

Synthesis of Ce/N Co-doped TiO₂ Using CTAB Template with Improved Visible Light-Driven Photocatalysis

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Abstract. Visible light active photocatalysts were prepared using N/Ce co-doped anatase TiO₂ nanoparticles and using cetyltrimethyl ammonium bromide (CTAB) as template. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transformation infrared spectroscopy (FTIR), and UV-visible absorbance spectroscopy (UV-vis). The results show that Ce/N co-doped in proper ratio can effectively improve the photocatalytic activity. The introduction of a certain amount of Ce is helpful to restrain the growth of catalyst grain and expand the light response range. The application of CTAB can control the nano-structure of TiO₂ which is helpful to increase the photoactivity.

Introduction

Recently, the development research of treating organic pollutants has been widespread attention. TiO₂ is a promising material in photocatalytic, due to its stability, nontoxicity, high efficiency and low prices. The wide band gap of TiO₂ (3.2eV for anatase) limits its practical application, for which it can only respond to UV radiation. To improve the photocatalytic activity of titanium, many efforts have been made. Anionic and cationic doping is a familiar method, which may enlarge the absorption scope of TiO₂. However, the preparation of visible light responsive photocatalyst with high degradation efficiency still remains an appealing challenge.

Anionic doping is an active research in recent years. Asahi et al. ^[1] discovered N doping can enhance optical response of TiO₂ from UV to visible in the solar spectrum. However anionic doping intrinsically brings the serious problem of massive charge carrier recombination, which largely limited the photocatalytic activity. On the other hand, rare earths doping have also been studied, rare earths have transition of *d* and *f* orbital electrons, which reduce the recombination rate of electron-hole pairs and enhance the photocatalytic activity. Among rare earth elements, Ce has unique 4*f* electron configurations which will introduce impurity level. The redox couple (Ce³⁺/Ce⁴⁺) has the ability to shift between Ce₂O₃ and CeO₂ under reducing and oxidizing conditions, which is helpful to catalytic property ^[2]. At the same time, the doping of Ce may introduce structure defects to form oxygen vacancies which may promote light degradation performance of the catalyst ^[3].

Many researchers have been made about the synergistic effect of Ce and N to improve photocatalytic activity of TiO₂ ^[4]. However, the photocatalytic performance of Ce/N co-doped TiO₂ modified by CTAB (cetyltrimethyl ammonium bromide) has seldom been reported.

Experiment

Preparation of Catalyst

Pristine TiO₂, N/Ce co-doped TiO₂ and N/Ce co-doped TiO₂ with the template CTAB were prepared by sol-gel method. Specific steps are as follows: In order to prevent the butyl titanate(Ti(Obu)₄) precipitation in aqueous solution. Firstly, acetylacetone(Hacac) was dissolved in butyl titanate. Then anhydrous ethanol (2/3) was dropwise added into the mixture slowly companying stirring at room temperature, which was called as solution A. Meanwhile, anhydrous ethanol (1/3), glacial acetic and

deionized water was mixed thoroughly together, which was called as solution B. Then, add solution B slowly into solution A with vigorous stirring at room temperature to carry out hydrolysis. The molar ratio of Ti (OBU)₄: Ethanol: Hacac: glacial acetic: H₂O was 1:47.5:0.2:1.5:3 finally. On the completion of addition process, keeping strong stirring for 2-3h to form a transparent solution. The solution was aged for 1 day at room temperature and then been dried at 80°C in air. The resulting powders were grinded and then sintered in air for 3h at 500°C. The TiO₂ catalysts were obtained. For the synthesis of N/Ce co-doped TiO₂ and CTAB-assisted synthesis of Ce/N co-doped TiO₂, a certain amount of nitrite cerium, urea or CTAB were dissolved in solution B. The molar ratio of Ti/N was 1:1 and Ti/CTAB was 100:1. Finally, Ce(x)+N+TiO₂ and Ce(x)+N+TiO₂(CTAB) were gotten, where x stood for the molar ratio of Ce and TiO₂.

Characterization

X-ray diffraction (XRD) patterns of all samples were collected using a D/Max-RA diffractometer (RIGAKU, Japan) with Cu K α ($\lambda = 0.1541\text{nm}$) radiation at 40KV, 100mA in the range 20-80° (2θ). The morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4800). Fourier transform infrared (FTIR) absorption spectra of the samples were measured in the range of 500~4000 cm⁻¹ by a BRUKER TENSOR-27 spectrometer. The UV-Vis absorption spectra of the samples were measured on a UV-Vis spectrophotometer (V-570, JASCO).

