



A simple method to prepare N-doped titania hollow spheres with high photocatalytic activity under visible light

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ABSTRACT

N-doped titania hollow spheres were prepared using hydrothermally prepared carbon spheres as template. The prepared hollow spheres were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectrum (DRS). The photocatalytic activity of as-prepared hollow titania spheres was determined by degradation of Reactive Brilliant Red dye X-3B (C.I. reactive red 2) under visible light irradiation, and was compared to commercial P25 titania. It was revealed that the photocatalytic activity of the titania hollow spheres enhanced a lot. The apparent rate constant of the titania hollow spheres was almost 17 times as that of P25 titania.

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1. Introduction

The photocatalytic properties of nano-sized titania (TiO₂) have been extensively investigated due to its promising application in the field of destruction of pollutants [1], production of hydrogen [2] and removal of metal [3]. In order to commercialize this treatment technique, it is of great importance to improve the preparative methods of titania. The morphology and microstructures, which are very important to the photocatalytic activity of titania, are significantly influenced by the preparative conditions and methods [4–6]. Fabrication of titania hollow microspheres has recently attracted enormous attention because of their low density, high surface area, good surface permeability as well as large light-harvesting efficiencies [7]. It is also expected that higher energy conversion efficiency and photocatalytic activity could be achieved using titania hollow microspheres as photocatalysts.

On the other hand, due to the wide bandgap of titania (3.2 eV for anatase), the technological application seems limited by several factors, among which the most restrictive one is the need of using an ultraviolet (wavelength (λ) < 387 nm) as excitation source [8]. So it can only capture less than 5% of the solar irradiance at the Earth's surface. For the sake of efficient use of sunlight, or use of the visible region of the spectrum, the technology of enlarging the absorp-

tion scope of TiO₂ may then appear as an appealing challenge for developing the future generation of photocatalysts. Several works reported that doping TiO₂ with nonmetallic elements, such as nitrogen [9–14], sulphur [15], carbon [16], shift the optical absorption edge of TiO₂ toward lower energy, thereby increasing the photocatalytic activity in visible region.

Recently, Sun et al. [17,18] reported the preparation of colloidal carbon spheres. The carbon spheres can be used as template to prepare metal oxides with hollow structures. The surface of colloidal carbon spheres is hydrophilic and has a distribution of –OH and –C=O groups, which makes surface modification unnecessary. In this paper, for the enhancement of visible-light-driven photocatalytic activity of titania, we prepared visible light responsive N-doped titania hollow spheres using colloidal carbon spheres as template. Then, we studied their application to photocatalytic decomposition of Reactive Brilliant Red dye X-3B (C.I. reactive red 2) in aqueous solution.

2. Experimental

2.1. Preparation of carbon spheres

In a typical synthesis of colloidal carbon spheres, 6 g of glucose was dissolved in 60 ml of water to form a clear solution. The solution was then sealed in a 50 ml Teflon-lined autoclave and maintained at 180 °C for 4 h. The products were then centrifuged, washed, and redispersed in water for five cycles. Afterwards, the products were

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centrifugated, washed, and redispersed in ethanol for five cycles. The carbon spheres were then dried at 80 °C for 2 h under vacuum.

2.2. Preparation of N-doped titania hollow spheres

Urea was chosen as nitrogen precursor. Distilled water was additionally cleaned prior to its use with a quartz sub-boil high-purity water purification system. In a typical synthesis of N-doped titania hollow spheres, definite urea was dissolved into the admixture of 24 ml ethanol and 0.3 g distilled water, and then 0.12 g carbon spheres were added. Ti (OBU)₄ diluted with ethanol was added dropwise into the above suspension under vigorous stirring. Then, the solution was kept under reflux condition (around 80 °C) for 6 h. Afterwards, the products were centrifugated, washed and redispersed in ethanol for three cycles. After being placed in the air at room temperature for 12 h and at 60 °C for 2 h, the titania-carbon composite particles were formed. In order to produce N-doped titania hollow spheres, the titania-carbon composite particles were calcined at 500 °C for 3 h in the air. The molar ratio of urea to titania was controlled to be 1 or 2, and the obtained samples were labeled as NHT-1, NHT-2, respectively. The hollow titania (HT) were prepared for comparison by the same way without adding urea.

