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Enhanced visible photocatalytic activity of TiO₂ hollow boxes modified by methionine for RhB degradation and NO oxidation

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ABSTRACT

Hierarchical TiO₂ hollow nanoboxes (TiO₂-HNBs) assembled from TiO₂ nanosheets (TiO₂-NSs) show improved photoreactivity when compared with the building blocks of discrete TiO₂-NSs. However, TiO₂-HNBs can only be excited by ultraviolet light. In this paper, visible-light-responsive N and S co-doped TiO₂-HNBs were prepared by calcining the mixture of cubic TiOF₂ and methionine (C₅H₁₁NO₂S), a N- and S-containing biomacromolecule. The effect of calcination temperature on the structure and performance of the TiO₂-HNBs was systematically studied. It was found that methionine can prevent TiOF₂-to-anatase TiO₂ phase transformation. Both N and S elements are doped into the lattice of TiO₂-HNBs when the mixture of TiOF₂ and methionine undergoes calcination at 400 °C, which is responsible for the visible-light response. When compared with that of pure 400 °C-calcined TiO₂-HNBs (T400), the photoreactivity of 400 °C-calcined methionine-modified TiO₂-HNBs (TM400) improves 1.53 times in photocatalytic degradation of rhodamine-B dye under visible irradiation ($\lambda > 420$ nm). The enhanced visible photoreactivity of methionine-modified TiO₂-HNBs is also confirmed by photocatalytic oxidation of NO. The successful doping of N and S elements into the lattice of TiO₂-HNBs, resulting in the improved light-harvesting ability and efficient separation of photo-generated electron-hole pairs, is responsible for the enhanced visible photocatalytic activity of methionine-modified TiO₂-HNBs. The photoreactivity of methionine modified TiO₂-HNBs remains nearly unchanged even after being recycled five times, indicating its promising use in practical applications.

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1. Introduction

In the last 30 years, semiconductor photocatalysis has become an important research topic due to its potential applica-

tion in solving the problems of environmental pollution and energy crises, such as degradation of the organic pollutants [1–5], air purification [6–10], reduction of CO₂ to hydrocarbon fuel [11–13], and splitting water to produce hydrogen [14–17].

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Among all the photocatalysts, TiO_2 is the most studied because of its nontoxicity, higher chemical stability, and oxidizability features [18,19]. However, the wide band gap of anatase TiO_2 (3.2 eV) hampers its wide practical application due to the fact that it absorbs only a very small ultraviolet part (3%–4%) of solar light [20,21]. To make use of the abundant amount of visible light (approximately 45%) from solar light, the development of visible-light-driven TiO_2 is of great importance, but remains a great challenge [3,22,23]. Up to now, many strategies have been used to extend the light-responsive region of TiO_2 from the ultraviolet (UV) to visible region, including dye sensitization [24,25], semiconductor coupling [17,26,27], doping TiO_2 with metals or non-metals [22,28,29], noble-metal deposition [30], and surface-plasma effects [8,31,32]. Recent study also shows that modification of anatase TiO_2 with graphene can also result in a visible-light response [33–35].

In recent years, hollow nanostructures have attracted much attention due to their unique properties and potential practical applications [36–39]. According to the literature, many hollow nanostructures have been prepared, such as nanotubes [40] and hollow micro/nanospheres [17,41–44]. Large fractions of void space in hollow structures have been successfully used to encapsulate and control release of sensitive materials such as drugs, cosmetics, and DNA [45]. Our group has previously reported the fabrication of TiO_2 hollow nanoboxes (TiO_2 -HNBs) assembled from TiO_2 nanosheets (TiO_2 -NSs) via a fluoride-induced self-transformation strategy by solvothermal treatment of cubic TiOF_2 in alcohol solution [45]. It was found that the photoreactivity of the obtained TiO_2 -HNBs under UV irradiation was improved when compared with that of the discrete building block TiO_2 -NSs. Upon considering that TiO_2 -HNBs can still only be excited by UV light, herein we prepared visible-light-responsive TiO_2 -HNBs by *in situ* modification of TiO_2 -HNBs with methionine ($\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$), a N- and S-containing biomacromolecule. We systematically studied the effect of calcination temperature on the structure and visible photocatalytic activity of methionine-modified TiO_2 -HNBs.

2. Experimental

2.1. Synthesis

All reagents and solvents were of reagent grade (Wuhan Guoyao Chemical Co., China) and used without further purification.

Precursor TiOF_2 nanocubes were synthesized by hydrothermal reaction. Briefly, 30 mL of acetate, 5 mL of hydrofluoric solution (40 wt%), and 15 mL of tetrabutyl titanate were mixed in a 100-mL PTFE beaker under magnetic stirring. The mixture was heated at 200 °C for 12 h in an autoclave. After cooling to room temperature, the resulting white powders were washed with water and ethanol several times and dried at 60 °C overnight.

To prepare methionine-modified TiO_2 -HNBs, the mixture of 1.0 g of TiOF_2 and 0.05 g of DL-methionine in a crucible was calcined at 400 °C for 2 h with a heating rate of 1 °C min^{-1} . Similarly, the mixture of TiOF_2 and methionine was also calcined at

different temperatures, and the prepared sample denoted TM_x , where x represents the calcination temperature (300–500 °C). For example, TM_{400} means that the sample was prepared by calcining the mixture at 400 °C for 2 h.

