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*Noncovalent nanohybrids graphene oxide/dye:*
*synthesis, spectroscopic, structural research and evaluation of their photocatalytic activity*

## ABSTRACT OF THE DOCTORAL DISSERTATION

Photocatalysis refers to the process in which light energy is used to drive chemical reactions. In general photocatalysis, although varying in details in terms of reactions and mechanisms, it can be described by main important steps: (I) light absorption; (II) transfer of electrons and holes between reactants; (III) separation of excited charges and (IV) utilization of charges for redox reactions. The long-lived photogenerated charges have the potential to promote different redox reactions. As far as photocatalysis is concerned, the light absorbing and/or catalytic units can be homogeneous molecules dissolved in $H_2O$ (or another medium). Under light irradiation, a molecular photocatalyst can be promoted to the excited state. The excited state of the photocatalyst can act as both a strong reductant and a strong oxidant which can drive redox reactions such as water splitting or $CO_2$ reduction. In reality, often light absorbing unit and catalyst are separate individuals. In that case charge transfer between the photoexcited sensitizer and catalyst is essential for high efficiency of the photocatalytic process. Efficient charge separation is the important challenge that need to be addressed before such homogenous photocatalytic systems can be used more widely. One of the concepts for overcoming the obstacle of inefficient charge transfer is to use mediator which would help to separate the charge and act as an electron transporter. Graphene oxide (GO) can act as such mediator, because of its unique properties, such as very good charge carrier mobility, formation of stable suspensions in aqueous media and the ability to be functionalized with various molecules. The covalent or non-covalent functionalization of graphene oxide with a dye leads to the formation of a dye/GO nanohybrid, which could find application e.g. in the processes of solar energy conversion. The occurrence of the photoinduced electron transfer in those nanohybrids is crucial for its potential application in photocatalytic systems. In order to determine the possible application of such nanohybrids in photocatalysis, it is necessary to fully characterize their spectroscopic properties since the adsorption of the dye on the GO surface could significantly affects its ground state and excited state properties. Moreover, it is of importance to determine whether photoinduced electron transfer occurs in such hybrids. To gain this knowledge it is necessary to conduct series of measurements using steady-state and time-resolved absorption and emission spectroscopy. In the literature there is a lack of detailed spectroscopic properties of such nanohybrids, including research on the mechanism of

energy/electron transfer from the excited molecule of the sensitizer to the GO sheet. These studies are necessary to understand in detail the spectroscopic properties of such nanohybrids, which will later affect the conscious and more effective design of nanomaterials with the desired properties.

Among a variety of organic dyes, porphyrins and xanthenes dyes are well known for their excellent photoactive properties. As planar, electron rich aromatic entities, they possess remarkably high extinction coefficient in the visible region, photoinduced electron transfer ability and have been widely used as photosensitizers in artificial photosynthetic devices. Therefore, those dyes and graphene oxide are attractive candidates to create new nanohybrid materials, preferably based on non-covalent interactions, which can be potentially used in solar energy conversion applications. The literature on dye/graphene nanocomposites still lacks comprehensive studies that combine detailed spectroscopic measurements (steady-state and time-resolved) with the characterization of materials' morphology and structure

In this doctoral thesis, noncovalent nanohybrids of graphene oxide were studied with the following dyes: *meso*-tetrakis(4-hydroxyphenyl) porphyrin (TPPH), *meso*-tetrakis(4-hydroxyphenyl) zinc porphyrin (ZnTPPH) and eosin Y. Series of steady-state and time-resolved absorption and emission spectroscopy measurements were conducted to characterize the interaction between the dye and graphene oxide sheets in the nanohybrid and to determine the energy/ electron transfer mechanism from the excited sensitizer molecule to the GO sheet.

In the first part of the work, comprehensive spectroscopic measurements were performed to investigate the interaction of graphene oxide with TPPH. Knowing that protonation of the imino nitrogens introduces the charge to the porphyrin molecule, the strength of the interaction between porphyrin and GO was compared at two different pH values (neutral vs acidic). Neutral porphyrin molecules were efficiently assembled onto the surface of graphene oxide sheets forming stable complexes. However, interaction of the same porphyrin with GO in acidic environment was found to be stronger which was attributed to the electrostatic interaction. By modifying only the pH, one can easily achieve a more efficient coupling of porphyrins with GO, resulting in a material with enhanced absorption in the visible range. The newly obtained material was characterized using various techniques, including elemental analysis, infrared spectroscopy, thermogravimetric analysis (TGA) which confirmed the successful noncovalent functionalization of graphene oxide sheets with porphyrins (TPPH) and determined the structure and morphology of the resulting new materials. Subsequently, the interaction between porphyrins in their ground and excited states with graphene oxide was thoroughly investigated using a range of spectroscopic methods. All of these techniques provided insights into the interaction of porphyrins with GO in both ground and excited states. Analysis of the steady-state and time-resolved absorption and emission data revealed that:

i) adsorption of the TPPH porphyrin on the GO sheets changes its UV-Vis spectra what constitutes a direct evidence of the interaction of the components in the ground state

*ii)* formation of the ground state complex between porphyrin and GO caused static quenching of the porphyrin emission,

*iii)* no dynamic fluorescence quenching took place

*iv)* fast quenching of the singlet excited state of the porphyrin adsorbed on the GO sheet occurred, which could be presumably attributed to the electron transfer process.