2.3. Characterization

The structure properties were determined by X-ray diffractometer (XD-3A, Shimadzu Corporation, Japan) using graphite monochromatic copper radiation (Cu-K α) at 40 kV, 30 mA over the 2 θ range 20°–80°. The hollow morphologies were characterized by transmission electron microscopy (TEM, JEM2000EX). The UV–vis absorption spectra of the hollow titania spheres were observed with Shimadzu UV-2100 equipped with an integrating sphere. BET surface area measurements were carried out by N₂ adsorption at 77 K using an ASAP2020 instrument. The binding energy was identified by X-ray photoelectron spectroscopy (XPS) with Mg-K α radiation (ESCALB MK-II).

2.4. Photocatalytic activity

The photocatalytic activity of prepared samples was evaluated by photocatalytic degradation of Reactive Brilliant Red dye X-3B (C.I. reactive red 2) solution. One gram of sample was added into 200 ml of 25 mg l⁻¹ X-3B solution. The suspension was stirred in dark for 30 min to obtain adsorption–desorption equilibrium of X-3B before illumination. A 250 W halogen lamp (Instrumental Corporation, Beijing Normal University) with a light filter cutting the light below 400 nm was used as visible light source. At a defined time interval, 5 ml suspension was removed, and then the concentration of X-3B was analyzed using the UV–vis spectrophotometer at 535 nm.

3. Results and discussion

3.1. Characterization of N-doped titania hollow spheres

The X-ray diffraction (XRD) analysis pattern in Fig. 1 shows the titania phases formed at temperature 500 °C. The fact that the peaks are very narrow indicates that the hollow titania spheres are crystalline. As also shown in the figure, the particles had formed anatase phase since the characteristic diffraction peaks of anatase (major peaks: 25.4°, 38.0°, 48.0°, 54.7°, 63.1°) were evident in the sample. No other peaks such as N–O and Ti–N appeared. It may be due to the reason that the content of N was too little to be detected in the photocatalyst. The calcination at 500 °C not only removed the template, but also made the formation of anatase phase. Furthermore,

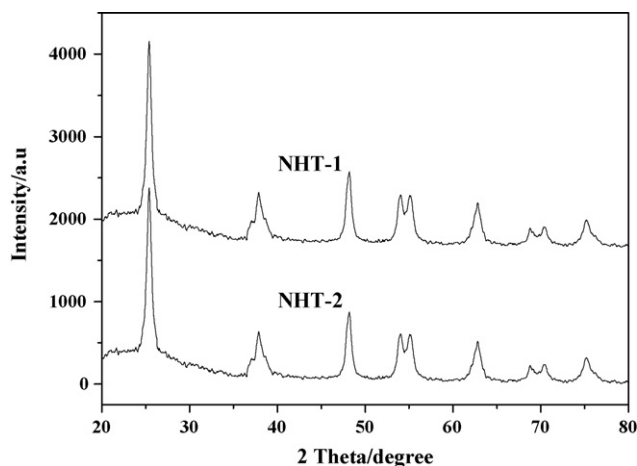


Fig. 1. XRD patterns of NHT-1 and NHT-2.

the crystal size of the resultant titania hollow spheres was determined by Scherrer's equation: $D = (K \lambda) / (\beta \cos \theta)$, where λ is the wavelength of the X-ray radiation ($\lambda = 0.15418$), K is the Scherrer constant ($K = 0.9$), θ is the characteristic X-ray radiation ($\theta = 12.7^\circ$) and β is the full-width-at-half-maximum of the (101) plane (in radians) [19]. The values are estimated to be 11.75 and 12.35 nm for NHT-1 and NHT-2, respectively. It demonstrated that the degree of crystallization of NHT-2 is little better than NHT-1. From the BET measurement, the specific surface areas are 361.27 m² g⁻¹ for NHT-1, while 319.32 m² g⁻¹ for NHT-2. The decreased surface area may be due to the increased crystalline size.