In order to study the effect of methionine on the structure and performance of TiO_2 -HNBs, direct calcination of TiOF_2 in the absence of methionine was also performed under identical conditions, and the resulting sample denoted T_x , where x represents the calcination temperature (300–500 °C).

2.2. Characterization

The crystalline structure of the catalyst was characterized by powder X-ray diffraction (XRD) employing a scanning rate of 0.05° s^{-1} in a 2θ range from 10° to 60°, in a Bruker D8 Advance diffractometer using monochromatized $\text{Cu K}\alpha$ radiation. The morphology and microstructure of the as-prepared sample were analyzed by field-emission scanning electron microscopy (SEM) (Hitachi, Japan) and transmission electron microscopy (TEM) (G20, Tecnai, USA). Nitrogen adsorption-desorption isotherms were obtained from a nitrogen-adsorption instrument (ASAP 2020, USA), from which all the photocatalysts were degassed firstly at 150 °C, followed by investigating the surface areas and pore-size distribution of the photocatalysts. The UV-Vis diffused reflectance spectrum (DRS) was collected using a spectrophotometer (Shimadzu UV-2550, Japan) from 200 to 800 nm using BaSO_4 as background. Fourier-transform infrared spectroscopy (FTIR) was recorded on a spectrometer (NEXUS 470) using the KBr pellet technique. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a photoelectron spectrometer (VG Multilab 2000, VG, Inc., USA) using monochromatic $\text{Al K}\alpha$ radiation under vacuum at 2×10^{-6} Pa. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon.

2.3. Measurement of the photocatalytic activity

The photocatalytic activity of the photocatalyst was evaluated both by photocatalytic decomposition of the organic dye rhodamine B (RhB) and NO oxidation under visible-light irradiation.

For RhB degradation, one cylindrical Pyrex® flask with a capacity of approximately 50 mL was used as the photoreactor vessel in the reaction system. Approximately 50 mg of the photocatalyst was put into 50 mL of RhB solution with a concentration of 1.0 g L^{-1} . After being ultrasonicated and stirred in the dark overnight to establish adsorption-desorption equilibrium, the solution was illuminated by an Xe lamp (300 W) with a cut-off filter ($\lambda > 420$ nm). At given time intervals, 3.0 mL of suspension sample was taken and centrifuged to remove the photocatalyst particles. The concentration of the RhB in solution was monitored by UV-Vis spectroscopy at 554 nm.

NO oxidation was performed in a consecutive flow reactor at ambient temperature. The volume of the rectangular reactor constituted of stainless steel with a quartz glass cover was 4.5 L ($L \times W \times H$, 30.0 cm $\times$ 15.0 cm $\times$ 10.0 cm). A simulated visible-light source was acquired from an LED lamp ($\lambda > 400$ nm).

First, 30 mL of deionized water was poured into 0.2 g of the as-obtained samples, and the mixed solution was subjected to ultrasonication for 30 min. The resulting suspension was then sedimented onto a culture dish with a diameter of 11.5 cm. The dish containing the sample was heated at 60 °C for 3 h to thoroughly evaporate any water, and then cooled to normal temperature. NO gas was supplied from a compressed gas cylinder having 50 ppm of NO (N₂ balance) in line with traceable standards recommended by the U.S. National Institute of Standards and Technology. An air stream produced by a zero-air generator (Advanced Pollution Instrumentation, A Teledyne Technologies Co., Model 701) can be used for diluting the initial NO concentration to approximately 600 ppb. In a gas blender, the gas streams were totally premixed, and the gas-flow rate was set as 1.0 L min⁻¹ by employing a mass-flow controller. When the gas system reached adsorption-desorption balance, the lamp was turned on. A chemiluminescence NO_x analyzer (Advanced Pollution Instrumentation, A Teledyne Technologies Co., Model T200) was used for monitoring the concentrations of NO continuously, at a gas-flow rate of 1.0 L min⁻¹.

2.4. Photoelectrochemical performance

The photocurrent of the film electrode was measured on an electrochemical system (CHI-760e, Shanghai, China) using a standard three-electrode cell. The ITO/sample, measuring 2.0 cm × 1.5 cm, acted as the working electrode, a Ag/AgCl electrode was used as the reference electrode, and a platinum wire was used as the counter electrode. The ITO/sample working electrode was prepared by a dip-coating method: 50 mg of the photocatalyst was suspended in 1.0 mL of ethanol, which was then dip-coated onto the ITO glass electrode. 0.1-mol L⁻¹ Na₂SO₄ was used as an electrolyte. The photoelectric responses of the sample at light-on and light-off were measured using an LED lamp (3 W) emitting mainly at 420 ± 10 nm as the light source.

The surface photovoltage spectroscopy (SPS) measurements of the sample were carried out with a home-built apparatus [4,46]. The SPS signals are the potential barrier change of the testing electrode surface between that in the presence of light and that in the dark.

