



Mesoporous black Ti³⁺/N-TiO₂ spheres for efficient visible-light-driven photocatalytic performance



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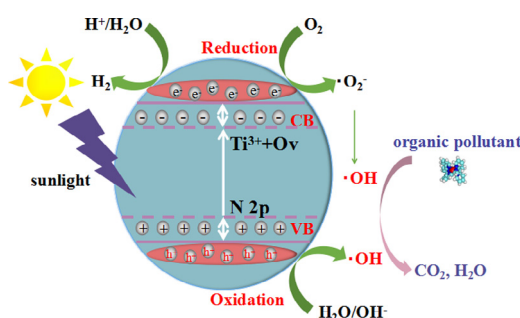
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HIGHLIGHTS

- Mesoporous black Ti³⁺/N-TiO₂ spheres are fabricated.
- The narrowed bandgap of 2.11 eV extends the photoresponse to near-infrared region.
- It possesses high surface area of 100 m² g⁻¹ and large pore size of 6.5 nm.
- It exhibits excellent visible-light-driven photocatalytic performance.
- It ascribes to the synergy of N, Ti³⁺ codoping and mesoporous frameworks.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous black Ti³⁺/N-TiO₂ spheres with high crystallinity are fabricated by a facile evaporation-induced self-assembly (EISA) method, using urea as nitrogen resource, combined with a mild calcinations (350 °C) after an in-situ hydrogenation under an argon atmosphere. The prepared materials are characterized by X-ray diffraction, Raman, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The results indicate the prepared sample is uniform mesoporous black Ti³⁺/N-TiO₂ spheres with high crystallinity of anatase, high surface area of ~100 m² g⁻¹, large pore size of 6.5 nm and narrow band gap of 2.11 eV, could be easily controlled with the diameter from 200 to 800 nm. Meanwhile, the photoresponse extends to near-infrared region owing to Ti³⁺ and N codoping. The visible-light-driven photocatalytic degradation ratio of methyl orange is up to 96% and photocatalytic hydrogen production rate is ~150 μmol h⁻¹, which are several times higher than that of pristine TiO₂. Besides, the possible photocatalytic mechanism is proposed. The excellent photocatalytic activity can be ascribed to N and Ti³⁺ doping resulting in high visible light utilization and enhanced separation of photogenerated charge carriers, and the mesoporous networks offering more surface active sites.

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1. Introduction

In recent decades, semiconductor photocatalysis has been utilized as an ideal way for environment-organic-pollutant decontamination and energy production to replace traditional

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technology which can cause environmental pollution problem [1]. Among them, titanium dioxide (TiO_2) has been considered to be a remarkable one on account of a variety of merits such as low price, nontoxicity, and universality, [2,3] and has found wide applications in organic pollutants degradation [4], solar cells [5–8], Li-ion batteries [9], hydrogen energy [10], water remediation [11], and so on. However, pure TiO_2 has two well-known nuisances that impede its large-scale application in photocatalysis [12]. One is that TiO_2 only has activity under UV light which accounts for less than 5% of sunlight as a result of its wide band gap of 3.0–3.2 eV [13]. Another is that the high electron-hole recombination rate can induce a low quantum yield and inefficiency of photocatalytic reactions [14]. Therefore, it is in urgent demand to prepare efficient TiO_2 with high visible light respond and slow photogenerated carriers recombination rate.

As is known to all, incorporation of other elements into TiO_2 is an effective strategy for extending the photoresponse of TiO_2 to visible light region including metal and non-metal doping [15]. Nevertheless, non-metal doping such as C, N, S, and F is thought to be more effective in expanding its light absorption region than metal doping. Furthermore, doping other metals always have higher cost and can induce thermal instability and the formation of secondary impurities [16]. Among numerous non-metals, N-doped TiO_2 has got the most widely investigation since Asahi et al. [17] proved its validity, considering that atomic radius of nitrogen is similar to that of oxygen, as well as the small ionization energy of nitrogen [18]. According to previous reports, nitrogen is responsible for the photoactivity in visible light because it can narrow the band gap of TiO_2 through forming an intermediate level of nitrogen 2p states which can elevate the oxygen 2p states valence band [19]. While it can merely extend the visible light absorption from 400 to 600 nm, it is still difficult to make catalytic reactions in wider range (e.g. >800 nm). Therefore, it is a significant challenge to broaden light absorption to 800 nm or even to the near-infrared region. In 2011, Mao et al. presented a groundbreaking research that demonstrating an approach involved hydrogen calcination to enhanced solar absorption by introducing disordered structure in TiO_2 [20]. Since then, much effort has been made directed toward Ti^{3+} self-doped TiO_2 with plenty of oxygen vacancies due to its unexpected property [21]. In general, Ti^{3+} self-doped TiO_2 appears black or dark blue so that it has strong absorption to visible light [22]. The combined effect of disordered surface layer and oxygen vacancies can give rise to narrowing the band gap of TiO_2 because energy level of the localized electronic state is below the conduction band minimum [23]. Furthermore, the formation of defects can capture electrons and prevent the recombination of electron-hole pairs, thus prolonging the life-time of them [24]. There are several methods to prepare black TiO_2 including high pressure hydrogenation, ionothermal, and N_2H_4 reduction. Of which high temperature calcination under the condition of hydrogen is a representative one [21,25,26]. However, the safety and practicability of such approach can't be assured. Hence, it is necessary to figure out a mild way to prepare Ti^{3+} doped TiO_2 , and ideally combined with N species doping, thereby the synergy of Ti^{3+} and N could ulteriorly narrow the band gap of TiO_2 .

