

# Nanostructured Architectures Based on Metal Oxides with Direct Wide Band-gap for the Engineering of Photocatalytic Reactions

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## Abstract

Heterogeneous photocatalysis is an active area of research regarding the oxidation and mineralization of a wide range of organic pollutants present in waste waters. The illumination of a semiconductor (normally  $\text{TiO}_2$  or  $\text{ZnO}$ ) with radiation of energy equal or greater than its band gap generates electron-hole pairs ( $e^-/h^+$ ), which diffuse to the surface and react with adsorbed species promoting the degradation of the organic contaminants.

The undesirable recombination of the  $e^-/h^+$  pairs, the problems arising from the use of the photocatalysts as suspensions, and the need of an artificial irradiation source, are some of the limitations in photocatalytic processes. To overcome these issues, the present research work was focused on the development of materials with superior photocatalytic performance. This was achieved by increasing their absorption in the visible range, the use of glass supports for immobilization of the photocatalyst and the utilization of irradiation sources to simulate solar light.

In the first part of this work, glass raschig rings were coated with different types of  $\text{TiO}_2$ , namely Aeroxide® P25 (EP), anatase  $\text{TiO}_2$  from Sigma–Aldrich (SA), and  $\text{TiO}_2$  obtained from a sol–gel procedure (SG). The efficiency of the coating was evaluated on phenol degradation, in a recirculation reactor system, operating under simulated solar light irradiation.

Regardless the material tested, phenol degradation gradually increases with the number of TiO<sub>2</sub> layer coatings. SA-coated glass rings showed the highest efficiency for phenol degradation, but do lose activity when reused due to particle disaggregation from the support. Rings coated with EP were the most stable over 3 cycles. Their efficiency was evaluated by comparing the apparent first order reaction rate ( $r$ ) as a function of several operating conditions. The reaction conversion was mainly influenced by the initial phenol concentration, the number of TiO<sub>2</sub>-coated rings, the irradiation intensity and the hydrogen peroxide concentration. Also is minimally affected by the solution's flowrate. A kinetic model was developed for the determination of  $r$  as a function of the operating parameters.

The EP-coated rings were used for the treatment of a synthetic effluent consisting of a solution with a mixture of seven phenolic derivatives: protocatechuic acid, 4-hydroxybenzoic acid, 4-methoxyphenol, 4-hydroxyphenethyl alcohol, benzoic acid, gallic acid and phenol. A relationship between the extent of photocatalytic degradation and the activating/deactivating nature of the aromatic ring substituents was proposed.

In order to increase the TiO<sub>2</sub> photo-efficiency, hydration–dehydration (HD) and sol-gel (SG) methods were used to prepare TiO<sub>2</sub>/multiwalled carbon nanotube (TiO<sub>2</sub>/CNT) composites with different carbon contents using functionalized (CNT<sub>f</sub>) and pristine carbon nanotubes (CNT). The TiO<sub>2</sub> based materials were immobilized on glass slides by using the doctor blade technique. The photocatalytic activity of the films was tested in the degradation of methylene blue by near-UV to visible irradiation. Depending on the nature of TiO<sub>2</sub>, the composites containing different amounts of CNT evidenced distinct spectroscopic, morphological and textural properties. In addition, it was shown that the introduction of oxygen surface groups in CNT is crucial to prepare TiO<sub>2</sub>/CNT composites with high photoactivity, promoting the dispersion of TiO<sub>2</sub> particles and inducing the CNT action as a photosensitizer.

The composites prepared by sol-gel and using CNT<sub>f</sub> were tested in the photocatalytic degradation of 4 *para*-substituted phenols: 4-aminophenol, 4-methoxyphenol, 4-chlorophenol and 4-nitrophenol. A relationship between the Hammett constant of each *para*-substituted phenol compound and its degradability by photocatalysis was obtained. A beneficial effect of the introduction of CNT in the matrix of TiO<sub>2</sub> was mainly observed for the degradation of 4-aminophenol and 4-methoxyphenol.

Because of the beneficial effect of the introduction of CNT into the TiO<sub>2</sub> matrix, composites using graphene oxide (GO) and nanodiamonds (ND) as carbon phase were also synthesized and tested in the degradation of a cyanobacterial toxin, microcystin-LA (MC-LA), under both visible and

simulated solar light irradiation. It was noticed that the photocatalytic efficiency is different depending on the carbon phase, following the order: GO-TiO<sub>2</sub>-4 > ND-TiO<sub>2</sub>-15 > CNT-TiO<sub>2</sub>-4. The high photocatalytic activity of GO-TiO<sub>2</sub>-4 was attributed to the optimal assembly and interfacial coupling between the TiO<sub>2</sub> nanoparticles and the GO sheets that can effectively inhibit e<sup>-</sup>/h<sup>+</sup> recombination. Reaction intermediates of MC-LA photocatalytic degradation using GO-TiO<sub>2</sub>-4 composite were also identified by mass spectrometry LC/Q-TOF and LC/MS/MS, most of them resulting from the attack of hydroxyl radicals to the MC-LA molecule.

The effect of the introduction of carbon materials, namely nanotubes (CNT), nanofibers(CNF), nanodiamonds (ND), fullerene (C<sub>60</sub>) and graphene (FLG) on ZnO synthesized by chemical vapor deposition (CVD) was evaluated. The photocatalytic efficiency of the carbon/ZnO composites was tested in phenol degradation under simulated solar light irradiation. In general, the carbon materials enhance the efficiency of ZnO, and the composite containing nitrogen-doped carbon nanotubes (N-CNT/ZnO) showed the highest photocatalytic activity. Photoluminescence analysis confirms the presence of efficient electron transfer between the carbon phase and the ZnO. Both ZnO and N-CNT/ZnO show high stability after reuses.

A beneficial effect on photocatalytic activity was observed when noble metal (Au and Ag) nanoparticles were deposited on different ZnO materials. The best activity for phenol oxidation was obtained with the Au-loaded on ZnO samples produced by CVD (Au/ZnO-cvd), and by thermal decomposition of zinc acetate (Au/ZnO-t). The efficiency of the ZnO materials was influenced by the gold nanoparticle dimensions and by the irradiation wavelength used. In case of the Ag/ZnO materials the efficiency was related to the ZnO type and Ag load. The best activity was obtained with ZnO prepared by thermal decomposition of zinc acetate with 0.25 *at%* Ag (0.25% Ag/ZnO-t). Selective trapping of photogenerated holes and radicals by specific scavengers show that holes are crucial, but free radicals do also participate on the phenol photodegradation pathway.

Finally, the ZnO-t and 0.25%Ag/ZnO-t materials were tested in a mixture containing phenolic compounds (4-methoxyphenol, 4-chorophenol, phenol, and resorcinol), using a batch and recirculation reaction systems with the catalyst in powder form and immobilized on glass raschig rings, respectively. Faster conversion was obtained when Ag particles were present in the photocatalyst.