

Phosphor-doped Titania —a Novel Photocatalyst Active in Visible Light

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A novel phosphor-doped titania in an anatase phase colored yellow was prepared by a simple modified sol-gel method with hypophosphorous acid as precursor. The as-prepared P-doped titania shows a narrower band gap than pure titania and an absorption tail in the visible range, which results in its effective photocatalytic degradation of 4-chlorophenol under visible-light (>420 nm) irradiation.

The photocatalytic decomposition of pollutants in water and air has attracted much interest for decades.¹ Among various semiconducting materials (oxides, sulfides, etc.) most attention has been given to anatase TiO₂ because of its high photocatalytic activity, resistance to photocorrosion, photostability, low cost and nontoxicity. However, because of its large band gap of 3.20 eV, only the small UV fraction of solar light, about 2–3%, can be utilized. Therefore, many attempts have been made to modify the electronic properties of TiO₂ in order to extend its optical absorption edge into visible light, the main part of the solar spectrum. Different from the modification by metal complexes in most literatures, it was reported recently that anionic species (C, N, F, S, or B) doped titania was also responsive to visible light.^{2–7} For example, Zhao et al.⁷ reported that incorporation of B into TiO₂ can extend the spectral response to the visible region and that the photocatalytic activity is greatly enhanced as it is further loaded with Ni₂O₃. To the best of our knowledge, phosphor-modified titania responsive to visible light has not been reported until now. In the literature, Yu et al.^{8a} reported that phosphated mesoporous titanium dioxide prepared by incorporating phosphorus from phosphoric acid directly into the framework of TiO₂ shows large surface area, but its band gap is larger than that of pure TiO₂. Recently, Parida et al.^{8b} found that titania pillared zirconium phosphate and titanium phosphate showed greater activity towards photooxidation of 4-nitrophenol under solar radiation. However, they didn't distinguish the effect of UV and visible light both in the solar light, and no data about the red-shift in the optical absorption edge of synthesized photocatalysts had been given. Herein we report a novel photocatalyst, phosphor-doped titania, which is active in the photocatalytic oxidative decomposition of organic contaminants under visible-light irradiation.

P-doped TiO₂ was prepared by a simple sol-gel method referring to that of B-doped TiO₂ reported by Zhao et al.⁷ In the present paper, hypophosphorous acid was chosen as the precursor of phosphor. Typical synthesis procedure for P-doped TiO₂ is as follows: at first, 36 mg of hypophosphorous acid was dissolved in 50 mL of ethanol. The solution was stirred magnetically for 30 min, followed by the addition of 3.4 mL of tetrabutyl titanate and 3.4 mL of titanous chloride. Under anaerobic conditions (purged with H₂), the mixture was stirred for 2 h. NaOH solution (1 mol L⁻¹, 5 mL) was then added slowly to the solution in

an ice bath. After aged at room temperature for 2 days, it was stirred in a by water bath until gelation, and then dried at 110 °C for about 4 h in air to vaporize water and alcohol in the gels and then ground to fine powders to obtain xerogel samples. The as-prepared samples were calcined under nitrogen flow at temperature of 400 °C for 5 h with a heating rate of 1 °C/min. The yellow powders were washed repeatedly with water until no Cl⁻ ions could be detected by 1 mol L⁻¹ silver nitrate solution in the filtrate. The content of phosphor was about 1.3 wt % as tested by XRF. Pure TiO₂ was also prepared by the similar procedure without the addition of hypophosphorous acid.

X-ray diffraction analysis was used to investigate the changes of phase structure of the as-prepared pure and P-doped TiO₂ samples. As shown in Figure 1, the anatase phase is dominant in both of these two samples, but a small peak at around 31° also indicates the existence of a small amount of brookite. With the doping of phosphor, the peak intensities of anatase decrease and the width of the (101) plane diffraction peak of anatase ($2\theta = 25.4^\circ$) becomes wider, which might be due to the mixing with brookite 120 and 111 peaks. Considering the small content of brookite, another possible explanation is that the incorporation of phosphorus inhibits the grain growth of anatase TiO₂, because the BET surface areas of pure and P-doped titania are 67 and 137 m²/g, respectively.

The chemical states of P atoms incorporated into TiO₂ were studied with XPS using C1s peak assigned to residual organic

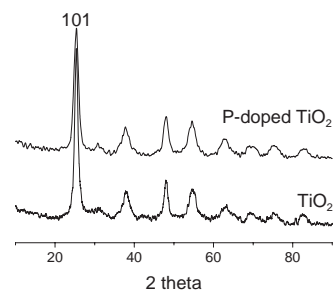


Figure 1. The XRD patterns of pure TiO₂ and P-doped TiO₂.