Measurement of Photocatalytic Activity

The experiments of degradation 20 mg/L solution of methyl orange was used to evaluate the photocatalytic activities of the catalysts. A 300W halogen lamp was used as the light source in the homemade photo-reactor, with a light filter cutting off the light below 420 nm. Take 0.05g catalysts add into a 150 mL of the methyl orange solution. The suspension was electromagnetic stirred in the dark for 30 min to establish the adsorption/desorption equilibrium. 5ml aliquot was sampled and centrifuged every 30 min. The filtrates were analyzed by recording variations in the absorption in UV-vis spectra of methyl orange, using a UV-vis spectrophotometer (V-570, JASCO). The degradation rate of methyl orange (%) = $(C_0 - C_t) / C_0$ was calculated. Where C_0 is the concentration of methyl orange after adsorption/desorption equilibrium before light irradiation, C_t is the concentration of methyl orange at time t .

Results and Discussion

XRD Analysis

The samples of pure, single doped and co-doped TiO₂ nanoparticles were shown in Fig. 1. It can be seen that the XRD of the prepared samples exhibit only anatase type of TiO₂ with the representative peaks of phases [101], [004], [200], [105] and [204] at diffraction scattering angles (2θ) of 25.3°, 36.6°, 48.0°, 54.5° and 62.6°, respectively. The average crystallite sizes of the samples can be calculated using the Debye-Scherrer formula^[5] on the anatase (101) diffraction peaks:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is the crystalline size, K is a constant usually taken as 0.89, λ is the wavelength of X-ray radiation (0.1541 nm), β is the peak width of the measured samples at half-maximum height (PWHMH) after subtraction of equipment broadening, and θ is the diffraction angle. No diffraction peaks about nitrogen and cerium can be found. For nitrogen components, it may indicate that new crystal phase is not form. However, when N is doped, the characteristic peaks of samples become narrower and higher.

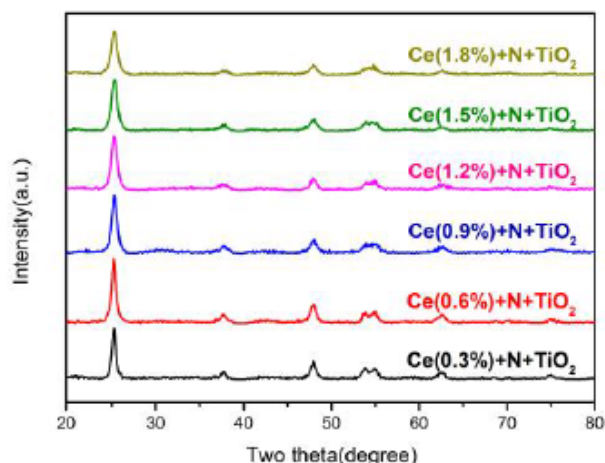


Figure1 (a) XRD patterns of co-doped photocatalysts

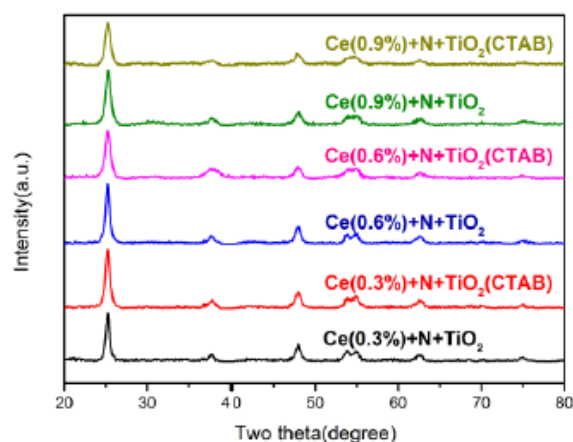


Figure 1 (b) XRD patterns of samples modified by CTAB

Table 1 Crystal of co-doped photocatalysts and samples modified by CTAB

Samples	Grain size/nm	Samples	Grain size/nm
Ce(0.3%)+N+TiO ₂	17.3	Ce(0.3%)+N+TiO ₂ (CTAB)	14.5
Ce(0.6%)+N+TiO ₂	17.0	Ce(0.6%)+N+TiO ₂ (CTAB)	9.5
Ce(0.9%)+N+TiO ₂	16.0	Ce(0.9%)+N+TiO ₂ (CTAB)	10.5
Ce(1.2%)+N+TiO ₂	12.0	Ce(1.2%)+N+TiO ₂ (CTAB)	11.7
Ce(1.5%)+N+TiO ₂	8.0	Ce(1.5%)+N+TiO ₂ (CTAB)	10.2
Ce(1.8%)+N+TiO ₂	14.8	Ce(1.8%)+N+TiO ₂ (CTAB)	12.4

