMs, and neither is there between the composites. However, it can be noticed that in the case of bare ZnOT (**Figure 57a**), the degradation is slightly lower than for ZnOT/PDA1 (5 minutes of polymerization) (**Figure 57b**).



Figure 57: Final [Rh6G] (%) after 2 h in darkness with 0 RPM, 250 RPM, and 700 RPM stirring rates. a) ZnOT deposited on the holder. b) ZnOT/PDA1 deposited on the holder.

These results do not indicate that the stirring does not move the tetrapods' arms and, thereby does not produce a piezoelectric effect. These findings show that the force is not enough to provide a noticeable catalysis improvement. Moreover, it was impossible to increase the stirring rate since that induced the tetrapods to fall from the holder. In addition to the conclusions explained in the previous chapter, it will also be necessary to develop a way to trigger the possible piezoelectricity of the composite.

5.2.3. ZnOT/PDA synthesis

To overcome the aforementioned problems, a new synthesis method was designed (**Figure 58a**). The setup was identical to the one already used before; however, a UV lamp was added. The round Petri dish attached to the thermoshaker described circular movements mixing the content of the dish and preventing the ZnOT from suffering harsh collisions (**Figure 58b**). Moreover, irradiating the sample with UV light (**Figure 58c**) is expected to activate the surface of the ZnO, thereby facilitating the deposition of the PDA layer.

In a round petri dish with a large diameter (15 cm), 100 mg of ZnO was dispersed carefully in 40 mL of tris buffer while the thermoshaker shook the petri dish at 250 RPM. Then, 110 mg of DA was added, and the sample was illuminated with the UV lamp at 365 nm. The reaction was carried out twice, obtaining ZnOT/PDA1 after 5 minutes and ZnOT/PDA2 after 15 minutes.

Then, the product was gently rinsed with water a minimum of 14 times and dried at 60 °C for 48 h. Following this drying period, the synthesized composites were stored in a dark environment for at least 1 week before their use in photocatalytic applications.

Figure 59, shows ZnOT/PDA1 and ZnOT/PDA2 SEM images. The PDA cover was successful for both composites, a homogeneous thin layer was obtained, and no PDA aggregates were observed in the final product. Besides, the most notable difference between ZnOT/PDA1 and ZnOT/PDA2 is that the PDA layer obtained for the first composite (**Figures 59a, 59b**, and **59c**) is smoother than for the second composite where it is possible to see smaller PDA aggregates attached to the structure (**Figures 59d, 59e**, and **59f**).

Finally, with this synthesis method, we were able to get rid of all the PDA aggregates, and it was also possible to obtain thinner and smoother layers with much fewer PDA aggregates at their surface, preserving the ZnOT structure. The ZnOT/PDA composites synthesis was optimized.

Nevertheless, before the photocatalytic experiments, a new photocatalytic setup needed to be designed to avoid the break of the structures and equal exposure to the irradiated light. Moreover, it was also necessary to determine the pure ZnO quantity in either ZnOT/PDA1 or ZnOT/PDA2 to carry out the photocatalytic experiments.



Figure 58: a) ZnOT/PDA synthesis scheme. b) Round petri dish attached to the thermoshaker. It is possible to observe that the liquid inside describes a circular mixing. c) Final setup where the UV lamp is placed above the petri dish and illuminates the sample with 365 nm light.

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Figure 59: SEM images of ZnOT/PDA1. a) Tetrapod. b) Core. c) Arm. SEM images of ZnOT/PDA2. d) Tetrapod. e) Core. f) Arm.

5.2.4. [Zn] determination by ICP-MS

The samples ZnOT/PDA1, ZnOT/PDA2, and an additional sample after 1 minute of polymerization (ZnOT/PDA1min) were analyzed by ICP-MS in collaboration with the group of prof Sergio Moya in the CICBiomagune in San Sebastián (Spain).

The ZnOT samples were dissolved by acids, causing ZnO to react, creating Zn^{2+} ions. Subsequently, this solution was vaporized and atomized into its elemental components, which are then ionized. Zn⁺ ions were formed and further determined by the mass spectrometer in the case of zinc.



Figure 60: Elemental Zn concentration (mg mL⁻¹) is plotted versus the time of DA polymerization of the three different samples. The calculated linear fit equation is displayed in the inset.

Figure 60 depicts the calculated data for the samples. The concentration of Zn is referred to the time of polymerization of the different samples: bare ZnOT (0 min), ZnOT/PDA1min (1 min), ZnOT/PDA1 (5 min), and ZnOT/PDA2 (15 min). These values were used to calculate each synthesized composite's weight to ensure the same amount of Zn was present.

