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Enhanced visible photocatalytic activity of TiO_2 hollow boxes modified by methionine for RhB degradation and NO oxidation

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Hierarchical TiO_2 hollow nanoboxes (TiO_2-HNBs) assembled from TiO_2 nanosheets (TiO_2-NSs) show improved photoreactivity when compared with the building blocks of discrete TiO_2-NSs. However, TiO_2-HNBs can only be excited by ultraviolet light. In this paper, visible-light-responsive N and S co-doped TiO_2-HNBs were prepared by calcining the mixture of cubic $TiOF_2$ and methionine ($C_5H_{11}NO_2S$), a N- and S-containing biomacromolecule. The effect of calcination temperature on the structure and performance of the TiO_2-HNBs was systematically studied. It was found that methionine can prevent $TiOF_2$-to-anatase TiO_2 phase transformation. Both N and S elements are doped into the lattice of TiO_2-HNBs when the mixture of $TiOF_2$ and methionine undergoes calcination at 400 °C, which is responsible for the visible-light response. When compared with that of pure 400 °C-calcined TiO_2-HNBs (T400), the photoreactivity of 400 °C-calcined methionine-modified TiO_2-HNBs (TM400) improves 1.53 times in photocatalytic degradation of rhodamine-B dye under visible irradiation (λ > 420 nm). The enhanced visible photoreactivity of methionine-modified TiO_2-HNBs is also confirmed by photocatalytic oxidation of NO. The successful doping of N and S elements into the lattice of TiO_2-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 TiO_2-HNBs. The photoreactivity of methionine modified TiO_2-HNBs remains nearly unchanged even after being recycled five times, indicating its promising use in practical applications.

1. Introduction

In the last 30 years, semiconductor photocatalysis has become an important research topic due to its potential application 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 CO_2 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 ($C_5H_{11}NO_2S$), 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, TM400 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 Cu K_α 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 Al K_α radiation under vacuum at 2×10^{-6} Pa. All the binding energies were referenced to the C 1*s* 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 (λ > 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 × 15.0 cm × 10.0 cm). A simulated visible-light source was acquired from an LED lamp (λ > 400 nm).