The TEM image of carbon spheres is shown in Fig. 2(a). It can be seen from the figure that diameter of as-prepared carbon spheres ranges from 250 to 400 nm. Fig. 2(b) shows example of TEM images of NHT-2. The strong contrast between the dark edges and bright centers indicates the hollow structure of titania spheres. The TEM image also revealed that the utilization of carbon spheres as a template has resulted in the formation of spherical shells with relatively smooth surface and dense arrangement of titanium dioxide nanolayers. It can be seen that the hollow spheres have average diameter of 280 nm and the shell thickness is about 30 nm.

Fig. 3 compares the UV–vis diffuse reflectance spectrum of NHT-1, NHT-2 and P25. The results indicated that doped nitrogen by this method can give rise to a clear red-shift in the optical response of the titania hollow spheres. High visible absorbance (400–550 nm) was observed for N-doped samples. In addition, we can observe that the red-shift and visible absorbance of NHT-2 are enhanced compared to NHT-1. This may be with higher initial urea that more N atom would be incorporated into the lattice of titania. Thus, it induces a larger red-shift and bandgap narrowing.

X-ray photoelectron spectroscopy analysis was employed as an important characteristic method to detect the chemical states of different atom in doped titania photocatalyst [20–23]. The active site and the nitrogen state responsible for the enhanced photocatalytic activity of nitrogen-doped TiO₂ is a recent subject of photocatalytic research. The XPS survey spectrum of NHT-2 (see Fig. 4(a)) indicates that the peak contains Ti, O, C and N atoms. Part of C atoms may come from the residual carbon of precursor solution. The other part of C atoms probably comes from carbon spheres during the calcinations. The high-resolution XPS spectra of the C1s and N1s regions on the surface of NHT-2 are shown in Fig. 4(b) and Fig. 4(c), respectively. From Fig. 4(b), we can see that there are two XPS peaks at about 284.6 and 288.2 eV. According to Li et al. [24] the peak at 284.6 eV arises from adventitious elemental carbon. The other peak around 288.2 eV attributed to the formation of carbonate species which can induce the narrowing of the bandgap of the doped titania.