5.2.5. XPS analysis

An X-ray photoelectron spectroscopy was carried out to determine if the DA was correctly polymerized on the surface of the ZnOT, forming a PDA layer. The content of zinc, oxygen, carbon, and nitrogen was analyzed for bare ZnOT, and ZnOT/PDA1 in collaboration with dr

Višnja Babačić from the Faculty of Chemistry of Adam Mickiewicz University, Poznań (Poland).



Figure 61: XPS spectra of ZnOT. a) Zn (2p). b) O (1s). c) C (1s). d) N (1s).

The results for bare ZnOT are displayed in **Figure 61**. Binding energies of 1021.46 eV and 1044.57 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively (**Figure 61a**). Moreover, the calculated difference of 23.11 eV between those bonding states suggests that the Zn might be in a +2 oxidation state.[177][178] Regarding oxygen, observed binding energies, in **Figure 61b**, of 530.07, 531.30, and 532.51 eV are compatible with O 1s signals. These binding energy values for Zn and O are comparable with the values found in the literature for ZnO NRs.[179] These findings are compatible with the structure of the tetrapods, which is formed by ZnO NRs conjoined by a central core. Binding energies of 284.80, 286.17, and 288.53 eV correspond to C 1s (**Figure 61c**) and indicate the presence of carbon in the sample. However, since there is

no signal for N 1s (**Figure 61d**), we can affirm that only the presence of carbon does not confirm the existence of PDA in the sample.

In contrast, more binding energies were found when ZnOT/PDA1 was analyzed. Regarding Zn (Figure 62a), binding energies of 1021.76 eV (Zn $2p_{3/2}$) and 1044.73 eV (Zn $2p_{1/2}$) were found. These values are similar to the values of the bare ZnO sample and can also be attributed to the presence of Zn^{2+} at the core level. However, additional values of 1023.26 (Zn $2p_{3/2}$) eV and 1046.39 eV (Zn 2p_{1/2}) were also found. These binding energies can appear due to a strong interaction between the ZnO surface and PDA. Polydopamine has amine and catechol groups that can create Zn-N and Zn-O bonds with the surface of the material, shifting the binding energy to higher values. This behavior has been observed for ZnO materials covered by polymers containing catechol where the electron-withdrawing nature of the catechol triggers the shift to higher binding energies. [83] Besides, in the case of O 1s (Figure 62b), observed binding energies of 530.40, 532.025, and 533.73 eV also shift to higher values compared to the uncoated sample. This can also be attributed to similar factors, such as the presence of adsorbed water at the surface of the ZnOT. Hydrogen bond acceptors exhibit increased binding energies at core levels; in this case, H₂O molecules could be hydrogen bonded to the surface oxygen of the ZnOT.[180] Regarding the two elements presented by PDA. First, the C 1s spectra (Figure 62c) present 284.8, 286.14, 287.34, 288.80, and 290.25 eV binding energies. These values can be attributed to a conjugated aromatic polymer like the PDA. The lower binding energy value at 287.30 eV might be due to the aromatic carbons and the rest of the higher binding energy peaks due to various oxidation states and because of the π - π stacking.[181] Secondly, in N 1s spectra (Figure 62d), the binding energy of 399.33 eV can be attributed to the C-N bonds in amines,[182] and the binding energy of 401.16 eV to the quaternary nitrogen.[183] These results prove that the PDA layer has been created covering the ZnOT.

This characterization method was carried out to analyze the correct polymerization of DA at the ZnOT surface with a successful result. However, these signals probably can unveil more knowledge about the interface constitution and the interactions between Au and PDA if analyzed deeply.



Figure 62: XPS spectra of ZnOT/PDA1. a) Zn (2p). b) O (1s). c) C (1s). d) N (1s).

5.2.6. Photocatalysis setup

Once the amount of Zn was determined for each sample and the polymerization of DA was proven, a new photocatalytic setup design was proposed since the mechanical stirring of the ZnOT was not an option (**Figure 63**). In this setup, the cuvette containing the composite and the organic dye was first sealed with parafilm and then attached via double-sided tape to a rotor. Subsequently, the light beam was directed to the center of the cuvette, as it is shown in **Figure 63**. By rotating the cuvette at 35 RPM and filling the volume of the cuvette, the composites and the solution were mixed, effectively preserving the tetrapod structure.



Figure 63: Photocatalytic setup. Pictures taken during a photocatalytic degradation using ZnOT/PDA1 as catalysts.

