



Annealing-free synthesis of C–N co-doped TiO₂ hierarchical spheres by using amine agents via microwave-assisted solvothermal method and their photocatalytic activities



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ABSTRACT

The annealing-free synthesis of C–N co-doped TiO₂ hierarchical spheres is proposed in this study. C and N were doped into the TiO₂ structure via a direct chelating process to the Ti-precursor by using different amine agents, including hexadecylamine (HDA), diethylamine (DEA), trimethylamine (TMA), and diethylenetriamine (DETA). C–N co-doped TiO₂ spheres (300 nm to 500 nm) composed of nanoparticles approximately 11 nm to 13 nm in size were obtained via an efficient microwave-assisted solvothermal reaction at 190 °C for 60 min. The effects of C and N doping by using different amine compounds on the bandgap energy and photocatalytic performance of TiO₂ were investigated. Among the amine compounds, DETA provided the highest chelating efficiency because it provides two primary amine groups, which resulted in the highest C and N doping concentrations and the largest degree of bandgap narrowing (2.77 eV); nevertheless, the high chelating ratio of C and N restrained the crystallization of TiO₂ and considerably decreased its photocatalytic activity. The use of TMA produced optimal C and N doping concentrations, which effectively reduced the bandgap of TiO₂ to 2.85 eV without affecting its crystallization. Its photodecomposition activity to rhodamine B was eightfold of that of commercial Degussa P25 powders under visible light irradiation.

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1. Introduction

Titanium oxide (TiO₂) has been given much attention because of its excellent photocatalytic depollution properties. Given the wide bandgap of TiO₂ (3.2 eV for anatase), its photocatalytic properties are only active under excitation by UV light, which occupies merely 3% of the solar spectrum. Accordingly, narrowing the bandgap of TiO₂ to enhance its absorption of solar light has been of much interest to researchers. The absorption edge of TiO₂ was successfully extended to the visible range by doping non-metal elements, such as C [1], B [2], S [3], and N [4]. Asahi et al. [5] found that the substitutional doping of N is effective in narrowing the bandgap compared with the substitutional doping of C, F, P, or S for O in the anatase TiO₂ structure. More recently, the C and N co-doped TiO₂ photocatalyst has been extensively studied. Chen et al. observed that C–N co-doped TiO₂ nanomaterials exhibit higher photocatalytic activities compared with singly C- or N-doped TiO₂; this high photocatalytic activity could be attributed to the synergistic effect of the doped C and N atoms [6,7]. Various

methods for the synthesis of N-doped TiO₂ nanoparticles have been proposed. Heat treatment under NH₃ flow [8] is often used to dope N into the TiO₂ structure; however, this method requires complex and expensive equipment, and controlling the N doping content in this method is difficult. In the past years, organic amine compounds are often applied as the complexing agents of Ti ions to control the shape of the TiO₂ crystallites [9,10]; however their resulting N doping effect was not examined. Recently, introduction of N into TiO₂ structure by adding organic amine compounds following the sol–gel process has been proposed [11–14]. Several studies have investigated the C or N doping effect of adding organic amine compounds on the TiO₂ materials. Majority of these investigations has shown that an extra thermal treatment is required to induce crystallization [12,13]. However, the annealing treatment often results in a sharp reduction in the N concentration because of the replacement of O for the doped N in the N-doped TiO₂, which consequently decreases TiO₂ photocatalytic activity [15]. Zhao et al. [15] successfully doped N into TiO₂ by incorporating a tertiary amine [trimethylamine (TMA)] to the hydrolyzed colloidal TiO₂ particles in ambient temperature. In this study, N was doped through the direct amination of TiO₂, and doping concentrations as high as 8% were achieved. However, the amount of the added

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amine agent was considerably excessive (the volume ratio of TMA to Ti-isopropoxide (TIP) was as high as 370–1500), which resulted in a relatively high synthesis cost. Cong et al. [16] synthesized N-doped TiO₂ nanoparticles via the microemulsion-hydrothermal process (120 °C for 13 h) by using different amine agents as the N source. They also found that TMA is more effective in improving the photocatalytic efficiency of TiO₂ compared with urea, thiourea, and hydrazine hydrate [17]. Very recently, Bao et al. [17] used several small-molecule amines for the preparation of N doped TiO₂ nanoparticles and found that the alkyl amines provided better doping efficiency comparing to the alcohol amines.

