



**MESOPOROUS TITANIA DIRECTLY DOPED WITH TUNGSTOPHOSPHORIC ACID  
BY UREA-TEMPLATED SOL-GEL SYNTHESIS AS PHOTODEGRADATION  
CATALYST**

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Titania (TiO<sub>2</sub>) is considered as one of the most suitable semiconductors to be used as photocatalyst due to its negligible toxicity, relatively high chemical stability and low cost. The photocatalytic activity of titania can be affected by several factors, such as the crystalline structure, the specific surface area, the particle size, the *band gap* ( $E_g$ ) and the surface density of hydroxyl groups, among others. The hole-electron recombination and the low specific surface area are considered as the main factors leading to the low photocatalytic activity of TiO<sub>2</sub>.

Mesoporous titania has been firstly prepared through a sol-gel process using a phosphate surfactant, and then different ionic or neutral surfactants have been employed. Recently, we started to use organic compounds of low cost as pore-forming agents, such as urea, in order to obtain mesoporous titania with high specific surface area.

Keggin heteropolyacids have been added to TiO<sub>2</sub> suspensions or anchored by chemical interactions on the support surface, with the purpose of reducing the charge recombination.

In the present work, mesoporous titania directly doped with tungstophosphoric acid (TPA), obtained through reactions of the sol-gel type using urea as pore-forming agent, was synthesized. During the gelation step, alcoholic solutions of TPA were added, in order to obtain TPA contents of 0, 10, 20 and 30% w/w in the prepared material. Urea was leached with water and the obtained solids were thermally treated between 100 and 600 °C.

Mesoporous solids with a mean pore diameter ( $D_p$ ) higher than 3.1 nm were obtained. The specific surface area ( $S_{BET}$ ) decreased and  $D_p$  slightly increased with a higher TPA content.  $S_{BET}$  also diminished with increasing calcination temperature, in a lower extent for the higher TPA



contents. X-ray diffraction patterns of the solids doped with TPA only exhibited the characteristic lines of the anatase phase, which is stabilized due to TPA addition. The crystallinity and the crystal size increased for higher calcination temperature. The species mainly present in the solids is the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anion, as was observed by Fourier transform infrared spectroscopy. The *band gap* values estimated from the spectra obtained with UV-Vis diffuse reflectance spectroscopy are slightly lower than those reported for anatase.

The activity of the materials in the methyl orange photodegradation was evaluated. For low dye concentration, a pseudo-first-order reaction rate may be assumed. The values of the apparent reaction constant ( $k_{\text{ap}}$ ) increased when the calcination temperature was raised for the samples without TPA, which is attributed to a higher crystallinity and, as a result, the number of defects, where the hole-electron recombination could take place, would diminish. Samples doped with TPA led to a photocatalytic activity increase in the degradation reaction. The  $k_{\text{ap}}$  values increased for both calcination temperature and TPA content increase. The latter is indicative of the TPA role in the decrease of the recombination degree of the photogenerated charges. This fact would allow increasing the formation of reactive species (as  $^*\text{OH}$ ,  $\text{O}_2^{*-}$ ,  $\text{HO}_2^*$ ), considered as responsible for the substrate degradation. In addition, the activity increase can also be due to the decrease of the *band gap* values, which would lead to the absorption of radiation with a higher wavelength.