XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

Photosensitization with porphyrins as a strategy to increase the light absorption of titanium dioxide (TiO_2) nanoparticles into the visible region

Alessandra N. S. Batista, Dayse C. S. Martins, and Marcelo M. Viana*

Chemistry Department, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, Brazil
*E-mail: alenayra.silva@gmail.com, marcelomachado@ufmg.br**

Thematic Area: Materials Chemistry

Keywords: photocatalysis, titanium dioxide, surface functionalization

Titanium dioxide (TiO_2) is a semiconductor widely used in heterogeneous photocatalysis studies. However, due to its wide band gap (3.0–3.2 eV), its application is restricted to the ultraviolet radiation region (100-400 nm), which makes the use of sunlight unfeasible. Therefore, photosensitization using porphyrins is a strategy that can be adopted to increase the absorption range to the visible region (400-750 nm), mainly due to the porphyrins' broad conjugated π system that allows good absorption in the visible region. Despite that, low stability of the obtained hybrid has been commonly observed, which makes the photosensitization process challenging and requires the study of new strategies that allow for obtaining a stable hybrid. Therefore, prior surface functionalization of the semiconductor with a coupling agent, such as organosilanes, becomes an alternative way to increase hybrids' stability by forming a "molecular bridge" between the porphyrin and the semiconductor. [1,2,3] In this work, a study was carried out on the photosensitization of a sample of titanium dioxide synthesized using the titanium tetrachloride precipitation method.[4] The surface of the TiO_2 nanoparticles was functionalized with the coupling agent 3-aminopropyltriethoxysilane (APTES) and, subsequently, sensitized with the porphyrin H_2T4SPP^{4-}.

The successive surface modifications were monitored using different characterization techniques. The insertion of APTES onto the TiO_2 surface was confirmed by infrared (IR), Raman, thermogravimetry, and energy-dispersive X-ray spectroscopy (EDS) techniques. The IR spectrum of the hybrid obtained showed bands referring to the Ti-O-Si, Si-O-Si, and C-N bonds, in the region of 750-1300 cm^{-1}, which are indicative of a covalent bond formation between the semiconductor and the organosilane, as well as the occurrence of its horizontal polymerization. Furthermore, TEM images showed the occurrence of vertical polymerization of the coupling agent. The immobilization of the porphyrin to the functionalized material was confirmed by diffuse reflectance UV-Vis spectroscopy, by Raman, and by calculating the loading. The absorption of light in the visible region for the obtained hybrid was confirmed by the appearance of the Soret (414 nm) and Q (500-600 nm) bands of the porphyrin in the diffuse reflectance absorption spectrum, evidencing the interaction between the porphyrin and the semiconductor from the formation of a type II heterojunction, which makes it possible to apply the material in heterogeneous photocatalysis studies using visible or UV light.

Acknowledgments: CAPES, CNPq, FAPEMIG, FINEP, LCPNano, CTNano, and INCT-CIMOL.

References

[1] Stepanova, A. *et al.*, ACS Omega, **8**, 44, 41664−41673 (2023).
[2] Ahmed, M. A. *et al.*, Journal of photochemistry and photobiology B: Biology, **176**, 25-35 (2017).
[3] Zhang, Y. *et al.*, Chinese Chemical Letters, **33**, 33-60 (2022).
[4] Almeida, A. I. A. R. *et al.*, Synthetic Metals, **269**, 116544 (2020).