3. Results and discussion

3.1. Phase structure and morphology

XRD was used to investigate the changes of the phase structure of the photocatalyst with calcination temperature. From Fig. 1(a), it can be seen that a sharp peak at $2\theta = 23.4^\circ$ corresponding to TiOF₂ was observed, indicating the successful synthesis of TiOF₂ precursor [23,47,48]. Upon calcination of the precursor TiOF₂ at 300 °C for 2 h (T300 sample), the peak intensity for TiOF₂ decreases, while a broad peak exists at $2\theta = 25.3^\circ$, corresponding to anatase TiO₂ (A-TiO₂), appears (Fig. 1(b)) [49]. This infers that anatase TiO₂ is a more stable phase than TiOF₂. When the calcination temperature increases to 350

°C (Fig. 1(c)), the precursor TiOF₂ almost completely transforms into anatase TiO₂. However, upon calcination of the mixture of TiOF₂ and methionine at 300 °C, no indication of the formed anatase TiO₂ was observed for the TM300 sample. Phase transformation of TiOF₂ to anatase TiO₂ begins at 350 °C (TM350 sample), and the phase transformation completes at 400 °C upon calcination of the mixture of precursor TiOF₂ and methionine. This indicates that methionine can prevent TiOF₂-to-anatase TiO₂ phase transformation, which is possibly due to the fact that the presence of methionine retards the diffusion of fluoride ions from the core to the shell.

Consistent with the reported literature [23,50–53], the cubic morphology of the as-prepared TiOF₂ precursor is confirmed by the corresponding TEM image (Fig. 2(a)). It can be seen that the synthesized TiOF₂ cubes have sidelengths of approximately 200–300 nm. When calcining the mixture of precursor TiOF₂ and methionine at 300 °C for 2 h, the morphology of the photocatalyst seems unchanged (Fig. 2(b)). However, careful examination shows the formation of core-shell structured nanocubes. When compared with the TEM image of the precursor TiOF₂ sample (Fig. 2(a)), the dark core of the cubes become much lighter, and the nanosheets around the cores can be observed, indicating that the phase transformation begins. This is in ac-

Fig. 1. XRD patterns of the calcined photocatalysts before (A) and after (B) modified by methionine, together with the expected diffraction peaks for TiOF₂ and anatase TiO₂ (A-TiO₂), respectively.

Fig. 2. SEM images of the photocatalysts for TiOF₂ precursor (a), TM300 (b), TM350 (c), TM400 (d), TM450 (e) and TM 500 (f), respectively. Inset of (d) is the side view HRTEM image of an erected TiO₂ nanosheet for TM400 sample, where the lattice spacing of ca. 0.235 nm corresponds to the (001) planes of anatase TiO₂.

cordance with the XRD characterization results ((a) and (b) of Fig. 1B). Upon increasing the calcination temperature to 350 °C, the hollow interiors of the nanocubes become obvious (Fig. 2(c)). Almost totally hollow structures are obtained upon further increase in the calcination temperature to 400 °C, indicating the completion of TiOF₂ to anatase TiO₂ ((c) of Fig. 1B).

We proposed that TiOF₂ cubes will transform into TiO₂-HNBs during a solvothermal reaction when using alcohol as solvent by *in situ* transformation of TiOF₂ to anatase TiO₂ nanocrystals [45]:

However, in the present study, TiOF₂ cubes transforms into more stable anatase TiO₂-HNBs by direct calcination. The possible reaction is

It has been reported that fluoride ions facilitate the formation of high-energy anatase TiO₂-NSs due to the fact that the adsorption of F⁻ on the surface of TiO₂ nanocrystals can sharply reduce the surface energy of (001) facets [54]. Therefore, it is understandable that precursor TiOF₂ can *in situ* transform into

anatase TiO₂-HNBs assembled from TiO₂-NSs with exposed high-energy (001) facets at high temperature. The inset of Fig. 2(d) clearly shows the sideview high-resolution TEM (HRTEM) image of an erected TiO₂ nanosheet for the TM400 sample, from which we can see a lattice spacing of approximately 0.235 nm, confirming the exposure of the (001) facets of anatase TiO₂ nanosheets.

The obtained TiO₂-HNBs are not stable, and decompose into discrete TiO₂-NSs at high temperatures, such as 450 and 500 °C (Fig. 2(e) and 2(f)).

Fig. 3 shows the SEM images of the TM400 sample at different magnifications, which further confirms the formation of TiO₂-HNBs assembled from TiO₂-NSs.

3.2. Nitrogen adsorption

To obtain more detailed structural information of the prepared TiO₂-HNBs, nitrogen adsorption was used to measure the Brunauer-Emmett-Teller (BET) surface area and pore structure of the photocatalyst. It was found that both the BET surface area and pore volume (PV) of TM_x nearly increase with increasing calcination temperature (Table 1). The BET surface

Fig. 3. SEM images of TM400 sample with different magnification.

Table 1

Physical properties of the photocatalysts.

