Multi-type carbon doping of TiO$_2$ photocatalyst

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Abstract

Carbon-doped TiO$_2$ nanoparticles in a pure anatase phase colored dark brown were successfully prepared using a convenient controlled nonhydrolytic sol–gel method followed by annealing at 400 °C. The UV–Vis diffuse reflectance spectra and X-ray photoelectron spectroscopy (XPS) indicate that substitutional and interstitial carbon atoms coexist in the lattice of TiO$_2$. The shift of photo response of TiO$_2$ from UV to near infrared region is responsible for the multi-type carbon doping by the formation of complex midgap states. The photo-initiated graft polymerization of methyl methacrylate (MMA) is also induced by the carbon impurities in the TiO$_2$ structure.

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1. Introduction

TiO$_2$ has been widely used as gas sensors [1], pigment [2], solar-energy conversion [3] and a promising photocatalyst for water and air purification [4–6], because of its high oxidative power, chemical stability, low cost, and nontoxicity [7]. Unfortunately, one severe disadvantage of the TiO$_2$ semiconductor material is the large band gap of 3.0 or 3.2 eV in the rutile or anatase crystalline phase, respectively and only absorbs the UV light which accounts for merely ~5% of the solar spectrum. Therefore, there have been many efforts to extend activity of TiO$_2$ into the visible region to improve utilization efficiency of TiO$_2$. One of the best-researched methods is to get the visible light response by dye-sensitization [8–11]. However, this method for more solar-energy harvesting is not suitable to decompose aqueous pollutants and wastewaters, since all of the known dye-sensitizers are toxic and in aqueous solution dye molecules will also be consumed in the photocatalytic process. The doping of TiO$_2$ is currently attracting considerable interest as a promising route to extend its optical absorption to the visible region [12]. This would allow the use of sunlight in photochemistry and photocatalysis with important fallout on the environment and economy. Doping with nonmetal atoms [13,14] in TiO$_2$ has been proved to be more effective than doping with transition metals [15], which suffers from a thermal instability, an increase of carrier trapping, or the requirement of an expensive ion-implantation facility [16]. Compared with doping with nitrogen [14,17,18], carbon-doped TiO$_2$ has not received the same attentions, although carbon-doped powders have been determined to be five times more active than nitrogen-doped TiO$_2$ in the degradation of 4-chlorophenol by artificial light (λ $\geq$ 455 nm) [19]. Among the several preparation methods of the carbon-doped TiO$_2$, it has been proved that the wet process synthesis has the excellent reproducibility and great applicability [19]. Because the wet process is controlled by the diffusion of carbon source [20], the using of different carbon sources is expected to have great effects on the carbon doping in the band structure of TiO$_2$, as well as its photocatalytic property.

Herein, we used a convenient controlled nonhydrolytic sol–gel method to prepare alkoxide-bonded TiO$_2$ nanoparticles. The whole reaction procedure between TiCl$_4$ and ethanol is simple without using any additional peptizing agent. After annealing at 400 °C, multi-type carbon doping of TiO$_2$ with pure anatase phase is obtained, which exhibits the photoactivity under sunlight illumination in the
photocatalytic graft polymerization of MMA. This will allow more effective utilization of sunlight as an energy source in the photocatalytic reaction of TiO$_2$.

2. Experimental

2.1. Chemicals

Titanium (IV) chloride (TiCl$_4$, chemical reagent grade), ethanol (EtOH, analytical reagent grade), methyl methacrylate (MMA, analytical reagent grade) and tetrahydrofuran (THF, analytical reagent grade) were purchased from Shanghai Chemical Reagent Company. MMA, EtOH and THF were purified by distillation and TiCl$_4$ was used without further purification. Degussa P25 with 75% anatase and 25% rutile was used for comparison purpose.

2.2. Synthesis of TiO$_2$ nanoparticles

In a typical preparation, 25 g TiCl$_4$ was slowly added to 100 g anhydrous ethanol under vigorous stirring at room temperature. The clear yellow solution was stirred at room temperature for 12 h and then dried at 100°C for 12 h to obtain the off-white powders. After these powders were calcined at about 400°C for 1 h in air in a muffle furnace without a gas flow, the dark brown TiO$_2$ nanoparticles were obtained.