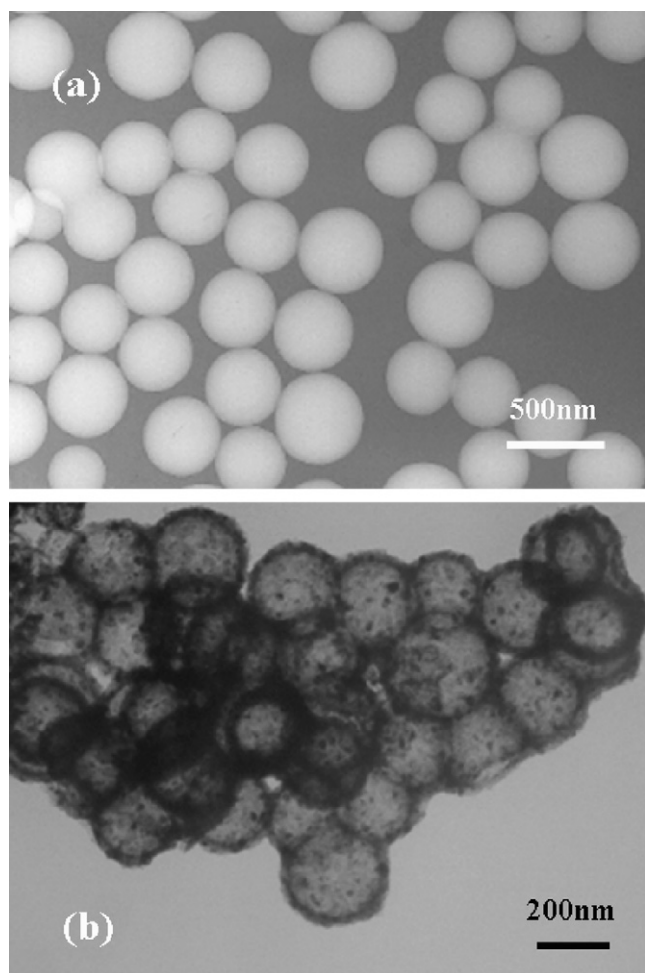


Fig. 2. TEM images of (a) carbon spheres and (b) NHT-2.

nia. The N1s region of NHT-2 (as shown in Fig. 4(c)) is wide and asymmetric, indicating that there are at least two kinds of chemical states. Using Origin software with Gaussian rule, N1s region is fitting to two peaks. One peak, at 396 eV, corresponds to the so-called β -N state, which represents atomic N in form of mixed titanium oxide–nitride ($\text{TiO}_{2-x}\text{N}_x$), O–Ti–N [25]. This indicates that using the synthesized method in this study indeed leads to the substitution of some oxygen sites by nitrogen. And the other peak

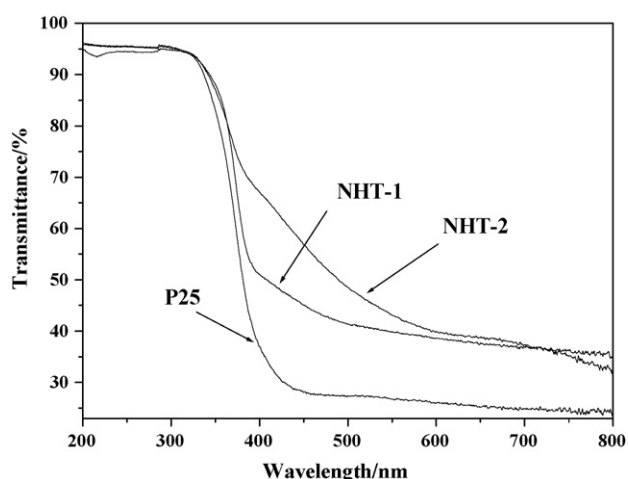


Fig. 3. The diffuse reflectance UV–vis spectra of NHT-1, NHT-2 and P25.

