

# Self-assembly of porphyrin-based MOF photocatalysts in Pickering emulsions stabilized by graphene oxide

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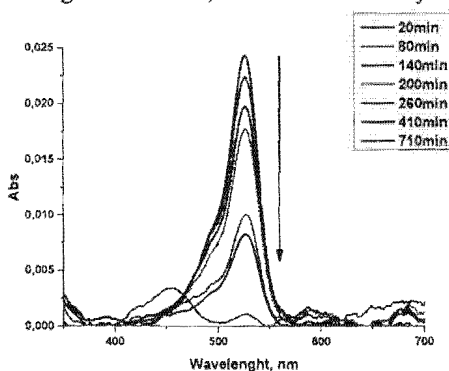
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Fabrication of efficient and ecologically safe catalysts for wastewater treatment and industrial waste is a demanding problem of modern chemistry. One of the most rapidly developing strategies for solving this problem is the use of visible light as very accessible and cheap source of energy for chemical conversion in combination of stable heterogeneous photocatalysts. Hybrid catalysts based on photoactive compounds and stabilizing inorganic matrix may be best candidates for this application.

Herein we used graphene oxide (GO) as a matrix and porphyrin metal-organic framework (MOF) as a photocatalytic unit. The GO-based colloids have significant sorption and catalytic activity by itself, so the synergy effect can occur.[1] *Meso*-tetra(4-pyridyl)-porphyrin and *meso*-di(4-pyridyl)-di(4-carboxyphenyl)-porphyrin were used as organic linkers, and zinc (II) acetate was used as metal source for the metal-organic framework component of the composite. The catalytic activity of zinc (II) porphyrinates is well known: it was used, for example, in organic synthesis reactions, photodegradation of aromatic compounds and water decomposition for hydrogen production [2,3].

We applied the emulsion synthesis technique to obtain the composite GO/porphyrin MOF catalysts. Two solvent systems were used: water/chloroform and DMSO/hexane for *meso*-tetra(4-pyridyl)-porphyrin and *meso*-di(4-pyridyl)-di(4-carboxyphenyl) porphyrin correspondingly. The structural characteristics and the morphology of the obtained materials were investigated using scanning electron microscopy and X-ray powder diffraction.

The model reactions of rhodamine-6G and 1,5-dihydroxynaphthalene (DHN) photobleaching were selected for evaluation of the catalytic activity of the obtained materials. It was found that the nature of porphyrin plays a key role in ensuring the catalytic activity of the hybrid material. While hybrid materials based on *meso*-tetra(4-pyridyl)-porphyrin do not exhibit any catalytic activity, materials containing *meso*-di(4-pyridyl)-di(4-carboxyphenyl)-porphyrin decompose solutions of rhodamine 6G (Fig.1) and 1,5-dihydroxonaphthalene under visible light irradiation, that was detected by UV-Vis spectroscopy.



**Figure 1.** UV-Vis spectra of the photobleaching of a solution of rhodamine 6G under visible light irradiation in the presence of the composite based on *meso*-di(4-pyridyl)-di(4-carboxyphenyl)-porphyrin MOF.

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