2.3. Photocatalytic polymerization of MMA

A general photocatalytic polymerization procedure was carried out as follows: 5.00 g purified MMA, 0.10 g photocatalyst (the as-synthesized carbon-doped TiO$_2$ or Degussa P25) and 20.00 g distilled water were taken in a flask. The polymerization was carried out by exposing the flask to the diffuse radiation arriving through the window with continuous stirring for 10 h at room temperature from 7:00 to 17:00. The raw products were obtained by centrifugation of the reacted mixture. They were washed by water thoroughly to remove unreacted monomers, and then the polymeric products were dissolved in THF and washed for three times to remove the free polymer chains if they had formed in the experimental procedure. The eventual precipitates were dried at 60°C under vacuum for 12 h.

2.4. Characterization

The X-ray powder diffraction (XRD) pattern of the TiO$_2$ powders calcined at 400°C indicates the formation of pure anatase phase as shown in Fig. 1. The average grain size about 9.3 nm is determined from the Scherrer equation ($D = 0.9/\beta_{1/2}\cos \theta$). It has been confirmed that crystalline anatase generally exhibits a much higher photocatalytic activity than amorphous TiO$_2$ and even higher than rutile [21]. Therefore, the prepared nanoparticles have potentially good photocatalytic ability.

To investigate the carbon states in the TiO$_2$ photocatalyst, C 1s core levels were measured by XPS as shown in Fig. 2. There is only one peak at 284.6 eV for the TiO$_2$ powders annealed at 100°C. Four XPS peaks at 279.9, 284.6, 287.8 and 288.6 eV for the as-synthesized carbon-doped TiO$_2$ annealed at 400°C are clearly found, and the peak at 284.6 eV arises obviously from adventitious elemental carbon [22,23] because it also exists in pure TiO$_2$ sample [24]. Hashimoto et al. [25] prepared carbon-doped TiO$_2$ by oxidizing TiC and observed a C 1s XPS peak with much lower binding energy of 281.8 eV. They assigned this peak to Ti–C bond in carbon-doped TiO$_2$ by substituting some of the lattice oxygen atoms by carbon. Khan et al.

![Fig. 1. XRD pattern of TiO$_2$ powders after calcination at 400°C.](image)
[13] synthesized carbon-modified rutile TiO$_2$ by controlled flame pyrolysis of Ti metal and thought that the carbon substituted for some of the lattice oxygen atoms. However, Sakthivel and Kisch [19] prepared carbon-modified TiO$_2$ by hydrolysis of TiCl$_4$ with tetrabutylammonium hydroxide followed by calcinations at 400 °C and found the two kinds of carbonate species with binding energies of 287.5 and 288.5 eV. Kim and coworkers [24] only observed one kind of carbonate species in their carbon-doped TiO$_2$ samples with binding energy of 288.2 eV. These results suggest that the preparation method plays an important role in determining the carbon state in TiO$_2$ band structure. Not like the preparation methods mentioned above, we synthesize the carbon-doped TiO$_2$ via a controlled nonhydrolytic sol–gel method followed by the calcination at 400 °C. Therefore, the XPS peaks at 279.9, 287.8 and 288.6 eV for the carbon-doped TiO$_2$ are a result of the diffusion of the carbon atoms during the thermal treatment. And the carbon comes from the alkoxide residues after the controlled nonhydrolytic sol–gel method. Recently, a theoretical study about carbon-doped TiO$_2$ has performed by Di Valentin et al. to clarify the origin of the red shift of optical absorption edge of the doped TiO$_2$ [26]. They found that carbon impurities in TiO$_2$ band structure were expected to result from substitutional and interstitial carbon atoms, as well as multi-doping species. Furthermore, their calculations predicted an unexpected stabilization induced by multi-doping effects, which was interpreted as interspecies redox processes. According to our XPS results, the substitutional carbon atoms with the binding energy of 279.9 eV [25] and two kinds of interstitial carbon atoms with the binding energies of 287.8 and 288.6 eV [19] are clearly found, which is in accordance with the multi-doping of TiO$_2$ species predicted by Di Valentin et al. [26]. However, this kind of multi-type carbon doping of TiO$_2$ has not been found in experiments before. The multi-doping may induce the larger number of electronic states in the band gap and different optical activity compared with the observation in other carbon-doped TiO$_2$. The carbon content in the as-synthesized sample is also estimated by XPS to be about 1.03% and the ratio of carbon substituted for lattice oxygen atoms to carbonate species is about 1:5.