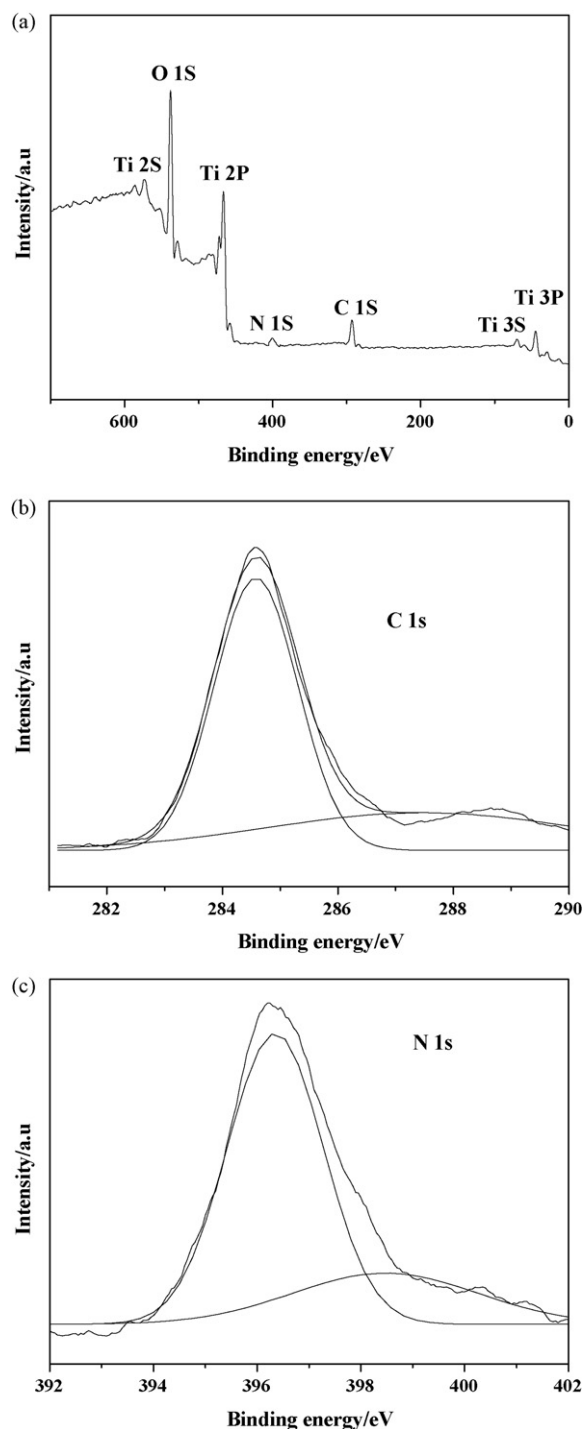


Fig. 4. (a) XPS survey spectrum of NHT-2. (b) High-resolution XPS spectrum of C1s region of NHT-2. (c) High-resolution XPS spectrum of N1s region of NHT-2.

around 399.2 eV may account for the presence of oxidized state of N or C–N bonds [26]. This can be attributed to the chemically adsorbed urea molecule on the surface of titania particles. From the above results, we can forecast the prepared N-doped titania hollow spheres would show high photocatalytic activity under visible light irradiation.

3.2. Photocatalytic activity of titania hollow spheres

In order to investigate the photocatalytic activity of as-prepared N-doped titania hollow spheres samples, degradation experiments

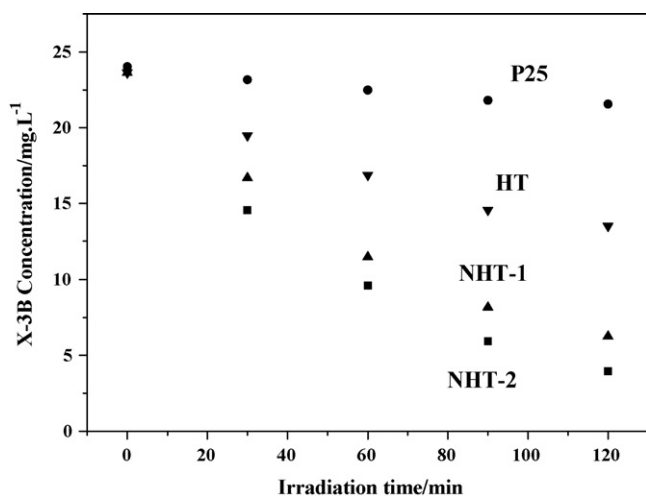


Fig. 5. Kinetics of X-3B disappearance in the presence of NHT-1, NHT-2 and P25.

of Reactive Brilliant Red X-3B (C.I. reactive red 2) were studied under visible light and results are shown in Fig. 5. The blank experiment without catalysts was also investigated and the value can be neglected with about 2% of conversion after 2 h illumination. For the absolute degradation ratio of X-3B, the trend is NHT-2 > NHT-1 > P25. From the results we can find that the photocatalytic activity of three samples corresponds well with the visible light absorption in UV–vis diffuse reflectance spectrum. Furthermore, we can see that the photocatalytic activity of HT was higher than P25, but lower than the doped samples. The results illustrated that both hollow spheres structure and N-doping affected the photocatalytic activity.