Although TiO₂ nanoparticles have attracted much attention because of their highly active surface area, which provides excellent photocatalytic efficiency, the nanoparticles are often dispersed and suspended in water, thereby making them difficult to reuse and even causing secondary pollution. Submicron- to micro-scale TiO₂ with a nanocrystalline framework is considered to be a good choice for photocatalytic applications because it overcomes the problem in terms of nanoparticle recycling. Zhu et al. [18] have investigated and indicated that the anatase mesoporous submicron spheres showed excellent photocatalytic activities comparing to commercial P25 attributed to its higher specific surface area, strong light harvesting capability and lower recombination rate of photogenerated carriers. Chen et al. [19] suggested an effective method that involves the use of hexadecylamine (HDA), which is an organic amine compound, as a structural conducting agent for TIP hydrolysis. Well-shaped TiO₂ spheres ranging from 320 nm to 1150 nm were obtained. With this method, mesoporous TiO₂ spheres were obtained via a solvothermal reaction at 160 °C for 16 h followed by calcination at 500 °C for 2 h. Li et al. successfully prepared C–N co-doped TiO₂ nanoparticles by heating ammonium titanyl oxalate at 250 °C [20], thereby indicating that the doping process can be achieved by directly heating the C–N containing Ti-precursor. In the current study, a time-effective and annealing-free synthesis method to obtain C–N co-doped TiO₂ spheres is proposed. C and N can be directly doped into the TiO₂ structure at the molecular level with relatively high modification efficiency via the direct chelating reaction of amine compounds with the TIP. Four different organic alkyl amines, namely, HDA, TMA, diethylamine (DEA), and diethylenetriamine (DETA), which belong to different molecular levels of amine structure, were used to directly dope C and N into the TIP precursor. Among these amine agents, HDA was particularly applied as the structural conducting agent for all samples to induce the formation of N-doped TiO₂ spheres. Moreover, a microwave reactor was used in the solvothermal process, which reduces the reaction time to 60 min with no further calcination treatment, instead of the typical reaction in a stainless autoclave in a conventional oven. Given the proposed method, hierarchical C–N co-doped TiO₂ spheres (in the submicron scale) were obtained. The submicron spheres exhibited remarkable band-gap narrowing by using a relatively small amount of dopants. The doping effects of the different types of amine agents are investigated and discussed. Through the photodecomposition of rhodamine B (RhB) under visible light, the photocatalytic activity of the prepared C–N co-doped TiO₂ spheres was considerably improved compared with the that of the commercially available Degussa P25 powder.

2. Experimental

2.1. Synthesis of C–N–TiO₂ photocatalysts

C–N co-doped TiO₂ was synthesized following the process proposed by Chen et al. [19] with modifications. In the first step, 1 mL of TIP was added to 8.45 mL of pure isopropanol, and the mixture was stirred for 10 min to ensure complete dissolution. DEA, TMA, and DETA were added to the TIP solution with a fixed N/Ti molar ratio of 0.9. The amount of the added amine agent was calculated based on the

