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Synthesis of C,N,S-tridoped mesoporous titania with enhanced visible light-induced photocatalytic activity

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ABSTRACT

C,N,S-tridoped mesoporous titania was synthesized via a combined sol–gel process with surfactant-assisted templating method using cetyltrimethylammonium bromide (CTAB) as the structure-directing agent. The prepared samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectra (DRS), N_2 adsorption–desorption measurements (BET) and Fourier transform infrared spectroscopy (FT-IR). The photocatalytic activity was evaluated by the photocatalytic degradation of Reactive Brilliant Red X-3B in aqueous solution. The results showed that the prepared titania was mesoporous structured and exhibited stronger absorption in the visible light region with red shift in the absorption edge. The prepared C,N,S-tridoped mesoporous titanias showed high photocatalytic activity under visible light irradiation. The high activity can be attributed to the synergetic effects of large surface area, red shift in absorption edge, strong absorption in visible light region and mixed phase structures of the C,N,S-tridoped mesoporous titania.

1. Introduction

Semiconductor mediated photocatalytic oxidation and reduction offers potentially a facile and cheap method for removing inorganic and organic pollutants from wastewaters. It has been an area of intense interest for the past twenty years, particularly for removing organic compounds as they can be completely mineralized under photocatalytic oxidation [1–5]. Among various oxide semiconductor photocatalyst, titanium dioxide has proved to be the most suitable catalysts for widespread environmental application because of its biological and chemical inertness, strong oxidizing power, non-toxicity and long-term stability against photo and chemical corrosion [6–11]. However, its technological application seems limited by several factors, among which the most restrictive one is the need of using an ultraviolet (UV), wavelength (λ) < 387 nm, as excitation source due to its wide band-gap (3.2 eV for anatase) [12], and 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 absorption scope of TiO_2 may then appear as an appealing challenge for developing the future generation of photocatalysts.

Several works reported that doping TiO_2 with nonmetallic elements, such as nitrogen, sulphur, carbon, boron and fluorine shift the optical absorption edge of TiO_2 toward lower energy, thereby increasing the photocatalytic activity in visible light region [13–17]. On the other hand, numerous approaches have been conducted to prepare mesoporous titania due to its high surface-to-volume ratio and offers more active sites, which are of great importance in photocatalysis and solar energy conversion [18–22]. For preparation of visible light responsive titania with high surface area, other authors prepared metal or nonmetal doped mesoporous titania [23–26]. Undeniably, the preparation of doped mesoporous titania resulting in a desired band-gap narrowing and an enhancement in the photocatalytic activity under visible light irradiation. This technology makes it is feasible for the development of practical application of solar-induced photocatalyst. However, to the best of our knowledge, the preparation of C,N,S-tridoped mesoporous TiO_2 has not been reported. This work provide a simple route for the preparation of C,N,S-tridoped mesoporous TiO_2 with enhanced photocatalytic activity under visible light irradiation.

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2. Experimental

2.1. Materials and chemicals

All chemicals used were of analytical grade from Shanghai Chemical Reagent Corporation. Water used in the experiments was deionized, doubly distilled prior to use.

2.2. Sample preparation

Nanocrystalline mesoporous titania was synthesized via a combined sol–gel process with surfactant-assisted templating method. $Ti(OBu)_4$ was chosen as a Ti precursor, which is less reactive than titanium chloride and titanium isopropoxide. Firstly, 2.62 g cetyltrimethylammonium bromide (CTAB) was dissolved into 200 ml water. The acidity of the solution was adjusted by phosphoric acid to pH 1. Then, definite amount of thiourea was added into the solution. The molar ratio of thiourea to titania was controlled to be 1 or 2, and the obtained samples were labeled as SMT-1, SMT-2, respectively. Afterwards, $Ti(OBu)_4$ diluted with PrOH was added dropwise into the above solution under vigorous stirring. Then, the solution was kept under reflux condition (around 60 °C) for 0.5 h. The titania sol was dried in a rotatory evaporator under vacuum for 1 h (at 60 °C). Then it was dried into powder at 100 °C. At last, the dried samples were calcined at 540 °C for 6 h, and the C,S,N-tridoped mesoporous titania was thus obtained. For comparison, undoped mesoporous titania (MT) was prepared by the same way without the addition of thiourea.