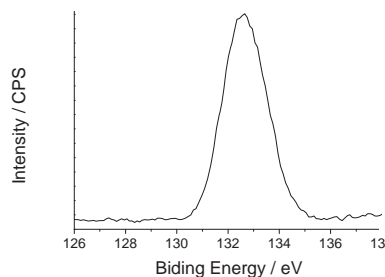


Figure 2. XPS spectrum of P 2p region of P-doped TiO₂.

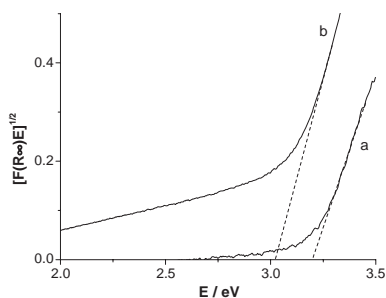


Figure 3. Diffuse reflectance absorption spectra of (a) pure TiO₂, and (b) P-doped TiO₂. Data are plotted as transformed Kubelka–Munk function versus the energy of exciting light.

species at 284.8 eV for the correction of the peak position. In the XPS spectrum of P-doped titania (Figure 2) a peak around 132.6 eV was observed. Compared to the binding energy of 133.8 eV of P 2p in a pentavalent oxidation state,⁹ it can be deduced that there must be some amount of P in lower oxidation state in the as-prepared P-doped titania. The XPS spectra of Ti 2p_{3/2} in pure and P-doped TiO₂ can both be fitted by only one peak at 458.5 eV, indicating the absence of Ti³⁺ in these two samples.

Compared with pure titania, the change in color of the P-doped TiO₂ demonstrates a profound effect on its optical response in the visible wavelength range, which can be confirmed by their UV–vis diffuse reflectance absorption spectra as shown in Figure 3. Obviously, P-doped TiO₂ shows a high tailing absorbance in the visible range and its band gap energy moves to 3.05 eV compared to 3.18 eV of pure TiO₂. On the contrary, Yu et al.^{8a} reported a phosphor-modified titania with P in a form of PO₄³⁻ had a band-gap larger than that of pure titania. Therefore, the narrowing of band gap of as-prepared P-doped titania might be resulted from the interaction of titania and phosphor in lower oxidation state as mentioned above. In the present paper, the source of phosphor employed is hypophosphorous acid and is different from the phosphoric acid adopted by Yu et al.^{8a} Our observation might accord with the recent results by Yates et al.^{10a,10b} and Martyanov et al.^{10c} who found that success in extending activity of TiO₂ into the visible range depends on the sources of nonmetals employed for doping. The absorption feature suggests that the as-prepared P-doped TiO₂ photocatalyst should be possibly responsive to the visible light.

Photocatalytic activities of pure and P-doped TiO₂ powders were evaluated by measuring the rates of 4-chlorophenol (4CP) decomposition in aqueous solution (2.5×10^{-4} mol L⁻¹, 100 mL) containing 100 mg of the photocatalysts. The concentration of 4CP was monitored by HPLC after stirring in darkness to secure the adsorption–desorption equilibrium. Figure 4 illustrates the photodegradation of 4CP under UV and visible light in the presence of pure and P-doped TiO₂. It can be found that the photocatalytic activity of pure titania was comparable to that of the P-doped titania under UV light irradiation. Differently, under visible light irradiation pure TiO₂ exhibits almost no activity, while in the P-doped titania system about 33% of 4CP is converted after 2 h of irradiation. The visible light source was a 150-W halogen-tungsten lamp (Phillips) equipped with a UV cut-off filter to remove the UV portion of the illumination (<420 nm). In addition, we found that in the presence of P-doped TiO₂, the pH value of the solution dropped after photocatalytic

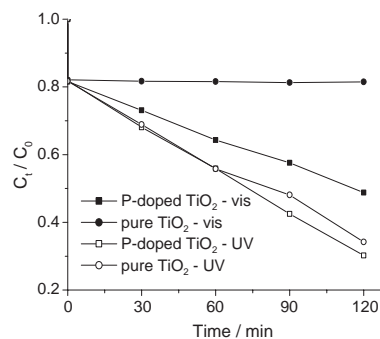


Figure 4. Temporal course of the photodegradation of 4CP (2.5×10^{-4} mol L⁻¹; 100 mL) in aqueous dispersions containing 100 mg of catalysts under UV and visible light irradiation.

reaction and CO₂ formation was also checked qualitatively by Ba(NO₃)₂ solution.

In summary, P-doped TiO₂ prepared by a modified sol–gel method exhibits a red-shift in the optical absorption edge from the undoped TiO₂ and an absorption tail in the visible range, which consequently induces the efficient photocatalytic degradation of 4CP under visible-light irradiation. We expect that the activity of P-doped TiO₂ will be further improved by optimizing its preparing conditions.

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