SiO_2@TiO_2 and SiO_2@TiO_2-Prussian Blue core-shell photocatalysts for environmental applications

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Heterogeneous photocatalysis using semiconductor materials is regarded as a promising approach for environmental remediation as it can promote both organic pollutants photodegradation and photo-assisted heavy metal ions removal[1]. However, the overall efficiency of photocatalytic processes is still low and there is great interest in the development of highly active photocatalysts for such environmental applications. In this study, we report the preparation of enhanced nanostructured photocatalysts by the sol-gel synthesis of SiO_2@TiO_2 core-shell particles and their further modification with Iron Ferrocyanide (Prussian Blue or PB). SiO_2@TiO_2 particles were prepared by the grafting and controlled hydrolysis of titanium isopropoxide on the surface of silica particles in ethanol/isopropanol mixtures[2] and further modified with PB by photodeposition method[3]. Characterization by electron microscopy and XRD analysis evidenced the formation of the core-shell particles by coating of SiO_2 submicron spheres with porous TiO_2 shells constituted of anatase nanocrystals, while modification with PB was confirmed by FTIR, XRD and XRF elemental composition analysis. Photocatalytic behavior of the prepared materials was evaluated using Crystal Violet dye photodegradation and Cr(VI) photoreduction as probe reactions. SiO_2@TiO_2 particles exhibited superior photocatalytic activity for Crystal Violet degradation compared to unsupported TiO_2 nanoparticles of similar size, which is attributed to improved adsorption of dye molecules and better dispersion of the silica-supported anatase nanoparticles[2]. Additionally, Prussian Blue modified samples showed further enhanced photocatalytic activity for Cr(VI) reduction, achieving a 98% removal of hexavalent chromium for a 10mg/L Cr(VI) solution in deionized water (pH =5,6) after 1h exposure to UV radiation. Highest Cr(VI) removal efficiency was achieved in acidic media (pH 1-3) and using SiO_2@TiO_2-PB photocatalyst with 6% Fe loading. Presence of Cr(III) in treated solutions and used solid catalysts was confirmed by electron paramagnetic resonance (EPR). The photoactive behavior of SiO_2@TiO_2-PB material is based on the photo-reduction of PB to Prussian White (PW) triggered by interband photo-excitation of the TiO_2 nanoparticles. By acting as electron receptor and mediator, the PB layer promotes effective charge separation in the titania interface, thus resulting in increased photocatalytic reduction activity.

1. Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. ;*Water Res.* **2010**, *44*, 2997.

2. Ullah, S.; Ferreira-Neto, E. P.; Pasa, A. A.; Alcântara, C. C. J.; Acuña, J. J. S.; Bilmes, S. A.; Martínez Ricci, M. L.; Landers, R.; Fermino, T. Z.; Rodrigues-Filho, U. P. ;*Appl. Catal. B Environ.* **2015**, *179*, 333.

3. Tada, H.; Saito, Y.; Kawahara, H. ;*J. Electrochem. Soc.* **1991**, *138*, 140.

The authors would like to thank São Paulo Research Foundation (FAPESP) for financial support (grant#2013/24948-3)