A fluorine free method to synthesize nitrogen and lanthanum co-doped TiO₂ nanocrystals with exposed {001} facets for enhancing visible-light photocatalytic activity

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ABSTRACT

This study introduces a simple and fluorine free route to synthesize nitrogen and lanthanum co-doped TiO₂ nanocrystals with exposed {001} facets through one-step hydrothermal method. The microstructure, chemical composition, and photocatalytic property of the co-doped TiO₂ nanosheets were analyzed using XRD, FESEM, TEM, XPS and UV–vis. The experimental results indicated that N had been successfully doped into TiO₂ lattice, while La was likely to form a binary nanocomposite with TiO₂. The co-doped TiO₂ nanosheets showed an additional visible light absorption band starting from 400 nm, which could improve the visible light photocatalytic activity of the sample. As the shape-controlling agent, DEA plays a crucial role in the formation of {001} facets. N and La co-doping could produce a synergistic effect. N doping can narrow the band gap of anatase TiO₂ and increase the utilization efficiency of visible light, while La doping can enhance the separation efficiency of photo-induced electrons and holes. N and La co-doped TiO₂ nanosheets exhibited higher visible light photocatalytic activity compared with P25, N doped TiO₂ nanosheets and N, La co-doped TiO₂ nanoparticles with the same doping concentration. In addition, N and La co-doped TiO₂ nanosheets showed well recycling performance.

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1. Introduction

A lot of efforts have been made in recent years to develop oxide semiconductor photocatalysts with excellent activities for environmental protection, such as water purification, water disinfection, air purification, and hazardous waste remediation [1–8]. Among various oxide semiconductor, TiO₂ has been considered as the most promising photocatalyst for widespread environmental applications due to its chemical stability, high oxidizing capacity, non-toxicity and low cost. However, because of the large band gap (3.2 eV), TiO₂ can only absorb a small proportion of the solar spectrum in ultraviolet region. To shift its absorption edge to the visible light region, many works involving surface modifications, compounds, metal and nonmetal doping have been proposed in the last few years [9–12]. Generally, nonmetal doping (such as N and C) can produce an energy level above the valence band. The presence of such energy levels resulted in an narrowed band gap and an additional absorption in the visible light region.

Another reason impeded the practical application of TiO₂ is its low quantum yield, which is due to the fast recombination rate of photogenerated electron–hole pairs. Rare-earth metal ions doping (like La, Ce) is one of the typical approaches to reduce the recombination rate of electron–hole pairs, and thus can enhance interfacial charge-transfer efficiency [13,14]. Therefore, doping with both nonmetal and metal ions could not only improve the visible light absorption of TiO₂, but also slow down the recombination rate of photoinduced charge carriers, and thus enhance the photocatalytic activity [15,16].

The surface free energy of the facets in anatase TiO₂ crystals has been calculated to be: 0.90 J/m² for {001} > 0.53 J/m² for {100} > 0.44 J/m² for {101} [17,18]. It has been demonstrated that the high energy {001} facets show the most active photocatalytic properties. However, owing to the higher energy, {001} facets usually diminish quickly during the crystal growth process [19]. Recently, anatase TiO₂ crystals exposing a high percentage of {001} facets were synthesized using a capping agent or a co-capping agent containing HF [20–26]. Later, other fluorine and amine capping agents such as NH₄F [25], NH₄HF₂ [27], BF₄[−] [28], and amine [29,30] were utilized to instead of HF. Despite these successes, highly corrosive and toxic fluorinated compounds have been employed in the

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synthetic process of TiO_2 crystals with high-energy facets. Furthermore, it was difficult to remove F^- from exposed $\{001\}$ facets due to the strong interactions between F^- and $\{001\}$ facets of TiO_2 . Therefore, it becomes increasingly necessary to develop a fluorine free method to prepare anatase TiO_2 crystals with exposed high energy facets.

Herein, we report a simple and fluorine free hydrothermal method to synthesize nanosized and highly dispersed nitrogen and lanthanum co-doped TiO_2 crystals with exposed $\{001\}$ facets. Diethanolamine (DEA) was used as nitrogen doping source and $\{001\}$ -facet-controlling agent. The co-doped TiO_2 nanosheets present high photocatalytic activity under visible light irradiation.