5.2.6.1. Photocatalysis and stability

Photocatalytic behavior of ZnOT, ZnOT/PDA1, and ZnOT/PDA2 were tested in the new setup where the parameters were established as follows: $[Rh6G] = 5.0 \ \mu g \ mL^{-1}$, $[Zn] = 2.5 \ mg \ mL^{-1}$, total volume 4 mL, 1 sun irradiation during 1h (data taken every 5 minutes). As depicted in **Figure 64a**, the bare ZnOT degraded 80% of the initial organic dye concentration in 1 h irradiation. In contrast, both PDA-covered ZnOT improved their performance. In both cases, after 1h of irradiation, the final concentration of Rh6G is negligible.

However, within the first 30 minutes, the degradation efficiency with the smooth PDA-covered composite (ZnOT/PDA1) was around 97%, much superior than with ZnOT/PDA2 (82%) and bare ZnOT (58%). ZnOT/PDA1 degradation showed a rapid initial degradation rate, depleting almost half of the initial concentration of Rh6G within the first 5 minutes and over 70% in the next 10 minutes. After the first 10 minutes, the degradation rate stabilized and constantly advanced to almost degrade everything within the first 30 minutes. This improved photocatalytic behavior is not observed in the other two samples, which, although they also exhibited a significant initial degradation, is not comparable with the efficiency shown by ZnOT/PDA1. These findings clearly indicate that ZnOT/PDA1 are the composites that achieved the best performance; hence, they will be used in further experiments.



Figure 64: a) Assessment of the [Rh6G] (%) during 1 h of 1 sun irradiation using ZnO, ZnOT/PDA1, and ZnOT/PDA2 as a possible catalyst. b) Assessment of the [Rh6G] (%) during 3 consecutive cycles of 1 h of 1 sun irradiation using ZnOT/PDA1 as the catalyst.

ZnOT/PDA1 reusability and stability in two additional consecutive cycles were tested. After each photocatalytic round, the composites were recovered by decantation and rinsed with water several times. Subsequently, the photocatalytic process started again with a fresh Rh6G solution and the recovered catalysts. In the next two cycles, the decrease in the photocatalytic yield was negligible for both of them (**Figure 64b**). Moreover, the sample was analyzed by SEM (**Figure 65**), unveiling that the ZnOT/PDA1 were stable and preserved their structure after the 3 photocatalytic cycles.

These results show that ZnOT/PDA1 exhibited an improved photocatalytic behavior, being able to degrade almost all the initial Rh6G concentration within 30 minutes of irradiation. Moreover, after 3 h of irradiation and 2 recovery processes, the composite remains stable and reusable with a negligible photocatalytic yield decrease.



Figure 65: ZnOT/PDA1 SEM images. a) Before photocatalysis. b) After 3 rounds of photocatalysis.

5.2.6.2. Reaction kinetics

The consistency of the degradation was studied toward additional Rh6G concentrations of 2.5, 7.0, and 10.0 μ g mL⁻¹ when [ZnO] = 2.5 mg mL⁻¹ (**Figure 66a**). The degradation followed the same trend as the previous experiments where [Rh6G] = 5.0 μ g mL⁻¹. The rates were consistent, and degradation occurred faster when the Rh6G concentration was lower, which became slower for the higher Rh6G concentrations. These values were used to study the kinetics of the reaction through the Langmuir-Hinshelwood method (**Equation 3**). This method has been widely used in literature to study the degradation of Rh6G by ZnO-based materials.[184–186] The plotted L-H equations for each concentration of Rh6G are displayed in **Figure 66b**. The correlated linear fits are shown in **Equations 13**, **14**, **15**, and **16**.

The consistency of the photocatalytic process is proven by plotting $1/K_{app}$ versus C₀ which shows a linear behavior (**Figure 66b**). Moreover, it is noticeable that K_{app} increases as Rh6G concentration decreases. This indicates that, as the catalyst concentration is equal, the degradation rate diminishes when the organic dye concentration becomes higher.

$$[Rh6G]_{2.5} \rightarrow ln\left(\frac{c_0}{c}\right) = (14.6 * 10^{-2} \pm 15.9 * 10^{-4}) t + (18.8 * 10^{-2} \pm 11.0 * 10^{-3}) (13)$$

$$[Rh6G]_{5.0} \rightarrow ln\left(\frac{c_0}{c}\right) = (9.2 * 10^{-2} \pm 75.8 * 10^{-4}) t + (21.3 * 10^{-2} \pm 7.7 * 10^{-2}) (14)$$

$$[Rh6G]_{7.5} \rightarrow ln\left(\frac{c_0}{c}\right) = (6.0 * 10^{-2} \pm 40.2 * 10^{-4}) t + (19.2 * 10^{-2} \pm 3.3 * 10^{-2}) (15)$$

$$[Rh6G]_{10.0} \rightarrow ln\left(\frac{c_0}{c}\right) = (4.6 * 10^{-2} \pm 21.1 * 10^{-4}) t + (11.3 * 10^{-2} \pm 2.8 * 10^{-2}) (16)$$