Recently, numbers of researches have focused on the morphology of TiO_2 materials, such as nanospheres [27], nanotubes [28], nanosheets [29], and mesostructures [30]. Among them, three dimensional (3D) spherical TiO_2 stands out for its peculiarities of large surface areas, special structure and high photocatalytic activities [31]. Therefore, TiO_2 sphere materials, which are a kind of self-assembly nanoparticles, have become hotspots because they are favorable for forming porous system that possesses relatively high surface areas. The 3D mesostructure can not only supply more accessible active sites in the process of the reaction in comparison with regular TiO_2 , but also facilitate the contact between catalysts

and reactants [32]. In particular, the mesopores fabricated in that way are usually firm enough to keep its structure during the photocatalytic reaction. Although there are already numerous studies on one or two of N-doped, Ti^{3+} self-doped, and mesoporous 3D spherical TiO_2 , an appropriate strategy to fabricate TiO_2 spheres with the character of above merits is still a great challenge.

Herein, we demonstrate a facile template-free evaporation-induced self-assembly (EISA) method, followed by an in situ reduction, for preparation monodisperse black Ti^{3+} /N- TiO_2 spheres with high crystallinity. The structure and morphology of the prepared materials are analyzed and the performance of various TiO_2 is measured by the photodegradation of methyl orange solution and photocatalytic hydrogen evolution. Besides, the possible photocatalytic mechanism has been proposed.

2. Materials and methods

2.1. Materials

Titanium isopropoxide (TTIP, 98%) was purchased from J&K Chemical Reagent Company, China. Absolute ethanol (EtOH), urea, and chloroplatinic acid (H_2PtCl_6) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd, China. Sodium boron hydride (NaBH_4 , 98%) and methyl orange were purchased from Aladdin Reagent Company, China. All reagents used in this research were analytical grade and employed without further purification, and the deionized (DI) water was used over the whole experiments.

2.2. Synthesis of the black Ti^{3+} /N- TiO_2 spheres

The nitrogen doped mesoporous TiO_2 nanospheres consisting of TiO_2 nanoparticles were prepared via one-step EISA method. In the term of N-doped samples, urea was used as the nitrogen source. First, 110 mL of absolute ethanol and 1.5 mL of water were mixed in a 200 mL baker. Then, 0.6 g of urea were dissolved in the mixed solution for several minutes under magnetic stirring. After that, a solution containing 9 mL of absolute ethanol and 1 mL of titanium isopropoxide (TTIP) was dropwise into the above solution with vigorous stirring at room temperature for 24 h. The resulting solution was dried at 80 °C for 12 h in an oven followed by washed several times with deionized water and absolute ethanol. The final product was obtained after calcining the powders at 450 °C for 2 h in the muffle furnace (denoted as N- TiO_2). For the pure TiO_2 nanospheres, the samples were synthesized under the same condition without adding urea as control experiment. Then, 0.6 g of the prepared sample were ground with 0.6 g of NaBH_4 for 30 min at room temperature (20 ± 2 °C) thoroughly. Then the mixtures were transferred into porcelain boats, and placed in a tubular furnace to calcine at 350 °C for 1 h under the Ar atmosphere with a heating rate of 5 °C min^{-1} . After naturally cooling down to room temperature, the mesoporous black Ti^{3+} /N- TiO_2 was obtained (Scheme 1). The obtained samples (denoted as b-N- TiO_2) were washed with deionized water and absolute ethanol for three times to remove excessive NaBH_4 . For comparison, the pure black TiO_2 (b- TiO_2) was also synthesized under the same condition.

2.3. Characterization

The prepared powders were characterized by utilizing various techniques. The X-ray diffraction (XRD-D8 Advance, Bruker) technique with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) from 20 to 70° at an accelerating voltage of 40 kV, coupled with emission current of 30 mA. The Raman spectra were carried out by a Jobin Yvon HR 800 micro-Raman spectrometer in the range of 100–800 cm^{-1} with a laser excitation at 457.9 nm. The morphology of TiO_2

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