It is well known that photocatalytic oxidation of organic pollutants in aqueous suspension follows Langmuir–Hinshelwood model:

$$-\frac{dC}{dt} = \frac{k_f K_a C}{1 + K_a C} \quad (1)$$

where $(-dC/dt)$ is the degradation rate of X-3B, C is the X-3B concentration in the solution, t is reaction time, k_f is a reaction rate constant, and K_a is the adsorption coefficient of the reactant. $K_a C$ is negligible when the value of C is very small. As a result, Eq. (1) can be described as a first-order kinetics. Setting Eq. (1) at the initial conditions of the photocatalytic procedure, when $t=0$, $C=C_0$, it can

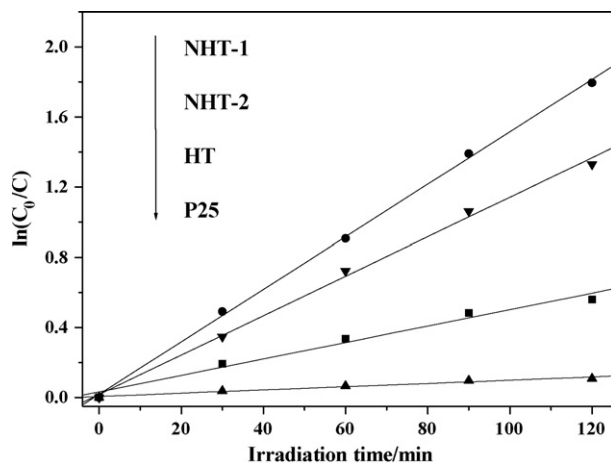


Fig. 6. Linear transform $\ln(C_0/C) = f(t)$ of the kinetic curves of X-3B disappearance for NHT-1, NHT-2 and P25 from Fig. 5.

Table 1
Degradation parameter of X-3B by different samples.

Samples	X-3B degradation (%)	Apparent rate constant k_{app} (min^{-1})	R
P25	8	0.00092	0.98671
NHT-1	76	0.01125	0.99838
NHT-2	85	0.01497	0.99951
HT	47	0.0047	0.98987

be described as follows:

$$\ln\left(\frac{C_0}{C}\right) = k_{app} \times t \quad (2)$$

where k_{app} is apparent rate constant, chosen as the basic kinetic parameter for the different photocatalysts, since it enables one to determine a photocatalytic activity independent of the previous adsorption period in the dark and the concentration of X-3B remaining in the solution [27]. The variations in $\ln(C_0/C)$ as a function of irradiation time are given in Fig. 6. The obtained apparent rate constants k_{app} are listed in Table 1. All together, we can conclude that N-doped titania hollow spheres exhibited a strong photocatalytic activity for decomposition of X-3B under visible light irradiation.

The different photocatalytic activity of different samples can be attributed to the following factors. It is well known that the doping of N and C elements in titania plays an important role in the visible light photocatalytic activity of titania. It can be seen from the UV–vis diffuse reflectance spectrum of the NHT-1 and NHT-2 that it results in a intense increase in absorption in the visible light region and a red-shift in the absorption edge. The bandgap narrowing of titania by N-doping leads to enhanced photocatalytic activity of the hollow titania sphere under visible light. Because the prepared doped samples can be activated by visible light, thus more electrons and holes can be generated and participate in the photocatalytic redox reactions. Furthermore, the hollow structure of NHT-1 and NHT-2 would show high energy-conversion efficiency [5,28].

4. Conclusions

In the present paper, we report a simple method for the preparation of N-doped titania hollow spheres using carbon spheres as template. The carbon spheres were synthesized by hydrothermal method. The photocatalytic activity of as-prepared hollow titania spheres was determined by degradation of Reactive Brilliant Red dye X-3B (C.I. reactive red 2) under visible light irradiation, and compared to commercial P25 titania. The apparent rate constant of the hollow titania spheres is almost 17 times as that of P25 titania.

This approach provides a green, simple and economical method to synthesize uniform N-doped titania hollow spheres with high visible light responsive photocatalytic activity.

Acknowledgments

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