Figure 66: a) Assessment of the [Rh6G] (%) within 1 h or 1 sun illumination for initial concentrations of Rh6G of: 2.5, 5.0, 7.5, and 10.0 μ g mL⁻¹. b) Langmuir-Hinshelwood equation and linear fit for initial concentrations of Rh6G of: 2.5, 5.0, 7.5, and 10.0 μ g mL⁻¹. The calculated linear fit is adjusted to the first 25 minutes of reaction since the majority of the degradation is taken within that time interval. At the inset, 1/K_{app} versus [RH6G].

5.2.6.3. Photo(sono)catalysis

Hitherto, ZnOT/PDA1 showed an outstanding photocatalytic performance, not only in the yield but also in the stability and reusability of the composites. ZnO is an n-type semiconductor with a wide bandgap that presents significant piezoelectric behavior due to its non-centrosymmetric wurtzite crystal structure. In the particular case of ZnO tetrapods, their arms do present that phase. However, the connecting central core is not. A study about tetrapods shows that when they are pulled or compressed, the highest and lowest piezoelectric potential happens at this central core, which is influenced by the shape features of the tetrapod.[110] Taking advantage of these properties, we used them to induce an electric field in the composite to enhance the separation of photo-generated electron-hole pairs. Since the preliminary experiments where the magnetic stirrer was used to provoke piezoelectricity did not work, it was decided to move on and try to trigger piezoelectricity by using sounds.

5.2.6.3.1. Photo(sono)catalysis under low-frequency sonication

Due to the alleged fragility of the ZnOT, ultrasounds were not used at the beginning, avoiding the breakage of their structure. The sonophotocatalytic setup was composed of the rotor setup with identical experimental parameters except for the irradiation time, which was reduced to 30 min, and the source of sonic waves.

As a gadget to produce the sonic waves, two brand-new bone-transmission speakers were attached to both sides of the cuvette (**Figure 67a**). The speakers were in direct contact with the cuvette walls filled fully with the solution ($V_t = 4 \text{ mL}$). The contact speaker-quartz wall allows the transmission of the sonic waves directly to the aqueous media where the photocatalysis occurs. The aim is to try to induce a piezoelectric response while the light triggers the photoresponse. By combining both phenomena, as explained before, an enhancement in the degradation of Rh6G is expected.

The output power of the speakers was 3 W for all the experiments, and the sonic waves (sinusoidal waves) frequency was 10 and 15 KHz. Bare ZnO exhibited negligible degradation in darkness when 10 KHz was applied (**Figure 67b**). Similarly, ZnOT/PDA1, under both light irradiation and sonication (10 and 15 KHz), did not improve the catalytic behavior of ZnOT/PDA1 under irradiation without sonic waves (**Figure 67c**).

These findings show that the addition of sonication at this frequency and power is negligible in terms of Rh6G degradation for the PDA-coating composites. Only by using sonication is there no degradation; when combined with light, the behavior is similar with and without them. However, there is one situation in which the application of sonic waves significantly enhanced the degradation, shown in **Figure 67d**.



Figure 67: a) Speaker attachment to the cuvette. Assessment of the Rh6G concentration (%) during 30 minutes of catalytic experiments. b) ZnOT under sonication at 10 KHz. c) ZnOT/PDA1 under 1 sun irradiation and sonication at 10 KHz and 15 KHz, ZnOT/PDA under 1 sun irradiation. d) comparison of the performance of ZnOT with and without sonication at 10 KHz while 1 sun illumination.

Bare ZnOT, under 1 sun irradiation, achieved a final degradation of 50% after 30 minutes of 1 sun irradiation; however, when the light was combined with the sonication at 10 KHz, the degradation increased up to 85%. These results suggest that sonication indeed facilitates the charge carrier separation induced by the irradiation and decreases the recombination rate, thereby increasing photodegradation. Nevertheless, in the case of PDA-covered composites, due to their rigid PDA layer, probably, the sonic waves at that frequency and, more importantly, at that sonication power are not strong enough to "shake" the tetrapods inducing piezoelectricity. To prove this hypothesis, another setup that applies ultrasounds at higher sonication power was necessary.

5.2.6.3.2. Photo(sono)catalysis under high-frequency sonication

A new setup capable of reaching higher frequencies and output power was built. As depicted in **Figure 68**, the main component was a sonication cleaner with an output sonication frequency of 45 KHz and an output electrical power of 30 W.