Catalyst	Starting material	Calcination temperature (°C)	Phase ^a	Nitrogen sorption		
				A_{BET} (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	APS (nm)
TM300	TiOF ₂ /methionine	300	TiOF ₂ /A-TiO ₂	7.0	0.022	8.0
TM350	TiOF ₂ /methionine	350	A-TiO ₂	8.9	0.022	6.9
TM400	TiOF ₂ /methionine	400	A-TiO ₂	12.9	0.038	6.5
TM450	TiOF ₂ /methionine	450	A-TiO ₂	14.3	0.043	7.1
TM500	TiOF ₂ /methionine	500	A-TiO ₂	13.0	0.041	7.5
T400	TiOF ₂	400	A-TiO ₂	11.6	0.028	6.0

^a A-TiO₂ means anatase TiO₂.

area increases from 7.0 to 12.9 m² g⁻¹, and the PV increases from 0.022 to 0.038 cm³ g⁻¹ when the calcination temperature increases from 300 to 400 °C, further confirming the heat-induced hollowing process, namely from a solid nanocube (TiOF₂) to hollow boxes (TiO₂-HNBS). The TM400 (12.9 m² g⁻¹) and T400 (11.6 m² g⁻¹) samples have similar BET surface areas, which are smaller than that of hollow TiO₂-HNBS (approximately 40 m² g⁻¹) reported by Jia et al. [55] and that of TiO₂ hollow microspheres (20–40 m² g⁻¹) reported by Zhang et al. [56]. This is possibly due to the different preparation methods.

Fig. 4 shows the nitrogen-adsorption isotherms and corresponding pore-size distribution curves of the TM400 and T400 samples. It can be seen that the shape of the isotherms for both samples is of type IV with H3 hysteresis loop shapes, suggesting narrow, slit-shaped pores that are generally associated with plate-like particles, which agrees well with their sheet-like morphology (Figs. 2 and 3).

3.3. UV-vis DRS and FTIR

Light-harvesting ability is of great importance to the photo-reactivity of photocatalysts. Here, UV-vis DRS were used to evaluate the effect of methionine modification on the light-responsive property of the photocatalyst. From Fig. 5, it can be seen that all the photocatalysts after methionine modification show obvious absorption in all the visible region, although this absorption steadily decreases with increasing calcination temperature. The long tail in the visible-light region of

the TiO₂ sample usually comes from the doping or surface oxygen vacancy [29].

When compared with the T400 and TM400 samples, we can clearly see that the absorption of the TM400 sample in the visible-light region is much stronger than that of the T400 sample, indicating that the TM400 sample is a potential visible-light-responsive photocatalyst.

Fig. 6 compares the FTIR spectra of methionine-modified photocatalysts calcined at different temperatures. The peak for the Ti-O and O-Ti-O flexion vibrations of the TM300 sample appears at 563 cm⁻¹ (Fig. 6(a)) [29]. The intensity of the peak becomes much stronger for samples calcined at high tempera-

Fig. 5. UV-visible diffused reflectance spectra (DRS) of the photocatalysts.

Fig. 4. Comparison of nitrogen sorption isotherms and corresponding pore size distribution curves of TM400 and T400 samples.

Fig. 6. FTIR spectra of the photocatalysts.

tures, which is due to the phase transformation from TiOF_2 to anatase TiO_2 (Eq. (3)). The peak at 980 cm^{-1} for the TM300 sample is attributed to the vibration of the Ti–F bond, which cannot be observed for TiO_2 samples calcined at high temperature. However, a newly formed peak at 1090 cm^{-1} is observed for all samples calcined at temperatures higher than $350\text{ }^\circ\text{C}$, which is attributed to the Ti–O–Ti vibration [29], further confirming the phase transformation from TiOF_2 to anatase TiO_2 during calcination. The peaks of 1630 and 3440 cm^{-1} are from the surface –OH groups/ H_2O due to the adsorption of moisture from the air [29,33].

3.4. XPS and EDX mapping analysis

Both of the XPS survey spectra of the unmodified (T400) and methionine-modified TiO_2 -HNBs (TM400) calcined at $400\text{ }^\circ\text{C}$ for 2 h are compared in Fig. 7. It can be clearly seen that the T400 sample contains only Ti, O, and C, with sharp photoelectron peaks appearing at binding energies of 458 eV (Ti 2p), 531 eV (O 1s), and 285 eV (C 1s). The carbon peak is attributed to the residual carbon from the precursor solution and adventitious hydrocarbon from the XPS instrument itself [33]. However, two obvious connected peaks with binding energies of 159 and 164 eV , corresponding to S 2p, are found in the spectrum of the methionine-modified TiO_2 -HNBs (TM400). Careful exami-

Fig. 7. Comparison of the XPS survey spectra between T400 (a) and TM400 (b) samples.

nation also shows a small peak centered at 400 eV in the TM400 sample, which is ascribed to the N 1s signal [29].

Fig. 8(A) and 8(B) compare the high-resolution XPS spectra of the T400 and TM400 samples in the Ti 2p and O 1s regions, respectively. From Fig. 8(A), two peaks of pure TiO_2 -HNBs (T400) at 458.3 and 464.0 eV are assigned to the $\text{Ti } 2p_{3/2}$ and Ti

Fig. 8. High resolution XPS spectra of the photocatalysts in Ti 2p (A), O 1s (B), N 1s (C) and S 2p (D) regions.