2. Experimental

2.1. Photocatalyst synthesis

All chemicals used were of analytical grade and were purchased from Beijing Chemical corporation (Beijing, China) without further treatment. Distilled water was used in all experiments. Nitrogen and lanthanum co-doped TiO_2 nanosheets (N,La- TiO_2 NSs) with dominant $\{001\}$ facets were synthesized through a hydrothermal route using titanium tetraisopropoxide (TTIP), diethanolamine (DEA), and $\text{LaCl}_3 \cdot n\text{H}_2\text{O}$ as precursors and sources of N, La, respectively. Details of the synthetic process are as follows [31]: 1.8 mL (6 mmol) of TTIP was added dropwise to an 80 mL mixture of tetrabutyl ammonium hydroxide (TBAH) (40 mL, 160 mmol), DEA (40 mL, 400 mmol) and $\text{LaCl}_3 \cdot n\text{H}_2\text{O}$ (0.016 g) at 2–5 °C. The transparent solution turned gummy white, indicating the formation of a complex. The gummy precipitated solution was stirred for 5 min. It was then transferred into a 100 mL teflon-lined autoclave. The autoclave was sealed and kept at 225 °C for 12 h, then cooled naturally to room temperature. The resulting reaction mixture was centrifuged and the obtained white-colored TiO_2 precipitation was washed several times with distilled water and ethanol. The product was dried under vacuum for 48 h at 60 °C. In order to remove the organics adsorbed on TiO_2 surface during the synthetic process, the sample was treated by ethanol and HCl (0.1 M), and then calcinated in the air at 400 °C for 2 h. The sample without the addition of $\text{LaCl}_3 \cdot n\text{H}_2\text{O}$ (N- TiO_2 NSs) was also prepared. For the purpose of comparison, N,La- TiO_2 nanoparticles (N,La- TiO_2 NPs) were prepared by the same experimental conditions excepting using triethylamine instead of DEA.

2.2. Characterization techniques

The crystalline phase of the synthesized samples were determined by X-ray diffraction (Phillips PW 1050-3710 Diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operated at a tube current of 40 mA and a voltage of 45 kV. Data were collected over 2θ values from 20° to 80°, at a scan speed of 4°/min. The morphology observation was performed on an S-4800 field emission scanning electron microscopy (FESEM, Hitachi, Japan) linked with an Oxford Instruments X-ray system, analysis was performed at accelerating voltage of 10 kV. The surface morphology and particle size were observed by high-resolution transmission electron microscopy (HRTEM, JEM-2011), with an accelerating voltage of 200 kV. The UV–vis diffuse reflectance spectra were obtained using a PerkinElmer Lambda 750S UV/vis spectrometer equipped with an integrating sphere assembly. The spectra were recorded at room temperature in air from 250 to 600 nm. X-ray photoelectron spectroscopy was performed using a PerkinElmer RBD upgraded PHI-5000C ESCA system with monochromatic $\text{Mg-K}\alpha$ excitation and a charge neutralizer was used to investigate the surface electronic states of the samples. All the bonding energies were calibrated to the C 1s internal

standard peak (284.8 eV) of surface carbon. The BET specific surface area and pore volume analysis of the samples were determined using a N_2 physisorption technique, the samples were degassed at 180 °C overnight before the actual measurement.

2.3. Photocatalytic activity measurements

The photocatalytic activity of the sample was evaluated by the degradation of rhodamine B (Rh B, 10 mg/L). A xenon lamp (Trustech, PLS-SXE300) with UV cut-off filters ($\lambda > 420 \text{ nm}$) was used as visible light source. The distance between the strip lamp and fluid level was kept as 15 cm. The lamp was cooled with flowing water in a quartz cylindrical jacket around the lamp. The photocatalyst (0.05 g) was added to a 200 mL quartz photoreactor that contained aqueous solution of Rh B (100 mL). The mixture was stirred for 120 min in the dark until the adsorption–desorption equilibrium, and then the residual concentration of dye was measured. The above suspension was stirred during the irradiation. At given time intervals, about 4 mL of the suspension was sampled, the photocatalyst was removed from suspension by a centrifugation. The concentration of Rh B in supernate was analyzed by using a Cary 100 UV/vis spectrometer.