2.3. Equipments

The dried samples were analyzed for their composition and microstructure. The structure properties were determined by X-ray diffractometer (XD-3A, Shimadazu Corporation, Japan) using graphite monochromatic copper radiation (Cu Kα) at 40 kV, 30 mA over the 2θ range 20–80°. The morphologies were characterized with a transmission electron microscopy (TEM, JEM2000EX). BET surface area measurements were carried out by N_2 adsorption at 77 K using an ASAP2020 instrument. The total pore volume was calculated from the amount of nitrogen adsorbed at relative pressure of 0.975. IR spectrum was recorded as KBr pellets on Shimadzu Fourier transform infrared (FT-IR) spectrometer. X-ray photoelectron spectrometer (XPS) measurements were done in a VG Microtech Multilab ESCALB-250 with Mg Kα radiation. A UV–vis spectrophotometer (Shimadzu UV-4100) was used to record the diffuse reflectance spectra (DRS) of samples.

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. 0.3 g of TiO_2 sample was added into 200 ml of 100 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 of 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 the concentration of X-3B was analyzed using the UV–vis spectrophotometer at 535 nm. The schematic image of the photocatalytic reactor is shown in Scheme 1.

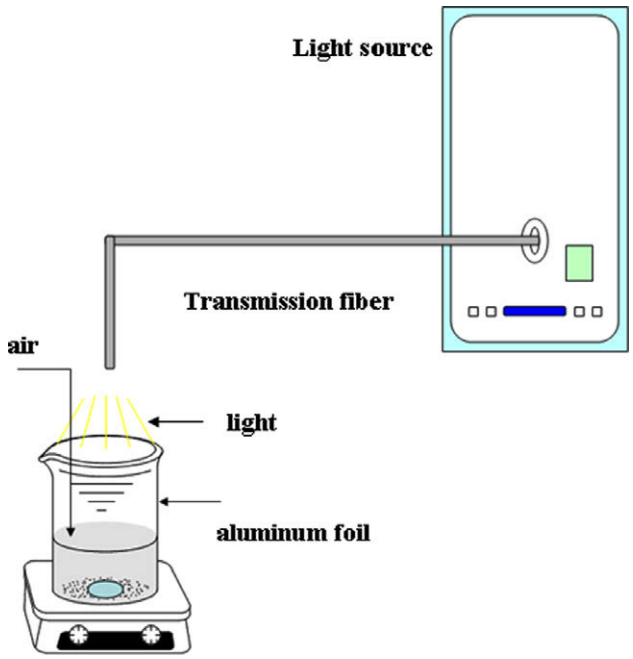
3. Results and discussion

3.1. Characterization of the prepared samples

XRD was used to investigate the phase structure of the as prepared samples (MT, SMT-1, SMT-2) and the results were shown in Fig. 1. It can be seen that MT exhibits only the characteristic peaks of anatase phase (major peaks: 25.4°, 38.0°, 48.0°, 54.7° and 63.1°). The other two samples (SMT-1, SMT-2) exhibit the characteristic peaks of both anatase and rutile phase. The weight percent of anatase in the rutile phase was obtained from the following equation [27]:

$$X_A = [1 + 1.26(I_R/I_A)]^-$$

where X_A is the weight fraction of anatase in the mixture, I_R and I_A are obtained from the peak areas of the characteristic anatase (1 0 1) and rutile (1 1 0) diffractions, respectively. The calculated weight percents of anatase phase are 90.2% and 87.7% for SMT-1 and SMT-2, respectively. It can also be seen that the ratio (R) of thiourea to titania slightly influences the crystallization of the mesoporous titania. With increasing R, the peak intensities of anatase slightly



Scheme 1. Schematic image of photocatalytic reactor.

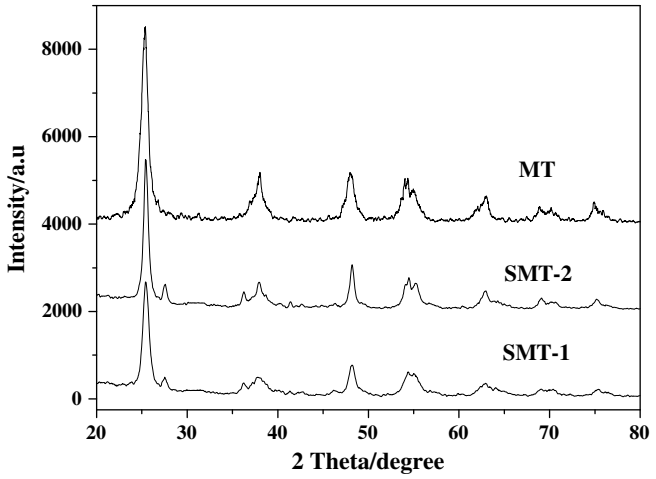


Fig. 1. XRD patterns of MT, SMT-1 and SMT-2.