$2p_{1/2}$ spin-orbital-splitting photoelectrons in the Ti^{4+} chemical state, respectively [33]. However, the $\text{Ti } 2p_{3/2}$ binding energy of the methionine-modified TiO_2 -HNBs sample (TM400) shifts from 458.3 to 458.8 eV when compared with the pure TiO_2 -HNBs (T400). This approximate 0.5-eV shift in the XPS measurement indicates the presence of a strong interaction at the interfaces between titania and methionine. This intense interaction results in the formation of the electron-transfer channel, which is beneficial to the improvement of the photo-induced charge-separation rate during the photocatalytic process [57]. The strong interaction between TiO_2 -HNBs and methionine also confirms from the increased O 1s XPS binding energy when comparing the spectrum of the TM400 sample with that of T400 sample (Fig. 8(B)).

Fig. 8(C) shows the corresponding high-resolution XPS spectrum of the N 1s region taken from the TM400 sample. The curve of the N 1s region can be deconvoluted into two peaks. The small peak (399.0 eV) is attributed to Ti–N, and the larger peak at 400.1 eV is assigned to the $\text{NH}_3/\text{NH}_4^+$ adsorbed on the surface of the TiO_2 -HNBs, respectively [22,58].

Fig. 8(D) is the high-resolution XPS spectrum of the S 2p region of the TM400 sample. The S 2p curve contains two isolated peaks at binding energies of 158.7 and 164.1 eV, which can be attributed to organic S(–II) and Ti–S, respectively [58]. The organic S(–II) comes from the methionine ($\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$), and the formation of the Ti–S bond reflects the fact that S atoms replace O atoms in the TiO_2 lattice.

To confirm the successful doping of N and S elements into the lattice of TiO_2 -HNBs, EDX mapping was used to observe the distribution of N and S elements in the TM400 sample. As shown in Fig. 9, it can be seen that not only Ti, but also N and S elements, are homogeneously distributed on the surface of TiO_2 -HNBs, which is consistent with the XPS characterization results (Fig. 8).

3.5. Photocatalytic activity

RhB is used as a probe to evaluate the visible-light photocatalytic activity of the photocatalyst under visible-light irradiation

Fig. 9. EDX element mapping of TM400 sample (a–d).

Fig. 10. Photocatalytic degradation profiles of RhB in photocatalysts before (a) and after (b) modified by methionine.

ation ($\lambda > 420$ nm). Fig. 10(a) and 10(b) are the degradation profiles of RhB in the presence of Tx and TMx photocatalysts. In the absence of any photocatalyst, RhB shows little degradation even under visible-light irradiation, reflecting the relative stability of RhB dye. Obvious degradation of RhB is observed in the presence of an illuminated photocatalyst, and the degradation obeys pseudo-zero-order kinetics. The apparent degradation rate constants are compared in Fig. 11. It can be seen that

Fig. 11. Effect of calcination temperature on the photoreactivity of the photocatalyst.

when calcination temperature is below 400 °C, the modification of methionine plays a negative role in the photoreactivity of TMx. This is because the presence of methionine prevents the phase transformation of TiOF_2 to anatase TiO_2 . It has been reported that TiOF_2 shows poor photocatalytic activity [49]. When the calcination temperature is between 400 and 450 °C, the positive effect of methionine on the photoreactivity of TiO_2 -HNBs becomes obvious. For example, the degradation rate constant (K_{app}) of RhB in the TM400 sample is calculated to be $0.15 \text{ mol L}^{-1} \text{ h}^{-1}$, which is 1.53 times higher than that of the unmodified T400 sample ($0.098 \text{ mol L}^{-1} \text{ h}^{-1}$). When the calcination temperature is higher than 500 °C, the positive effect of methionine modification can be neglected. This is due to the fact that it is difficult to dope N and S into the lattice of TiO_2 lattice at high temperature.

3.6. Photocurrent and surface photovoltage spectroscopy

The efficient separation of photo-generated electrons and holes is very important to improve the photoreactivity of the photocatalyst [4]. To account for the high visible-light photocatalytic activity of methionine-modified TiO_2 -HNBs, we compared the photocurrent response and surface photovoltage spectroscopy between the T400 and TM400 samples. From Fig.

Fig. 12. Comparison of the transient photocurrent (A) and photovoltage (B) responses between T400 (a) and TM400 (b) photocatalysts.

12A, prompt generation of photocurrents with good reproducibility when the ITO/ TiO_2 -HNBs electrodes are illuminated can be seen. The photocurrent value of the TM400 based film is as high as $1.5 \mu\text{A cm}^{-2}$, which is 3 times higher than that of T400 based film ($0.5 \mu\text{A cm}^{-2}$). The photocatalytic activity of TiO_2 is highly related to the number of the separated photo-generated charge carriers. Thus, it can be deduced that the photocatalytic activity of T400 is higher than that of the T400 sample.

The SPS was also measured to confirm the separation efficiency of photo-generated carriers of the photocatalyst. From Fig. 12B, it can be seen that the SPS signal of T400 can only be observed in the UV region due to the large band gap of anatase TiO_2 . However, TM400 not only shows a much higher SPS signal in the UV region, but also extends the signal to the visible-light region, indicating its visible photocatalytic activity.