3. Results and discussion

3.1. Phase structures and morphology

The XRD analysis was used to characterize the phase structures of the samples. Fig. 1 shows a comparison of XRD patterns of N- TiO_2 NSs, N,La- TiO_2 NPs and N,La- TiO_2 NSs. Both anatase and rutile phase were detected in N,La- TiO_2 NPs. In contrast, only anatase was found in N- TiO_2 NSs and N,La- TiO_2 NSs. This difference is mainly due to the fact that DEA molecules prevent the phase transition from anatase to rutile. The phase transition of TiO_2 proceeds by rearranging octahedral units under hydrothermal conditions [32]. The affinity of DEA molecules to TiO_2 in aqueous solution plays an important role in the phase transformation. The weaker affinity of the molecules is, the easier rearrangement of TiO_6 octahedra is [32]. Therefore, the strong affinity of DEA molecules restrains the structural rearrangement, and subsequently inhibiting the phase transformation. A detailed analysis shows that XRD peak intensity of N,La- TiO_2 NSs is stronger than that of N,La- TiO_2 NPs, and the width of anatase characteristic of diffraction peaks is narrower than that observed for N,La- TiO_2 NPs, suggesting the formation of larger TiO_2 crystallites in N,La- TiO_2 NPs.

The (101) and (200) diffraction peaks were used to determine the anatase lattice parameters of the doped TiO_2 [32]. The calculated cell parameters of N- TiO_2 NSs and N,La- TiO_2 NSs: ($a = 3.783 \text{ \AA}$, $c = 9.477 \text{ \AA}$) and ($a = 3.784 \text{ \AA}$, $c = 9.484 \text{ \AA}$), respectively, are slightly different compared with the cell parameters of pure anatase TiO_2 ($a = 3.785 \text{ \AA}$, $c = 9.514 \text{ \AA}$), indicating that N was doped into lattice of TiO_2 . In addition, there is no peak that can be ascribed to La oxides,

Fig. 1. XRD patterns of N- TiO_2 NSs, N,La- TiO_2 NPs, and N,La- TiO_2 NSs.

Fig. 2. FESEM (a and b) and TEM (c and d) images of N,L a-TiO₂ NPs (a and c) and N,L a-TiO₂ NSs (b and d) (the inset shows the corresponding HRTEM (high resolution TEM image) and SAED (fast Fourier transform) pattern).

this is because the content of La₂O₃ is little and cannot be detected, or La³⁺ are incorporated into the crystal lattice of TiO₂.

DEA was chosen as the capping/shape-controlling agent because DEA can stabilize the {001} facets of TiO₂ through H-bonding [31]. Such H-bonding onto {001} facets of TiO₂ can inhibit the growth along {001} and therefore exposed the thermodynamically unstable {001} facets. Fig. 2 shows FESEM and TEM images of N,L a-TiO₂ NPs and N,L a-TiO₂ NSs. It can be seen that N,L a-TiO₂ NPs is spherical with particle size of 20–40 nm (Fig. 2a) and there is absence of {001} facets. The SEM image of N,L a-TiO₂ NPs indicates that one-step hydrothermal method without presence of DEA can synthesize nanocrystalline TiO₂ but without the exposed {001} facets (Fig. 2a). Fig. 2b shows SEM image of N,L a-TiO₂ NSs, which is cube-shaped with the exposure of {001} facets. The side length of the nanosheets is in the range of 30–50 nm. It is necessary to compare the morphology of DEA-capped TiO₂ nanosheets with traditional F-capped TiO₂ crystals. F-capping is generally realized using HF, the shape of the synthesized TiO₂ crystals is either truncated tetragonal bipyramids primarily with exposed {101} facets or sheets mainly with exposed {001} facets depending on the quantity of HF used in the synthesis [8,24,32,33]. A higher quantity of HF produces nanosheets due to the efficient capping of {001} facets [22–24,34,35]. The sizes of the truncated tetragonal bipyramids are in the range of 1–3 μm, whereas the sizes of nanosheets are in the range of 10–1000 nm (length) and 3–260 nm (thickness) [22–24,34,35]. Fig. 2c and d shows the TEM images of N,L a-TiO₂ nanoparticles and nanosheets. It is worth noting that the N,L a-TiO₂ NPs are aggregated into spherical particles (Fig. 2c), but N,L a-TiO₂ NSs present as regular nanosheets mainly with exposed {001} facets (Fig. 2d). They are in good agreement with SEM analysis. The above SEM and TEM results indicate the presence of TiO₂

nanocrystals with exposed {001} facets after addition of diethanolamine and tetrabutylammonium to TiO₂ precursor using the one-step hydrothermal method. From the inset of Fig. 2d (HRTEM and SAED), it can be indicated that the top and bottom facets of the nanosheets were the (001) planes, the high-resolution TEM image directly showed that the lattice spacing parallel to the top and bottom facets was ~0.235 nm, the SAED pattern can be indexed as the [001] zone axis diffraction, which indicates that the top and bottom surface of the anatase TiO₂ NSs are highly reactive {001} facets.