As Fig.1 (a) shows, when the N content is constant, the characteristic peaks of the samples become narrower and higher with the increase of Ce content and reach highest when the doping ratio of Ce is 0.6%, then get wider and lower with the increased of Ce content. As Fig.1 (b) shows, the introduction of CTAB may broaden characteristic peaks. It may be due to the reason that doping too much will cause crystalline grains growing not so well. However, it does not introduce no additional peaks and keep the original characteristic peaks of Anatase. At the same time, the average particle size is calculated listed in Table 1. From the results, when N content is kept constant, the size of the titania crystallites becomes smaller with the increase of doping amount of cerium ion, and get smallest when Ce content is 1.5%, and then get bigger with the increase of doping amount of cerium ion. Meanwhile, the samples which are modified by CTAB can reach smaller size. The one exception, particle size of Ce (1.5%) +N+TiO₂ (CTAB) is get bigger, this may be ascribed to measuring errors. Above these, we can see that a certain amount of cerium can suppress the crystallite growth of anatase titania. This is because the adsorption of cerium species on the surface of titania inhibits crystallite growth of titania nanoparticles. CTAB is a kind of surfactant, which can reduce the surface tension of the solution and make the precursors of TiO₂ highly dispersive. When

a certain amount of CTAB was added into the synthetic system, the highly dispersive precursors of TiO_2 can form smaller particles.

SEM Analysis

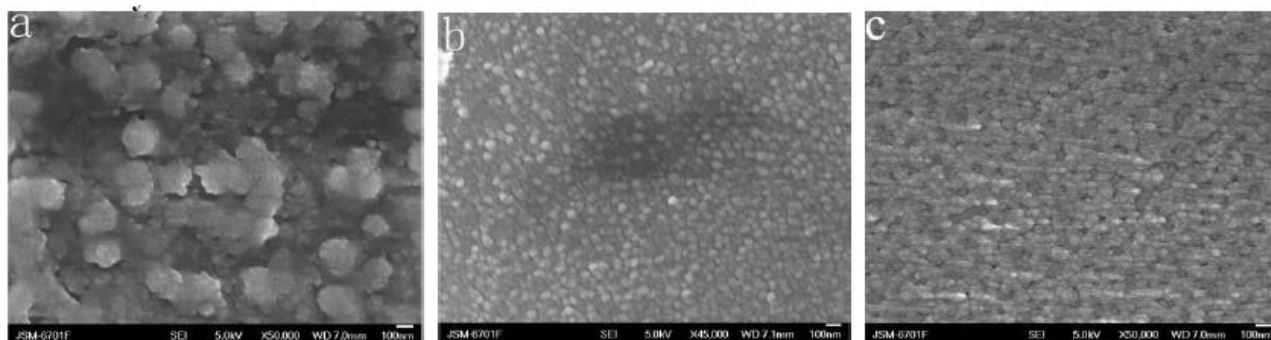


Figure 2 SEM images of: (a) TiO_2 (b) $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2$ and (c) $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2(\text{CTAB})$

Fig. 2 shows the SEM images of the samples of pure TiO_2 , $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2$ and $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2(\text{CTAB})$ nanoparticles calcined at 500°C . The SEM images show that samples are composed of nanoscale spherical particles. The co-doping has a significant influence on titanium dioxide particles morphology. It effectively controls the growth of particles. The average particle size of pure TiO_2 particles is 21nm and the size of the particles is uniform while with a slight reunion. The particle size of $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2$ is about 17nm with smaller and uniform crystal form while with a slight reunion. $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2(\text{CTAB})$ compare to co-doping has smaller particle size and more uniform crystal form. This shows that the added CTAB effectively control the phenomenon of agglomeration of particles. It also confirmed the XRD data.

FTIR Analysis

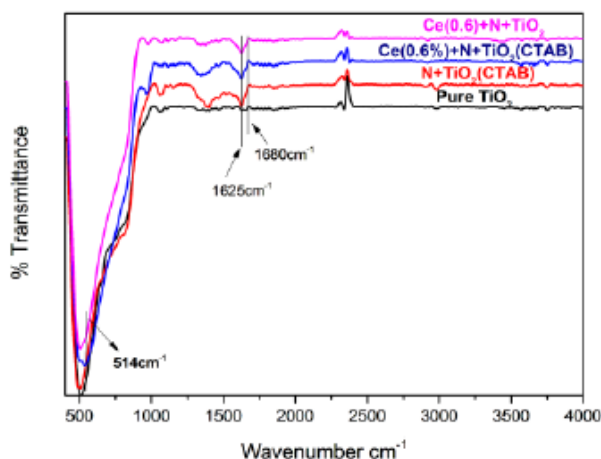


Figure. 3 FTIR Spectra of pure TiO_2 , $\text{N}+\text{TiO}_2(\text{CTAB})$, $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2$ and $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2(\text{CTAB})$ samples

