Size-selective hybrid photocatalysts based on porphyrin SURMOFs and graphene oxide

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Abstract. In this work, we report on a new method to synthesize new sponge-like photocatalytic materials comprising graphene oxide (GO) and zinc porphyrin complexes ordered into surface-attached metal organic frameworks (SURMOFs). To obtain the SURMOF/GO hybrids in a powdered form, we developed a one-pot synthesis of these materials in the GO-stabilized oil-in-water Pickering emulsions. The oxidized groups on the GO sheets promote the adsorption of metal clusters followed by anchoring of porphyrins to the surface of 2D carbon [1]. The results of experimental studies involving X-ray diffraction, UV-vis spectroscopy, BET nitrogen absorption, gas chromatography-mass-spectrometry and MALDI-TOF spectroscopy. The data suggest that these mesoporous SURMOF/GO hybrids can exploit two different mechanisms yielding different products of photocatalytic degradation of model organic compounds such as rhodamine 6G (Rh6G) and 1,5-dihydroxynaphtalene (DHN). The oxidation through photoinduced generation of singlet oxygen on porphyrin centres occurs in the presence of oxygen [2]. In anaerobic conditions, the catalysts can promote reduction by a direct electron transfer to the substrates in the SURMOF pores. Their size controls the efficiency of the anaerobic process. The SURMOF/GO with the pore size of 1.6 nm can transform both Rh6G and DHN, whereas the material with 1.1-nm pores is active only with respect to the small DHN molecules. The results provide a rational basis for the substrate-selective GO-based hybrid photocatalytic materials integrated with SURMOF components with tunable porosity.

1. Synthesis of hybrid photocatalysts based on porphyrin SURMOFs and GO

The application of hybrid materials based on GO as photocatalysts is of great interest, because GO has necessary optical transparency and a low Fermi energy level, which is needed for efficient separation of the photoinduced charge. The use of porphyrins as an organic component will expand the range of optical absorption in the visible region and use the intrinsic photocatalytic properties of porphyrins. The organization of porphyrins into metal-organic frameworks (MOFs) will make it possible to create selective photocatalysts by varying functional substituents and pore size.

New photocatalysts were synthesized from GO, zinc acetate as metal cluster and zinc porphyrins, either meso-tetra(4-pyridyl)porphyrin (ZnTPyP) or meso-di(4-pyridyl)di(4-carboxyphenyl)porphyrin (ZnDPyDCPP), by non-covalent self-assembly in Pickering emulsions. X-ray powder diffraction and BET nitrogen sorption methods confirmed the formation of SURMOFs with different micropore sizes of 1.1 nm for ZnTPyP - SURMOF1/GO and 1.6 nm for ZnDPyDCPP - SURMOF2/GO.

2. Study of photocatalytic activity

The activity of materials in the photodegradation of rhodamine 6G (Rh6G) and 1,5-dihydroxynaphthalene (DHN) based on SURMOF/GO was studied by UV-Vis spectroscopy. The photocatalysts initiate aerobic oxidative photodestruction with k up to 2.3×10^{-1} min^{-1} through generation of singlet oxygen ($^1O_2$) on porphyrin centers. Generation of $^1O_2$ was confirmed by analysis of the sample with Sensor Green. Under anaerobic conditions, these materials assist photoreduction of the same dyes in the SURMOF micropores. To confirm the mechanism of the reaction in an anaerobic area, a set of methods was used - MALDI-TOF, GC-MS spectroscopy and terephthalic acid probing. The size of the SURMOF pores controls the reduction, which occur due to the effective charge separation between porphyrin SURMOFs and GO. A large pore photocatalyst, SURMOF2/GO, can destruction both Rh6G and DHN, while SURMOF1/GO is active only against small DHN molecules.

The ability of the formed SURMOF/GO photocatalysts to use two mechanisms that give different photodegradation products creates the basis for obtaining new ambivalent photocatalysts for selective transformations of target compounds in molecular mixtures.

Acknowledgments

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References

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