The synthesized TiO$_2$ powders exhibit off-white color when annealed at 100 °C and turn to dark brown when calcined at 400 °C. From the diffuse reflectance spectra given in Fig. 3, it is obvious that the TiO$_2$ powder annealed at 100 °C has practically no absorption at the wavelength longer than 400 nm. However, the TiO$_2$ sample calcined at 400 °C exhibits significant absorption in the visible region, in addition to the absorption band at wavelength below 400 nm. The optical behavior of our carbon-doped TiO$_2$ is similar with the result reported by Kisch et al. [19], as well as the very recent work of Khan et al. [20]. However, it should be pointed out that our samples absorb much larger light fraction from UV to near infrared region in excess of 950 nm and their samples only start absorbing at about 735 and 800 nm, respectively. This may be induced by the multi-type carbon doping, and therefore more complex midgap states are formed in TiO$_2$ band structure.

The heterogeneous photochemistry of TiO$_2$ has attracted more and more interests, which dealt with photocatalytic syntheses of organic compounds [27,28], initiation of polymerization [29,30] and the other photochemical reactions. We use the photo-polymerization of MMA under indoor sunlight irradiation to evaluate the photocatalytic activity of the carbon-doped TiO$_2$ powders in the visible region. Fig. 4 shows FTIR spectra of TiO$_2$ powders calcined at 400 °C and the product after photocatalytic polymerization. It is clearly found that besides the absorption band of pure TiO$_2$, the spectrum of the product after polymerization has the characteristic absorption bands of PMMA, such as significant peaks around 2920, 1222, 1158 and 1058 cm$^{-1}$, which correspond to C–H band, –CH$_2$ bond and C–O–C band of PMMA [31,32]. This indicated that the photocatalytic polymerization of the
monomer was successfully induced by these dark brown TiO$_2$ powders. From the FTIR spectrum, C=O bond in PMMA at 1720 cm$^{-1}$ is not found, which may result from the strong interaction between TiO$_2$ nanoparticles and C=O bonds. Because the product after polymerization has been carefully washed using the good solvent of PMMA (THF), it suggests that the polymer chains detected by FTIR spectrum were grafted on the surface of TiO$_2$ nanoparticles. It has been proved that the polymer chains were free when the polymerization reaction of the same monomers was initiated by traditional anatase TiO$_2$ under the UV irradiation [33]. This great difference may come from the formation of localized midgap states in carbon-doped TiO$_2$ and the detailed mechanism is not clear yet.

The products after the photocatalytic polymerization initiated by carbon-doped TiO$_2$ were further investigated by TGA and the results are showed in Fig. 5. And furthermore, the polymerization procedure with photocatalyst Degussa P25 was also carried out for comparison. The result indicates that the polymer component can hardly be detected when the reaction was initiated by Degussa P25. However, the formation of polymer is clearly found when carbon-doped TiO$_2$ nanoparticles are used as photocatalyst because the weight loss about 10% at 400–550 °C is derived from the degradation of PMMA. Therefore, the carbon-doped TiO$_2$ have an effective performance for the photocatalytic polymerization of the monomers compared with the undoped one. The more interesting thing observed from the TGA curve is the polymer begins to degrade at about 400 °C, which is much higher than that of traditional PMMA (below 300 °C). This is induced by the incorporation of TiO$_2$ nanoparticles and their strong interactions with polymer chains. So it can be concluded that the carbon-doped TiO$_2$ material as a photocatalyst can be excited by indoor sunlight irradiation and initiate the polymerization of monomers. The PMMA-grafted TiO$_2$ nanoparticles have potential applications to prepare polymer/TiO$_2$ nanocomposites as functional materials.

4. Conclusions

We have presented a convenient, novel and cost efficient method to prepare a high crystalline and visible-light-responsive nanosized dark brown TiO$_2$ photocatalyst. It was prepared via a controlled nonhydrolytic sol–gel process followed by the thermal treatment at 400 °C. These TiO$_2$ nanoparticles exhibit significant photo response from UV to near infrared region in excess of 950 nm, which results from the multi-type carbon doping and the subsequent complex midgap formation. The interesting photocatalytic graft polymerization of monomers can be initiated by this kind of carbon-doped TiO$_2$ under the indoor sunlight irradiation. This multi-carbon doping of TiO$_2$ would be beneficial to allow the more efficient use of sunlight in photocatalysis and photochemistry.

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References