Moreover, methodology of conducting meaningful emission experiments in the presence of graphene type materials was demonstrated, emphasizing a correct approach to quantitative data analysis in such systems.

In the second part of the work, the interaction of ZnTPPH porphyrin with graphene oxide was investigated. The interaction of light with free ZnTPPH molecules and with ZnTPPH molecules adsorbed on graphene oxide sheets was probed via UV-Vis spectroscopy, fluorescence spectroscopy, femtosecond transient absorption spectroscopy and nanosecond flash photolysis. The experimental results were additionally supported by extensive theoretical calculations that included optimizations of the ground state structures of porphyrin and its complex with a molecular Lerf-Klinowski model of the GO. There were no prior studies that would focus on comparison of theoretical and spectroscopic results for the porphyrin/graphene-based materials.

It has been proven that an interaction between ZnTPPH and GO exists and the isolation of a noncovalent ZnTPPH-GO nanohybrid is possible. Moreover, time-resolved studies showed the occurrence of the electron transfer process from the singlet excited ZnTPPH molecule to the GO sheet as evidenced by detection of the transient absorption spectrum of the radical $ZnTPPH^{\bullet+}$. Comparison of the results from the first part of the work led to the conclusion that the interaction of metalloporphyrin ZnTPPH with graphene oxide is weaker than in the case of porphyrin TPPH.

The possibility of the photoinduced electron transfer process from TPPH and ZnTPPH porphyrin molecules to GO sheets led to hypothesis that the TPPH-GO and ZnTPPH-GO nanohybrids could be useful in solar energy conversion. However many attempts with different parameters were carried out, but no photocatalytic activity was demonstrated for these nanohybrids. This could be attributed to very efficient back electron transfer and thus no efficient charge separation in those systems. Further research is planned in the future to determine the factors influencing the rate and efficiency of back electron transfer in porphyrin/GO systems. The failure in the application of the studied hybrids in photocatalysis resulted in a change in the direction of the research which was subsequently focused on how the preparation of the graphene oxide suspension by sonication could affect the efficiency of the photocatalytic hydrogen production.

The last part of the work presents the influence of the morphology of graphene oxide, i.e. size and thickness of the flakes, on the efficiency of photocatalytic hydrogen production. Despite the fact that it is well accepted that graphene-based materials have the potential to boost the efficiency of photocatalytic hydrogen systems, the link between morphological properties of graphene-based materials (size and thickness) and photocatalytic performances has not been explored yet. Since there was no prior study that focused on the GO size and thickness selection, it was unclear whether those parameters actually matter in photocatalytic hydrogen production. The goal of this work was to fill this gap. For the research, a system in which the sensitizer was eosin Y, the catalyst was cobalt sulfate, and the electron donor was triethanolamine was applied. Graphene oxide was added to the system to increase the efficiency of the photocatalytic process. First of all, it was demonstrated previously by the A. Lewandowska-Andralojc group (*J.Phys.Chem. C, 2020, 124, 2747*) that for the system EY and GO in the presence of triethanolamine efficient charge transfer from the EY to GO occurs and therefore significant enhancement for hydrogen production in the presence of GO is observed. Subsequently, it was of interest to verify the hypothesis that the morphology of the GO does matter for its photocatalytic activity. To explore this the isolated fractions of graphene oxide differing in the size and thickness of the flakes were characterized using an atomic force microscope and a scanning electron microscope, and then used in the photocatalytic reaction. Interestingly it was found that too long ultrasound treatment decreased hydrogen production by 40% which was related to the fragmentation of GO flakes. The photocatalytic system produced the highest amount of $H_2$ when graphene oxide occurs as monolayers and the efficiency becomes lower with the decrease of GO sheets size. These studies, for the first time, clearly indicate a relationship between the morphology of graphene material and the activity of the photocatalytic system. The findings indicate the importance of controlling and optimizing the sonication time of GO prior to preparation of GO-based materials for photocatalytic applications. Observed effect of the morphology of GO dispersions on photocatalytic efficiency could be employed for other 2D-material based composites with various potential application.

The research presented in the doctoral dissertation was focused on the synthesis and spectroscopic characterization of the porphyrin-graphene-oxide nanohybrids with the ultimate goal of the detection of the photoinduced electron transfer process from the singlet excited state of the porphyrin to the graphene oxide sheet. The studies showed that by modulation the pH, which results in a change in the charge of the porphyrin molecule (protonation of the ring or substituents), it is possible to influence on the strength of the interaction of porphyrin with GO and the stability of the obtained material. The proper methodology of conducting meaningful emission experiments were demonstrated in the presence of graphene type materials including the choice of excitation wavelength and correction for GO absorption. It was also pointed out that the possibility to over-interpret the emission data with regard to intensity decrease being a proof of the electron transfer process between a dye and graphene. It was clearly shown that the decrease of the fluorescence intensity of the porphyrins in the presence of GO is solely attributed to the static quenching.

In addition, the research pointed to the importance of the optimization of the preparation of the graphene oxide suspension for photocatalytic research. Moreover, simple method based on UV-vis spectroscopy for monitoring efficiency of the exfoliation of the graphene oxide flakes in the aqueous suspension was demonstrated.