Figure 68: High-frequency setup images while performing a ZnOT photo(sono)catalysis. The cuvette is submerged in water inside a sonication cleaner in addition to a gear system and a parabolic mirror. It is possible to rotate the cuvette while the sonication and the irradiation are applied to the sample.

Inside, the cuvette was placed horizontally in a mobile structure attached to gears capable of rotating the cuvette without hindering any of the faces. The light was directed perpendicularly to the cuvette walls by the parabolic mirror. Apart from that, the sonicator was filled with water until the cuvette wall nearest the mirror, leaving that cuvette face completely dry. Thereby, the light beam could reach one of the walls of the cuvette; meanwhile, the rest of the cuvette is submerged in water, where sonication occurs. During the reaction, the rotor moved the cuvette, allowing the tetrapods to be suspended in the solution while the sonication and the light were applied. In conclusion, with this setup, it was possible to combine the photo and piezo stimulation of the ZnOT and ZnOT/PDA1 at the same time.

As a result, by increasing the output sonication frequency up to 45 KHz from 10 KHz, the bare ZnOT improved its degradation efficiency (**Figure 69a**). The most notable change was within

the first 5 minutes of the reaction, which was able to degrade almost 60% of the concentration of Rh6G. Conversely, when covered with PDA, ZnOT/PDA1 efficiency experienced a slight increment much lower than bare ZnOT (**Figure 69b**).



Figure 69: Assessment of the Rh6G concentration (%) during 30 minutes of catalytic experiments. ZnOT under 1 sun irradiation. ZnOT under 1 sun irradiation combined with 45 KHz. ZnOT/PDA1 under 1 sun irradiation. ZnOT/PDA1 under 1 sun irradiation combined with 45 KHz.

These findings reveal that the photodegradation offered by ZnOT improves by increasing the frequency and power of the sonication. The application of light and sonication will probably unveil a combined effect in catalysis. Taking advantage of the tetrapod structure and the piezoelectric nature, its vibration could boost the separation of the already photogenerated charges and decrease the recombination rate. Hence, the catalytic depletion of the organic dye would be favored.

This effect is more noticeable with the uncovered tetrapods. A possible explanation could be that the PDA cover supplies more stability and rigidity to the composite, not allowing enough freedom to move, thereby producing less piezoelectricity. Moreover, the samples were examined by SEM after the photo(sono)catalysis (**Figure 70**). As observed for ZnOT (**Figures 70a**, and **70b**) it was possible to find some areas where the tetrapods were broken, probably because of the effect of the sonication. However, most of the sample preserved the tetrapod structure (**Figure 70c**). In contrast, for ZnOT/PDA1, there was not any area where the structure was not preserved (**Figures 70d**, **70e**, and **70f**).



Figure 70: SEM images after the high-frequency photo(sono)catalysis. a) b) and c) ZnOT. d) e) and f) ZnOT/PDA1.

We could not estimate how much of the bare ZnOT did break. Several trials using dynamic light scattering (DLS) were carried out to measure the hydrodynamic diameter of the composites, but none of them were successful. The reason is quite simple, the tetrapods are so big that they precipitate, making the measure unsuccessful. However, several trials were performed to change the solution of the sample to keep the tetrapods dispersed. Trials with PEG and PVP with different concentration levels (5%, 10%, 30%, and 50%) were carried out to add steric stabilization to the sample. Nevertheless, they were unsuccessful. On the one hand, lower concentrations do not retain the composites in suspension. On the other hand, tetrapods tend to create tangled structures. Due to the long arms, they typically gather between themselves, creating large aggregates, so they need a fluid media to detach from each other by the movement of the liquid. This is impossible in the concentrated samples, which obtain results with very large diameters that do not correspond to the diameter of the tetrapods but for the large macroscopic aggregates.
5.2.7. Summary

ZnOT/PDA composites were synthesized after a complex synthesis process developed to avoid breakage of the tetrapod structure. and the effect of the PDA cover in the band gap was studied through the Tauc plot method.

Moreover, two different samples were obtained with smooth (ZnOT/PDA1) and rough (ZnOT/PDA2) PDA cover. Their photocatalytic behavior was tested towards Rh6G under 1 sun illumination ([Zn] = 2.5 mg mL⁻¹, [Rh6G] = 5.0 μ g mL⁻¹, 100 mW cm⁻², 1h). As a result, the smoother composite (ZnOT/PDA1) degraded 97% of the organic dye within the first 30 minutes of irradiation, much higher than ZnOT/PDA2 (82%) and bare ZnOT (58%). The consistency of the reaction was tested with additional Rh6G concentrations of 2.5, 5.0, 7.5, and 10.0 μ g mL⁻¹ and the kinetics of the process were studied with the L-H method. This exhibited faster degradation when the Rh6G concentration was lower with higher calculated K_{app} values. Moreover, the stability and the photocatalytic yield after three consecutive cycles were also assessed, and no photodegradation yield decay was observed. After the cycles, the composites were examined by SEM exhibiting stable PDA-covered tetrapods.