3.2. BET surface areas and pore size distributions

N₂ adsorption–desorption isotherms were used to determine the specific surface areas and pore size distributions of N,L a-TiO₂ NSs and N,L a-TiO₂ NPs (see Fig. 3). These isotherms (Fig. 3a) can be classified as type IV according to Brunauer–Deming–Deming–Teller (BDDT) classification, and the hysteresis loops suggest the presence of mesopores (2–50 nm) [36]. N,L a-TiO₂ NSs and N,L a-TiO₂ NPs exhibit quite different N₂ adsorption isotherms (Fig. 3a), implying the differences in their porous structures. First, the isotherm of N,L a-TiO₂ NSs is below that of N,L a-TiO₂ NPs, indicating lower surface area (108.37 m² g^{−1} for nanosheets, and 123.42 m² g^{−1} for nanoparticles) and pore volume of the former. Second, the hysteresis loop for N,L a-TiO₂ NSs is significantly shifted in higher relative pressures, indicating larger mesopores in N,L a-TiO₂ NSs in comparison to those in N,L a-TiO₂ NPs.

The maximum of the pore size distribution (PSD) curve (Fig. 4b) is about 10 nm for N,L a-TiO₂ NPs, which consist of nanoparticles. However, the PSD curve for N,L a-TiO₂ NSs is shifted in direction

Fig. 3. N₂ adsorption-desorption isotherm (a) and the corresponding pore size distribution curve (b) for N,La-TiO₂ NSs and N,La-TiO₂ NPs.

of larger mesopores due to the larger size of the building units for N,La-TiO₂ NSs. Actually, the single-crystal nanosheets are non-porous. Therefore, the existing mesopores in N,La-TiO₂ NSs are due to the aggregation of TiO₂ nanosheets.

3.3. XPS spectra

The XPS spectrum for N 1s region of N,La-TiO₂ NSs and its fitting curves are shown in Fig. 4a. There is a broad peak from 397 to 403 eV. After fitting, two peaks were acquired at 399.6 and 401.5 eV, respectively. The peak at 399.6 eV can be attributed to substitutional N replacing O in the form of O-Ti-N, and the other peak at 401.5 eV suggesting the presence of oxidized and interstitial state such as Ti-O-N-O and Ti-O-N [37]. Fig. 4b shows the La 3d XPS spectrum of N,La-TiO₂ NSs. There are two peaks centered at 853.4 eV and 836.7 eV, which can be attributed to La 3d_{3/2} and La 3d_{5/2}, respectively. Compared with the literature values 851.8 eV and 834.9 eV [13], the binding energies shift to higher energy region due to the formation of Ti-O-La bond. The ionic radius of La³⁺ (0.106 nm) is larger than that of Ti⁴⁺ (0.068 nm), it is difficult for La³⁺ to enter into the lattice of TiO₂. It is probably due to the substitution of La³⁺ in La₂O₃ lattice by Ti⁴⁺, and thus forming a Ti-O-La bond at the interface [13]. The electronegativity of La is lower than that of Ti, therefore, the electron density of La in the Ti-O-La reduces and the binding energy shifts. It is confirmed that N was doped into TiO₂ nanocrystals, while La₂O₃ is likely to form a binary composite with TiO₂.

3.4. UV/vis diffuse reflectance spectra

The light absorption characteristic of TiO₂ usually changes after doping of nonmetals [32]. Fig. 5a exhibits a comparison of the

UV-vis absorption spectra of P25, N-TiO₂ NSs and N,La-TiO₂ NSs. A strong absorption in ultraviolet region can be clearly observed for all of the three samples. However, in comparison to P25, N-TiO₂, N,La-TiO₂ NSs show two prominent features: (1) the visible-light absorbance intensities were enhanced; (2) the absorption edges at about 400 nm show an obvious red shift. These features further confirm that N element was successfully doped into the lattice of TiO₂. La³⁺ doping can lead to lattice deformation and form vacancy, and this will probably produce an impurity level in the band gap of TiO₂. The existing impurity level can narrow the band gap and enhance the absorption of visible-light [13]. Consequently, N and La co-doping provides prerequisite for the improvement of visible light photocatalytic activity of TiO₂ since the absorption ability for visible light is strengthened (the scheme of visible light absorption mechanism of nitrogen and lanthanum co-doped TiO₂ NSs can be seen in Fig. 5c). Assuming that TiO₂ is an indirect semiconductor, the band gap energy can be estimated from the intercept of the tangent to the plots of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$). The band gap energies calculated from these intercepts (see Fig. 5b) are 3.18, 2.88 and 2.84 eV for P25, N-TiO₂ and N,La-TiO₂ NSs, respectively. The first-principle DFT calculations have demonstrated that N 2p states can effectively merge with O 2p states and form a N impurity level near the valence band edge and thus narrow the band gap, which results in the visible light absorption of N-doped TiO₂ [33].