3.7. Reusability of the photocatalyst

The stability of the photocatalyst is of great importance from the viewpoint of practical applications. Therefore, we studied the reusability of the TM400 photocatalyst in the degradation of RhB for five consecutive cycles under visible-light irradiation (Fig. 13). We observe that the degradation rate of RhB in the presence of the TM400 photocatalyst almost remains unchanged even after being recycled five times, reflecting its good stability. The high stability of the methionine-modified TiO_2 -HNBs photocatalyst makes it promising for use in the treatment of wastewater.

3.8. Photocatalytic oxidation of NO

Upon considering that RhB can also be degraded via the photosensitization pathway, we measured the visible photocatalytic activity of the photocatalyst by photocatalytic oxidation of NO under visible-light irradiation, and the results are shown in Fig. 14. It can be seen that, similar to the results of RhB degradation, the TM400 sample shows the highest visible-light photoreactivity among all the photocatalysts with a

Fig. 13. Five consecutively cycling runs for the photocatalytic degradation of RhB using TM400 as photocatalyst under visible light irradiation.

Fig. 14. Photocatalytic oxidation of NO under visible light irradiation.

NO decomposition rate of 20%, which is 2 times higher than that of the T400 sample (a NO decomposition rate of less than 10%). This result also confirms the enhanced visible photocatalytic activity of methionine-modified TiO₂-HNBs.

4. Conclusions

Visible-light-responsive TiO₂-HNBs assembled from TiO₂ nanosheets with exposed high-energy (001) facets were fabricated by simple calcination of a mixture of TiOF₂ cubes and

methionine. During calcination, TiOF₂ cubes transform into more stable anatase TiO₂-HNBs via an *in situ* dissolution-recrystallization process, and both N and S elements are simultaneously doped into the TiO₂ lattice. Modification of TiO₂-HNBs with methionine not only greatly improves their light-harvesting ability, but also facilitates the efficient separation of photo-generated electron-hole pairs, therefore greatly enhancing the visible photocatalytic activity in the degradation of RhB and oxidation of NO. The present study provides a simple approach to designing highly efficient visible-light-responsive photocatalysts.

References

- [1] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.*, **2016**, 116, 7159–7329.
- [2] F. He, F. Ma, T. Li, G. X. Li, *Chin. J. Catal.*, **2017**, 34, 2263–2270.
- [3] K. Z. Qi, B. Cheng, J. G. Yu, W. K. Ho, *Chin. J. Catal.*, **2017**, 38, 1936–1955.
- [4] T. T. Huang, Y. H. Li, X. F. Wu, K. L. Lv, Q. Li, M. Li, D. Y. Du, H. P. Ye, *Chin. J. Catal.*, **2018**, doi: 10.1016/S1872-2067(17)62913-9.
- [5] D. A. Erdogan, E. Ozensoy, *Appl. Surf. Sci.*, **2017**, 403, 159–167.
- [6] F. Dong, Z. W. Zhao, Y. J. Sun, Y. X. Zhang, S. Yan, Z. B. Wu, *Environ. Sci. Technol.*, **2015**, 49, 12432–12440.
- [7] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiave, *Appl. Catal. B*, **1999**, 20, 15–27.
- [8] Z. L. Ni, W. D. Zhang, G. M. Jiang, X. P. Wang, Z. Z. Lu, Y. J. Sun, X. W. Li, Y. X. Zhang, F. Dong, *Chin. J. Catal.*, **2017**, 38, 1174–1183.

Graphical Abstract

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Enhanced visible photocatalytic activity of TiO₂ hollow boxes modified by methionine for RhB degradation and NO oxidation

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N and S co-doped TiO₂-hollow nanoboxes assembly from high energy TiO₂ nanosheets were prepared by calcining the mixture of TiOF₂ cubes and methionine (C₅H₁₁NO₂S), which showed improved visible photoreactivity in RhB degradation and NO oxidation.