Since the ZnO is a piezoelectric material, special setups were built to try to combine that with photocatalytic properties. The main idea was to trigger the piezoelectric response of the ZnOT/PDA1 nanocomposites by sonication meanwhile, the light irradiated the sample. We expected to induce an electric field in the composite, enhancing the separation of the photogenerated electron-hole pairs.

In the case of ZnOT/PDA1, the improvement was almost negligible. However, it worked for bare ZnOT. When sonication was not applied, degradation after 5 minutes of reaction was 17%. However, when an output frequency of 10 KHz was applied, degradation reached 23% within 5 minutes, but when it was turned to 45 KHz, degradation after 5 minutes increased up to 58%.

Finally, the structural stability of the composites after the photo(sono)catalytic experiments was examined by SEM, providing information about the possible breakable structure of the bare ZnOT when high-frequency sonication is applied, and the possibility form part of the PDA to offer mechanical stability. Subsequently, by using DLS, we tried to measure the size of the tetrapods, but we were unsuccessful after changing the solvent many times. It was not possible to keep the tetrapods in dispersion.

These findings suggest that the photocatalytic behavior of the ZnOT can be enhanced via sonication. In the scenario of ZnOT/PDA1, the PDA shell could supply rigidity to the composite, hindering the possibility of boosting the charge separation, which allegedly improves catalytic behavior. Nevertheless, the rigidity would preserve the tetrapod structure after high-frequency sonication is applied.

6. Conclusions and perspectives

A detailed AuNRs/PDA synthesis plan was developed to synthesize several samples with different structural and optical characteristics. First, six AuNRs samples with tunable transverse and longitudinal LSPR values, shapes, and sizes were synthesized by studying the influence of seed solution concentration and silver nitrate in the process. Secondly, the stabilization effect on AuNRs of two different molecular weights PEG (Mn = 800, and Mn = 6000) was tested before inducing DA polymerization at its surface. Finally, DA self-polymerization was induced at AuNRs surface, creating six different samples with different PDA shell thicknesses going from ≈ 4 nm to ≈ 30 nm with varying LSPR values. Here, by controlling the PDA thickness, it was possible to control the redshift of the nanocomposite under our requirements and exploit the interface towards photodegradation and photothermal applications.

AuNRs/PDA6, with the largest PDA shell thickness and longitudinal LSPR value (917 nm) offered the best photocatalytic performance. Subsequently, AuNRs/PDA6 underwent a complete study to unveil the processes at the interface between Au/PDA, which triggered the photodegradation process. The process consistency, stability, and reproducibility were studied through a three-round photostability experiment and several photodegradation reactions with varying organic dye concentrations. Moreover, the kinetics of the reaction were studied through the L-H method, and the TOC content determined the mineralization rate after 3h of photodegradation. Besides, the integrity of the nanocomposites was analyzed by TEM after the photodegradation. AuNRs/PDA6 were stable under all circumstances, offering consistent degradation rates. Finally, the temperature was assessed during these experiments, unveiling a possible thermal mechanism for the Rh6G depletion. Therefore, several experiments were designed to prove the hypothesis.

The source of irradiation was changed to a NIR laser exhibiting higher temperature rise but lower degradation. Thus, a set of experiments assessing the temperature increment and Rh6G degradation under NIR and UV-VIS irradiation with varying power densities going from 0.02 W cm⁻² to 2.5 W cm⁻² was carried out. Results showed that, although the effect of the temperature was not negligible, it was not the main force driving the photodegradation. Theoretical simulations shed some light on how the temperature increased at the bulk of the AuNRs/PDA6 solution, resulting in a macroscopic thermalization. EM losses and LSPR values were calculated based on the characteristics of the AuNRs/PDA6 nanocomposites, shape, size,

and different thicknesses of PDA. Results showed that the thicker PDA layers trigger higher light absorption and, even at low intensities, the nanocomposites induced a temperature increment on a global scale within 1h of irradiation. Moreover, due to that limited plasmonic enhancement and localized heating AuNRs could play another main function in the process. Therefore, it was suggested that AuNRs could produce hot electrons, which are then transported to the PDA surface, where they are available to carry out chemical reactions.