FTIR spectrum of pure TiO_2 , $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2$ and $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2(\text{CTAB})$ which are calcined under 500°C are shown in Figure. 3. The wide absorption region between 400cm^{-1} and 1000cm^{-1} can be assigned to the Ti-O stretching vibrations. Meanwhile, the sample of $\text{Ce}(0.6\%)+\text{N}+\text{TiO}_2(\text{CTAB})$ shows a new sharp peak at 514cm^{-1} represents the Ce-O stretching vibrations which means Ce is doped in TiO_2 . The absorption bands due to the stretching vibration of alkyl ($-\text{C}_n\text{H}_{2n+1}$) groups were not observed at around 2921 and 2845cm^{-1} . The absorption band of alkyl groups disappeared due to burning out of the surfactant, which indicates that annealing is an effective way to decompose the surfactant CTAB from the sample [6]. The peaks of 1625cm^{-1} represent the presence of -N-H stretching vibrations and C-N stretching vibrations. The peak of 1680cm^{-1} can be attributed to the Urea carbonyl stretching vibration. These means the new chemical

bond vibration is born about Ti-N ^[7].

UV-visible analysis

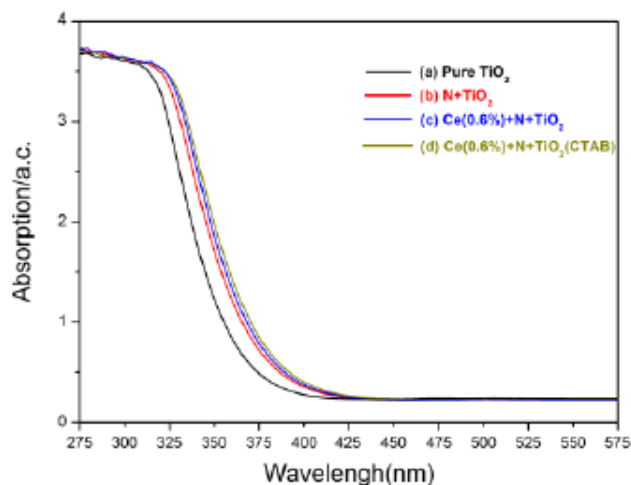


Figure 4 UV-visible absorption spectra of pure TiO₂, N+TiO₂, Ce (0.6%) +N+TiO₂ and Ce (0.6%) +N+TiO₂ (CTAB) samples

Figure 4 shows the UV-visible absorption spectrums. It can be seen from figure that pure TiO₂ show a strong absorption edge below 380nm while does not show absorption in the visible area. The doping of N is attributing to broaden absorption edges which cause obviously red shift. After the introduction of cerium, the absorption edge further broadens. At the same time, the samples which are assisted by CTAB show further red shift. The increased visible light absorption of the multi-doped TiO₂ is due to the introduction of new energy levels by dopant species in the band gap of titania. N atoms replaced a portion of O atoms from TiO₂ crystal forming a new N 2*p* energy level on top of the valance band. Ce 4*f* electrons energy levels are formed below the conduction band of TiO₂. Valence band electronics and the ground state of Ce₂O₃ electronics in visible light can be stimulated transition to Ce 4*f* which results in the red shift. The function of CTAB is helpful to the doping of Ce and N which is contributing to the improvement of photocatalytic activity.

Photocatalytic activity

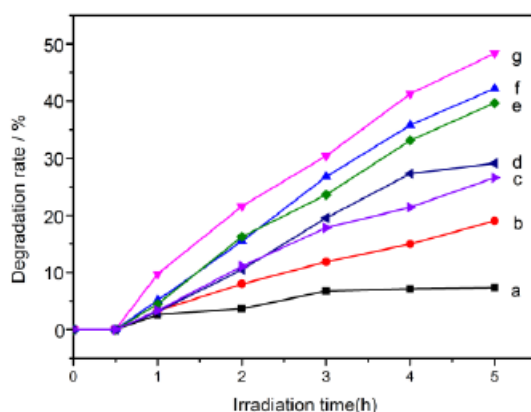


Figure 5(a) Photocatalytic degradation of methyl orange under visible light by (a) pure TiO₂, (b) N+TiO₂, (c) Ce(1.5%)+N+TiO₂, (d) Ce(1.2%)+N+TiO₂, (e) Ce(0.9%)+N+TiO₂, (f) Ce(0.3%)+N+TiO₂, (g) Ce(0.6%)+N+TiO₂