- [9] Y. H. Li, W. K. Ho, K. L. Lv, B. C. Zhu, S. C. Lee, *Appl. Surf. Sci.*, **2018**, 430, 380–389.
- [10] F. Dong, Z. Y. Wang, Y. H. Li, W. K. Ho, S. C. Lee, *Environ. Sci. Technol.*, **2014**, 48, 10345–10353.
- [11] J. G. Yu, J. X. Low, W. Xiao, P. Zhou, M. Jaroniec, *J. Am. Chem. Soc.*, **2014**, 136, 8839–8842.
- [12] Q. J. Xiang, B. Cheng, J. G. Yu, *Angew. Chem. Int. Ed.*, **2015**, 54, 11350–11366.
- [13] Y. M. He, L. H. Zhang, B. T. Teng, M. H. Fan, *Environ. Sci. Technol.*, **2015**, 49, 649–656.
- [14] Q. J. Xiang, F. Y. Cheng, D. Lang, *ChemSusChem*, **2016**, 9, 996–1002.
- [15] Y. Xia, Q. Li, K. L. Lv, D. G. Tang, M. Li, *Appl. Catal. B*, **2017**, 206, 344–352.
- [16] Q. Hao, S. M. Hao, X. X. Niu, X. Li, D. M. Chen, H. Ding, *Chin. J. Catal.*, **2017**, 38, 278–286.
- [17] Y. Xia, Q. Li, K. L. Lv, M. Li, *Appl. Surf. Sci.*, **2017**, 398, 81–88.
- [18] J. Schneider, M. Matsuoka, M. Takeuchi, J. L. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.*, **2014**, 114, 9919–9986.
- [19] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature*, **2008**, 453, 638–641.
- [20] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*, **2001**, 293, 269–271.
- [21] X. B. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science*, **2011**, 331, 746–750.
- [22] X. F. Wu, S. Fang, Y. Zheng, J. Sun, K. L. Lv, *Molecules*, **2016**, 21, 181.
- [23] C. Z. Wen, Q. H. Hu, Y. N. Guo, X. Q. Gong, S. Z. Qiao, H. G. Yang, *Chem. Commun.*, **2011**, 47, 6138–6140.
- [24] Y. Kondo, H. Yoshikawa, K. Awaga, M. Murayama, T. Mori, K. Sunada, S. Bandow, S. Iijima, *Langmuir*, **2008**, 24, 547–550.
- [25] Q. Sun, Y. M. Xu, *J. Phys. Chem. C*, **2009**, 113, 12387–12394.
- [26] G. Colon, S. Murcia Lopez, M. C. Hidalgo, J. A. Navio, *Chem. Commun.*, **2010**, 46, 4809–4811.
- [27] R. R. Hao, G. H. Wang, C. J. Jiang, H. Tang, Q. C. Xu, *Appl. Surf. Sci.*, **2017**, 411, 400–410.
- [28] D. Li, H. Haneda, S. Hishita, N. Ohashi, *Chem. Mater.*, **2005**, 17, 2588–2595.
- [29] K. L. Lv, H. S. Zuo, J. Sun, K. J. Deng, S. C. Liu, X. F. Li, D. Y. Wang, *J. Hazard. Mater.*, **2009**, 161, 396–401.
- [30] D. Z. Li, Z. X. Chen, Y. L. Chen, W. J. Li, H. J. Huang, Y. H. He, X. Z. Fu, *Environ. Sci. Technol.*, **2008**, 42, 2130–2135.
- [31] J. G. Yu, G. P. Dai, B. B. Huang, *J. Phys. Chem. C*, **2009**, 113, 16394–16401.
- [32] Y. H. Li, K. L. Lv, W. K. Ho, Z. W. Zhao, H. Yu, *Chin. J. Catal.*, **2017**, 38, 321–329.
- [33] K. L. Lv, S. Fang, L. L. Si, Y. Xia, W. K. Ho, M. Li, *Appl. Surf. Sci.*, **2017**, 391, 218–227.
- [34] W. Li, F. Wang, Y. P. Liu, J. X. Wang, J. P. Yang, L. J. Zhang, A. A. El-zatahry, D. Al-Dahyan, Y. Y. Xia, D. Y. Zhao, *Nano Lett.*, **2015**, 15, 2186–2193.
- [35] T. D. Nguyen-Phan, S. Luo, Z. Y. Liu, A. D. Gamalski, J. Tao, W. Q. Xu, E. A. Stach, D. E. Polyansky, S. D. Senanayake, E. Fujita, J. A. Rodriguez, *Chem. Mater.*, **2015**, 27, 6282–6296.
- [36] H. G. Yang, H. C. Zeng, *J. Phys. Chem. B*, **2004**, 108, 3492–3495.
- [37] X. W. Lou, L. A. Archer, Z. C. Yang, *Adv. Mater.*, **2008**, 20, 3987–4019.
- [38] L. Liang, K. N. Li, K. L. Lv, W. K. Ho, Y. Y. Duan, *Chin. J. Catal.*, **2017**, 38, 2085–2093.
- [39] X. F. Li, K. L. Lv, K. J. Deng, J. F. Tang, R. Su, J. Sun, L. Q. Chen, *Mater. Sci. Eng. B*, **2009**, 158, 40–47.
- [40] J. Sun, X. Yan, K. L. Lv, S. Sun, K. J. Deng, D. Y. Du, *J. Mol. Catal. A*, **2013**, 367, 31–37.
- [41] J. F. Lan, X. F. Wu, K. L. Lv, L. L. Si, K. J. Deng, *Chin. J. Catal.*, **2015**, 36, 2237–2243.
- [42] R. W. Yang, J. H. Cai, K. L. Lv, X. F. Wu, W. G. Wang, Z. H. Xu, M. Li, Q. Li, W. Q. Xu, *Appl. Catal. B*, **2017**, 210, 184–193.
- [43] K. L. Lv, J. G. Yu, J. J. Fan, M. Jaroniec, *CrystEngComm*, **2011**, 14, 7044–7048.
- [44] L. L. Si, Z. A. Huang, K. L. Lv, H. P. Ye, K. J. Deng, Y. Y. Wu, *J. Alloys Compd.*, **2014**, 612, 69–73.
- [45] Z. A. Huang, Z. Y. Wang, K. L. Lv, Y. Zheng, K. J. Deng, *ACS Appl. Mater. Interfaces*, **2013**, 5, 8663–8669.
- [46] S. Fang, Y. Xia, K. L. Lv, Q. Li, J. Sun, M. Li, *Appl. Catal. B*, **2016**, 185, 225–232.
- [47] K. L. Lv, J. G. Yu, L. Z. Cui, S. L. Chen, M. Li, *J. Alloys Compd.*, **2011**, 509, 4557–4562.
- [48] Z. Y. Wang, B. B. Huang, Y. Dai, X. L. Zhu, Y. Y. Liu, X. Y. Zhang, X. Y. Qin, *CrystEngComm*, **2013**, 15, 3436–3441.
- [49] Z. Y. Wang, K. L. Lv, G. H. Wang, K. J. Deng, D. G. Tang, *Appl. Catal. B*, **2010**, 100, 378–385.
- [50] Z. Y. Wang, B. B. Huang, Y. Dai, X. Y. Zhang, X. Y. Qin, Z. Li, Z. K. Zheng, H. F. Cheng, L. W. Guo, *CrystEngComm*, **2012**, 14, 4578–4581.
- [51] Z. A. Huang, Q. Sun, K. L. Lv, Z. H. Zhang, M. Li, B. Li, *Appl. Catal. B*, **2015**, 164, 420–427.
- [52] L. Chen, L. F. Shen, P. Nie, X. G. Zhang, H. S. Li, *Electrochim. Acta*, **2012**, 62, 408–415.
- [53] J. Zhu, D. Q. Zhang, Z. F. Bian, G. S. Li, Y. N. Huo, Y. F. Lu, H. X. Li, *Chem. Commun.*, **2009**, 5394–5396.
- [54] X. G. Han, Q. Kuang, M. S. Jin, Z. X. Xie, L. S. Zheng, *J. Am. Chem. Soc.*, **2009**, 131, 3152–3153.
- [55] C. C. Jia, X. Zhang, P. Yang, *Appl. Surf. Sci.*, **2018**, 430, 457–465.
- [56] Y. Zhang, Z. Y. Zhao, J. R. Chen, L. Cheng, J. Chang, W. C. Sheng, C. Y. Hu, S. S. Cao, *Appl. Catal. B*, **2015**, 165, 715–722.
- [57] Y. H. Li, X. F. Wu, W. K. Ho, K. L. Lv, Q. Li, M. Li, S. C. Lee, *Chem. Eng. J.*, **2018**, 336, 200–210.
- [58] K. L. Lv, J. C. Hu, X. H. Li, M. Li, *J. Mol. Catal. A*, **2012**, 356, 78–84.