Subsequently, these hypotheses were confirmed by ft-TAS spectroscopy, which demonstrated that hot carriers are transferred from Au to PDA, reducing their recombination rate and promoting redox reactions at the PDA surface. The ultrafast thermalization observed before could compete with another ultrafast electron transfer channel to PDA where, eventually, the charge carriers are available to undergo redox reactions.

Finally, a ROS production study demonstrated that these hot electrons at the PDA surface created ROS that unleashed the photodegradation of Rh6G. The amount of hydroxyl radicals, superoxide anion, and holes produced under lamp and laser was determined and studied, unveiling a higher production of ROS under UV-VIS irradiation, explaining the superior photodegradation.

These findings exalt the applicability of AuNRs/PDA nanocomposites in both photocatalysis and photothermal applications. However, even though this research has shed light on how the Au/PDA interface behaves, there is still plenty of room for investigation. Electrochemical impedance spectroscopy can study the charge transfer processes, and the topographical changes can be analyzed by atomic force microscopy, for example. Additionally, apart from photocatalysis and photothermal applications, AuNRs/PDA nanocomposites appear to be an outstanding material with possible applications in biosensors or drug delivery systems.

Conversely, we successfully synthesized ZnOT/PDA composites with a homogeneous PDA cover. Moreover, two levels of roughness composites were synthesized and tested in photocatalysis. After choosing the composite that offered the best performance (ZnOT/PDA1), a complete study of the photocatalytic consistency and reproducibility was carried out. ZnOT/PDA1 were able to degrade the organic die totally during three consecutive photocatalytic cycles without losing any yield. Besides, their consistency toward different concentrations was tested. In addition, these data were further used to study the kinetics of the

reaction through the L-H method. After the photodegradation, the tetrapods' SEM stability was shown, allowing them to preserve their structure and the PDA layer.

Apart from taking advantage of the piezoelectric properties of the ZnO, several studies were developed to trigger the piezoelectric response and combine it with the proven photocatalytic properties. Different output frequencies and electrical powers were applied, low-frequency and high-frequency, unveiling some results in the catalysis.

When bare ZnOT were tested, a notable improvement in the degradation of the organic dye was observed for both frequencies. However, for the covered composite (ZnOT/PDA1), this improvement was not observed when low-frequency was applied, and it was negligible when high-frequency was applied. Both of the materials were examined after the photo(sono)catalysis. In the case of ZnOT/PDA1 all the tetrapods preserved the structure. In contrast, for bare ZnOT, even though most of the sample was unbroken, there were areas where the tetrapods were broken, probably because of the sonic waves.

These findings suggest that the photocatalytic behavior of the ZnOT can be combined with its piezoelectric properties by triggering them via sonication. The combination resulted in an improved catalytic behavior but only for the uncovered ZnOT. The possible reason for this phenomenon could be the rigidity that the PDA shell supplies to the composite, hindering the possibility of moving and boosting the charge separation that would allegedly be taking place in the bare ZnOT. However, that rigidity would protect the tetrapods from breaking.

From future perspectives, XPS signals can be analyzed deeply to better understand the interaction between ZnOT and PDA. The interface between ZnO and PDA has been studied before showing the construction of different heterojunctions with different schemes. Therefore, the possible heterojunction created in ZnOT/PDA1 might be studied and cataloged. Besides, we must develop a method to assess and quantify the number of broken tetrapods in each sample and if the sonication is the reason for the bare ZnOT collapse. Moreover, the possible reason why the ZnOT/PDA1 are not significantly improving the degradation is that the sonication power cannot vibrate the composite, and this does not trigger piezoelectricity. It is important to note that the 30 W is the electrical intensity of the device but not the sonication intensity that reaches the tetrapods inside the cuvette. Hence, it would be expected to ameliorate the catalytic properties if the sonic waves reached the tetrapods more intensely. Nevertheless, the results are promising since they unveil the ZnO's capability to combine the photo properties with the piezo

properties, improving the photocatalytic behavior by gathering them. Although there is some more work to do, these findings unveil a promising path in different applications like sensors, environmental remediation, and biomedicine.

Additional experiments aiming at understanding the effect of further and more complex composites based on PDA, could be important in exploiting the results presented here. For example, $TiO_2/PDA/AuNRs$ or other hierarchical composites. These structures could show a different behavior, whether conformally coated or partially (i.e., dumbbell), showing superior and more versatile applicability in biomedical and environmental applications. Thus, this is a topic that might be of further interest in the following years.