number of amino groups in each of the amine compounds. Given that the DETA molecular structure provides three amino groups, its volume was divided by three. The mixture was stirred for 60 min to complete the chelating reaction. The hydrolysis rates of the amine-modified TIPs were examined by adding a fixed amount of deionized water to produce an H₂O/TIP molar ratio of 3 in the solution. For the unmodified TIP, precipitation occurred within 10 min to 15 min. However, the amine agents stabilized the hydrolysis rate of TIP because the precipitation was delayed from 12 h to 48 h for the amine-modified TIP. This observation implies the occurrence of the chelating reaction between the selected amine agents and TIP. The modified TIP solution was then incorporated into a 38 mL KCl aqueous solution and HDA. The molar ratio of TIP:HDA:KCl:H₂O was controlled at 1:1:5.5 × 10⁻³:3. In the presence of HDA and KCl, precipitation immediately occurred except in the solution prepared with DETA. DETA remarkably stabilized the hydrolysis and condensation reactions of TIP. Neither precipitation nor gelation occurred even after aging for 14 days. When the doping ratio was reduced to N/Ti at 0.45, precipitates formed within 5 min. Therefore, only one doping ratio (i.e., N/Ti = 0.45) was prepared for the sample with DETA as the doping source. The mixture was then placed in a static environment for 18 h to complete the hydrolysis and condensation reactions as well as the sphere-formation process. Given that HDA also contains an amino group that may cause N doping to TiO₂, the synthesis with unmodified TIP was also conducted for comparison. The preparation process was the same, and the sample was labeled as N(0). The as-obtained precipitates were washed thrice with deionized water to remove the unreacted compounds and then redissolved in ethanol at 70 wt.% for the following solvothermal reaction. The suspension was transferred into Pyrex® tubes at a fixed filling ratio of 60%. A microwave synthesizer (Discover SP, CEM) was used to perform the solvothermal reaction at 190 °C for 60 min, and the working pressure was set to about 300 psi. The as-obtained yellowish powders were again washed thrice with ethanol and then dried at room temperature overnight.

2.2. Characterizations

X-ray diffraction (XRD) was performed using a powder X-ray diffractometer (Siemens D5000) for the phase identification and estimation of the crystalline sizes according to the Scherrer equation. The morphologies of the products were observed via scanning electron microscopy (SEM, Hitachi SU 8000). The optical absorption spectra were obtained using a UV–visible absorption spectrometer (S3100, Scinco) in diffuse-reflectance mode with an integrating sphere. X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha) was performed to determine the molecular bonding structure. The Braunauer–Emmett–Teller (BET) specific surface areas of the C–N co-doped TiO₂ spheres were measured according to the adsorption and desorption isotherm curve of nitrogen at 77 K, which was obtained using Beckman Coulter SA3100.

2.3. Evaluation of photocatalytic activity

The photocatalytic performances of the prepared N–TiO₂ spheres were evaluated via the photodegradation of RhB. N–TiO₂ powders (0.02 g) were dispersed in a 20 mL RhB aqueous solution (5 ppm) with continuous stirring for 2 h in the dark to reach the adsorption–desorption equilibrium between N–TiO₂ powders and RhB. Visible light irradiation was applied to the suspension by using eight LED tubes (8 W) at 420 nm wavelength and with constant stirring. At a given time interval, 2 mL of the RhB solution was extracted from the top of the suspension after short gravity settling for a few minutes. To avoid the scattering effect caused by the slight amount of dispersed nanoparticles in the RhB solution, the suspension was filtered through a 0.2 μm membrane filter. The absorption spectra of the RhB solution was measured in transmission configuration by using a custom-made UV–visible absorption spectrometer equipped with a xenon lamp and a CCD detector. After the measurements, the extracted solution was poured back to keep the reaction volume of the RhB solution constant. The RhB concentration as a function of irradiation time was estimated according to the integrating area of the absorption peak at 420 nm to 600 nm. To compare the photoactivity of the samples, Degussa P25 TiO₂ powder was used as a reference.

3. Results and discussion

The SEM images of the prepared powders are shown in Fig. 1. The images indicate that the morphologies of the synthesized products were spherical with sizes of approximately 500 nm to 1 μm. The images, under a relatively high magnification (Fig. 1, inset), show a hierarchical structure that is comprised of nanoparticles. The XRD patterns (Fig. 2) confirm that the products were crystallized in the pure TiO₂ anatase phase (JCPDS 21-1272) except for the DETA sample. The addition of DETA considerably stabilized the TIP precursor. These results imply that the chelating rate between DETA and TIP is remarkably high, thereby resulting in poor

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