蛋氨酸改性 TiO₂ 空心纳米盒高效可见光催化 RhB 分解和 NO 氧化

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摘要: 由高能面 TiO₂ 纳米片 (TiO₂-NSs) 组装成的 TiO₂ 空心纳米盒 (TiO₂-HNBs) 显示出比单独 TiO₂-NSs 更强的光催化性能, 但是 TiO₂-HNBs 依然属于紫外光催化剂, 无法充分利用太阳能. 因此, 开发具有可见光响应的由高能面 TiO₂-NSs 组装而成的 TiO₂-HNBs 具有重要意义. 本文将立方体 TiOF₂ 与含有 N 和 S 元素的生物分子蛋氨酸混合, 通过一步焙烧制备了具有可见光响应活性的 N 和 S 元素共掺杂的 TiO₂-HNBs (掺杂催化剂标记为 TMx, 未掺杂催化剂标记为 Tx, x 代表焙烧温

度).

由立方体 TiOF_2 到锐钛矿相 TiO_2 空心纳米盒的转变是一个自模板转化过程. 氟离子的存在降低了 TiO_2 高能面(001)面的表面能, 从而使得高能面 TiO_2 纳米片的形成变得可能. 因此, 热处理立方体 TiOF_2 可得到由高能面 TiO_2 纳米片组装的 TiO_2 空心纳米盒.

本文系统研究了焙烧温度 (300–500 °C) 对所制 TiO_2 -HNBs 结构与光催化性能的影响. 结果发现, 在 350 °C 下焙烧, TiOF_2 完全转化成锐钛矿相 TiO_2 -HNBs. 但是焙烧蛋氨酸与 TiOF_2 的混合物, 需 400 °C 才能完全实现 TiOF_2 到锐钛矿相 TiO_2 -HNBs 的转变. 这说明蛋氨酸的加入阻碍了 TiOF_2 向锐钛矿相 TiO_2 -HNBs 的转变. XPS 结果显示, 经过 400 °C 焙烧的蛋氨酸改性样品 (TM400), N 和 S 元素成功掺入了 TiO_2 -HNBs 晶格, 使其产生可见光催化活性.

相对于 400 °C 焙烧 TiOF_2 所得样品 T400, 蛋氨酸改性的 TM400 催化剂可见光降解罗丹明 B 染料 (RhB) 和 NO 氧化的性能分别提升了 1.55 倍和 2.0 倍, 这与其更强的可见光吸收性能和光生载流子分离效率有关. 400 °C 焙烧的蛋氨酸改性的 TM400 可见光催化活性稳定, 连续 5 次可见光催化 RhB 降解后, 其活性没有明显改变, 显示了潜在的应用前景.

关键词: TiO_2 空心纳米盒; TiOF_2 ; 光催化降解; 罗丹明B; 一氧化氮氧化

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