7. Annexes

7.1. Annex I. MXenes/PDA synthesis

As a part of a collaboration, MXenes/PDA were synthesized. $Ti_3C_2T_x$ Mxenes were covered with PDA to further conjugate the composite with anti-CEACAM1 Ab. $Ti_3C_2T_x$ -PDAantiCEACAM1 ab complexes were biocompatible and capable of selectively ablating the CEACAM1-positive melanoma cells using NIR irradiation. Thus, the synthesized MXenes-PDA-Ab complexes showed an outstanding potential to be applied in cancer therapy.[7]



Figure A1: MXenes, MXenes/PDA (1h) and MXnes/PDA (2h). a) TEM images. b) EDX mapping analysis. c) AFM and profile analysis of a MXene flake. d) SEM images and EDX analysis on the inset. Reprinted with permission from ref [7].

Synthesis was based on inducing DA's self-polymerization on the MXenes' surface. Two different samples were created after varying the time of polymerization 1 and 2h. Therefore, PDA NPs with average sizes within 100-200 nm were synthesized on the surface of the Mxene

flakes, changing their morphology after 2h of PDA deposition. This might be influenced by the creation of a conformal PDA layer over the MXenes because it is possible to observe in **Figure A1** the creation of a few micrometres of shapeless globules. This conformal PDA layer was confirmed by the detection of titanium, carbon, and nitrogen all over the MXene surface by EDX analysis (**Figure A1b**). Using AFM, the average lateral sizes of the flakes were found to be between 400 and 1000 nm with a thickness of around 1.5 nm (**Figure A1c**). Finally, the presence of carbon, oxygen, fluorine, chlorine, and titanium on MXenes was also confirmed by EDX (**Figure A1d**).

8. Supplementary information

Sample	PDA shell (nm)		Transversal LSPR (nm)		Longitudinal LSPR (nm)	
	Experimental	Theory	Experimental	Theory	Experimental	Theory
AuNRs	-	-	510	508	790	789
AuNRs/PDA3	4.1 ± 1.7	4	514	513	806	838
AuNRs/PDA5	12.2 ± 2.6	12	518	517	846	900
AuNRs/PDA6	30.4 ± 4.9	30	526	520	917	958

Table S1: Transverse and longitudinal LSPR values. Calculated and experimental



Figure S1: EM simulation geometric model. Reprinted with permission from ref.[6]



Figure S2: Calculated light absorption in Au and PDA. a) AuNR core. b) for the used lamp spectrum. c) with a total power of 20 mW and a focus diameter of 1 cm (**Figure S3**). The grey line shows the wavelength-dependent imaginary refractive index of PDA. Reprinted with permission from ref.[6]

The power of each wavelength is selected to reproduce the lamp spectral shape and total power for the calculations. The observed reduced absorption of Au (a) and the enhanced absorption of PDA (b) is due to the increased imaginary part of the refractive index of PDA near the lamp spectrum maximum (c).



Figure S3: Final-state calculations of heating close to the Au/PDA nanostructures. Calculated temperature increment on the surface of the PDA (30nm) when 520 nm light irradiation with transverse polarization (incident E-field normal to longitudinal NR axis), 20 mW power and varying focus diameters from 1 cm (< μ K temperature rise) to 1 μ m. At the inset, the local temperature distribution for the highest light intensity. Reprinted with permission from ref.[6]

Since the light intensities in these experiments are not enough to create considerable ultrafast heating in the nanostructures vicinity, to achieve discernible localized heating, the VIS light around tens of mW need to be focused on $10 \,\mu m$ spot sizes or even less. This is demonstrated here in the final-state calculations.



Figure S4: Time-domain simulation of macroscopic heating for the aqueous solution. a) this simulated system consisted of a quartz cuvette filled with 3 mL of water and the heat source. b) The time-resolved temperature rises of the liquid averaged over its entire volume. Reprinted with permission from ref.[6]

The simulation of the macroscopic heat transfer consisted in a quartz cuvette (Hellma analytics 101-10-40) on a thermoplastic surface (polyethylene) filled up with 3 mL of water and a dispersion of NRs (7 μ g mL⁻¹, \approx 40 * 10⁹ NR mL⁻¹). Besides, the light focus (either lamp or laser) was considered a cylindrical, macroscopic heat source within the water. Because of the low concentration, the NRs contribution to the thermal properties of water is negligible. Therefore, the faster thermalization times observed in the experiments are due to the magnetic steering of the solutions. In the main manuscript, the final-state calculations are shown for the same system and parameters.



Figure S5: TA color plots for samples under 400 nm, 500 nJ excitation. a) AuNRs. b) AuNRs/PDA. Reprinted with permission from ref.[6]



Figure S6: TA spectra at selected time delays under different excitation for AuNRs and AuNRs/PDA. Reprinted with permission from ref.[6]

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