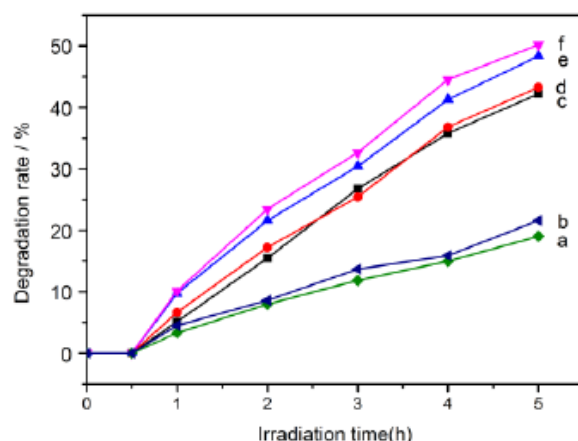
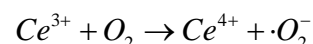
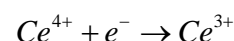


Figure 5(b) Photocatalytic degradation of methyl orange under visible light by (a)N+TiO₂, (b)N+TiO₂(CTAB), (c)Ce(0.3%)+N+TiO₂, (d)Ce(0.3%)+N+TiO₂(CTAB), (e)Ce(0.6%)+N+TiO₂, (f) Ce (0.6%) +N+TiO₂(CTAB)

The photocatalytic activity of the pure TiO₂, N+TiO₂, Ce(x)+N+TiO₂ and Ce(x)+N+TiO₂(CTAB) were evaluated by the degradation of 20 mg/L solution of methyl orange under visible light irradiation, as shown in Fig. 5. Initially, the adsorption experiments were performed in the dark for 30 min before the photoinduced degradation reaction. Comparing the performances of the catalysts, we can find that the photoactivity of N+TiO₂ is superior to that of pure TiO₂. It can be explained from the UV-Vis diffuse reflectance spectrum that the doping of nitrogen broaden the absorption band to visible light region. The photoactivity of the samples was further enhanced by the introduction of Ce in the catalysts. It shows that the Ce (0.6%) +N+TiO₂ have the highest photoactivity in Fig. 5(a). There are some factors. (1) In TiO₂ nanoparticles, Ce⁴⁺ and Ce³⁺ can coexist. The electrons can be excited from the valence band and nitrogen impurity level into Ce 4f level under visible light irradiation. Then these electrons probably shifted to Ce⁴⁺ on the TiO₂ surface and converted into the Ce³⁺. Electrons from Ce³⁺ may transfer to the O₂ molecules which may benefit the charge separation and increase the absorption of O₂ on the surface of TiO₂. Reaction process is as follows:



The combined action between Ce⁴⁺ and Ce³⁺ inhibits h⁺/e⁻ compound and improves the ability of TiO₂ photoactivity. However too much amounts of doping, Ce 4f level will act as a light recombination center of electrons and holes which will decrease photocatalytic activity of TiO₂. This situation is illustrated in Fig. 5(a). (2) The atomic radius of Ce⁴⁺ is greater than Ti⁴⁺ atomic radius. The doping of Ce will cause lattice expansion and form lattice defects, to produce more Ti³⁺ oxidation activity center. Ti³⁺ is easy to capture the electrons and transfer to surface to absorb molecular oxygen which is helpful to improve the efficiency of photocatalysis. Fig. 5(b) shows photocatalytic activity of co-doping samples and the samples which are modified by CTAB. We can see that the samples which are modified by CTAB have better photocatalytic activity. The introduction of CTAB will increase the surface area of samples, which is helpful to improve the efficiency of photocatalysis [8].

Conclusion

In summary, we reported the preparation of Ce/N co-doped TiO₂ powders with anatase crystallinity via sol-gel method using CTAB as template. The introduction of N broadens the absorption band to visible light region. Meanwhile, the introduction of Ce is helpful to restrain the catalyst grain

growth and expand light response range. It improves the oxygen adsorption on the surface of the catalyst and enhances the circulation of the oxygen on the surface of the catalyst which contributes to capture light carrier to derive kinds of highly reactive free radicals. However, doping too much amounts of Ce, recombination center of Optical electronic-hole can be formed. It is unfavorable to increase photocatalytic activity and light quantum efficiency. The introduction of CTAB can restrain the catalyst grain growth of the samples. Samples which are prepared using CTAB as template showed an obvious spectral absorption up to 450 nm and better photocatalytic activity.

Acknowledgements

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