3.5. Photocatalytic activity

The visible light photocatalytic activity of the samples was examined by decolorization of Rh B aqueous solution. Fig. 6a shows a comparison of the photocatalytic activities of P25, N-TiO₂ NSs, N,La-TiO₂ NSs and N,La-TiO₂ NPs. As can be seen from Fig. 6a, the presence of both visible light illumination and TiO₂ samples is

Fig. 4. N 1s (a) and La 3d (b) XPS spectra of N,La-TiO₂ NSs.

Fig. 5. UV-vis diffuse reflectance spectrum (a), the plots of $[F(R_{\infty})h\nu]^{1/2}$ vs. photon energy (b) of samples P25, N-TiO₂ and N,La-TiO₂ NSs, and the scheme of visible light absorption mechanism of nitrogen and lanthanum co-doped TiO₂ (c).

Fig. 6. Degradation of Rh B with different photocatalysts under visible light irradiation (a) and with recycled N,La-TiO₂ NSs under visible light (b).

necessary for the effective degradation of Rh B. P25 also shows visible light photocatalytic activity. Theoretically, P25 do not exhibits visible light photocatalytic activity since anatase can not be excited under visible light illumination due to the large band gap (about 3.2 eV). The observed photocatalytic activity of P25 can be due to the self-sensitized effect, which extends the absorption edge of P25 to visible light region [32].

The N-TiO₂ NSs, N,La-TiO₂ NSs and N,La-TiO₂ NPs show an enhancement of visible light photocatalytic activity due to the doping of N into TiO₂, and N,La-TiO₂ NSs shows even higher visible light photocatalytic activity than N,La-TiO₂ NPs. Theoretical and

experimental studies demonstrate that {001} facets of anatase TiO₂ is more reactive than the thermodynamically stable (101) facets, because of its special electronic and superficial structures [38]. The 2p states of the surface O atoms on the {001} facets are unstable and very reactive [38], which suggests more oxygen vacancies existing on the surface of {001} facets. The defects caused by oxygen vacancies can act as an activated center in the photocatalysis process due to the adsorption of OH [38], which leads to the high photocatalytic activities of N-TiO₂ and N,La-TiO₂ NSs under visible light. Therefore, N-TiO₂ and N,La-TiO₂ NSs with exposed {001} facets show high photoactivity under visible light.

As a photocatalyst, its stability is very important for the practical application. Therefore, the stability of N,La-TiO₂ NSs was further investigated by conducting the recycle experiments of the photocatalyst (see Fig. 6b). After five recycles, N,La-TiO₂ NSs did not show any obvious loss of photocatalytic activity, indicating its high stability during the photocatalytic degradation of pollutant molecules.

4. Conclusions

Anatase TiO₂ with exposed {001} facets has become a hot research topic, because of its high activity in heterogeneous reactions. However, it is still challenging to synthesize metal and nonmetal co-doped TiO₂ nanocrystals with exposed {001} facets. In this study, N and La co-doped TiO₂ nanosheets with exposed {001} facets have been fabricated by a one-step hydrothermal method without any addition of fluorides. As the crystal-growth-directing agent, DEA plays a crucial role in the formation of {001} facets. N,La-TiO₂ NSs showed greatly higher visible light photocatalytic activity compared with N-TiO₂ NSs and N,La-TiO₂ NPs with the same doping concentration. N and La co-doping could produce a synergistic effect. N doping can narrow the band gap of anatase TiO₂ and enhance the utilization efficiency of visible light, while La doping can improve the separation of photoelectrons and holes [13]. The finding provides a simple approach for the fabrication of shape-defined TiO₂ nanostructures with high-energy facets preferentially exposed, and also affords a viable way to synthesize other metal oxide nanocrystals with strong catalytic or photocatalytic activity.

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