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Facile synthesis of hierarchically meso/nanoporous s- and c-codoped TiO_2 and its high photocatalytic efficiency in H_2 generation

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ABSTRACT

Here, hierarchically meso/nanoporous TiO_2 was successfully fabricated by a facile and efficient hydrolysis and calcination method using $Ti(OC_4H_9)_4$ and $K_2S_2O_8$ as precursors. The hydrosol was firstly prepared by drop-wise adding ethanol dissolved $Ti(OC_4H_9)_4$ solution into acetone dissolved $K_2S_2O_8$ solution under a vigorous stirring and heating condition. After being sufficiently hydrolyzed, the hydrosol was calcined to promote the crystallization of TiO_2 and successfully dope S and C on TiO_2. The calcination temperature significantly affects the doping of S and C on TiO_2, crystallization of TiO_2, formation of hierarchically meso/nanoporous structure of TiO_2 and its light absorption capability. The S- and C-codoped TiO_2 exhibits high photocatalytic H_2 generation efficiency in a water/methanol sacrificial reagent system under the irradiation of UV light. The high photocatalytic efficiency is dependent on the comprehensively competing effects of the codoping of S and C, crystallization, specific surface area and light absorption capability. The S- and C-codoped TiO_2 calcined at 600 °C demonstrates the highest photocatalytic H_2 generation efficiency, which is ascribed to the balanced synergy of the abovementioned factors.

1. Introduction

The well-known issues related to environmental pollution and global warming concerns have motivated numerous efforts concentrating on photocatalytic H_2 generation to utilize abundant clean energy [1,2]. H_2 energy is an ideal candidate to alleviate the overdependence on fossil fuels in future because of its high energy intensity, environmental friendliness, and recycling possibility [2–4]. Since the benchmark paper published on Nature in 1972 reporting the photocatalytic water splitting on titania electrodes under UV light irradiation [5], it becomes a promising and sustainable approach to use TiO_2 photocatalytic water splitting to generate H_2. Owing to its unique properties including suitable band position, non-toxicity, biological and chemical stability in solution, and high photocatalytic efficiency [6,7], TiO_2 has essentially demonstrated to be one of the most efficient and viable photocatalyst [7–11]. In the past decades, huge research efforts were undertaken to fundamental research and practical applications of TiO_2 for clean energy generation and environmental purifications, etc [12–17].

However, the large band gap of 3.2 eV (anatase) restricts that TiO_2 can only absorb the UV fraction of solar light (about 2–3% of the total solar energy) to generate electron–hole pairs, which will migrate from the conduction and valence bands to the surface of TiO_2 to respectively initiate reductive and oxidative reactions [6,8,18]. The poor light absorption capability to generate electrons and holes as well as their fast recombination result in comparatively-low photocatalytic activity of TiO_2 [19,20]. Therefore, it is still challengeable to widely apply TiO_2 for large-scale clean energy generation and practical environmental purification in a cost-effective and efficient way [19,20]. Photosensitized TiO_2 by doping inorganic element such as hydrogen [20], carbon [21–24], sulfur [25], and nitrogen [1,11,18,26–28] proved to be an effective approach to tackle this challenge, as these doped elements act as electron donor or acceptor in the forbidden band of TiO_2 thus inducing absorption in the visible region [18]. A merit for carbon doping is that it can significantly stabilize the photoactive anatase TiO_2, inhibit the sintering of nanocrystals and expedite the adsorption of organic pollutant molecules by catalysts [6,24,29]. At the same time, the good conductivity of carbon also makes it possible that the carbon doped TiO_2 would accelerate the charge transfer from bulk of TiO_2 to the desired location where oxidation reactions take place [6,30]. Similar to the merits of inorganic element doping, the Pt deposition on the surface of TiO_2 would enhance the separation of photogenerated electrons and holes to prolong their lifespan, and suppress the reverse reaction between H_2 and O_2 so as to lead to improve the photocatalytic activity of TiO_2 [31].

Besides, considering the significance of the microstructure on the performance of photocatalyst, it is very interesting to search for new photocatalyst with an appropriate crystal structure and

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high specific surface area to improve the photocatalytic activity [14,32–36]. Porous TiO_2 with large specific surface area would ease the adsorption and encourage the accessibility of reactants to the catalysts via providing enough active sites [8,37,38]. Furthermore, the porous nanosized TiO_2 photocatalyst also allows multiple scattering and reflection of light so as to urge its light absorption capability [39,40].

In this study, a facile hydrosol and calcination method is developed to fabricate hierarchically meso/nanoporous S- and C-codoped TiO_2 to integrate the above mentioned virtues to synergistically improve the photocatalytic activity, which was witnessed by its photocatalytic H_2 generation activity in a water/methanol sacrificial reagent system under the irradiation of UV light. Furthermore, the effect of Pt loading on photocatalytic H_2 generation activity of the hierarchically meso/nanoporous S- and C-codped TiO_2 will also be investigated.

2. Experimental

2.1. Materials synthesis

Except stated elsewhere, all chemicals were from Sigma–Aldrich with reagent grade and used directly without further purification. Deionized (DI) water (Millipore, USA) with a conductivity reaching 18 Ω m/cm, acetone and ethanol were used as solvents for the materials synthesis. In brief, a typical procedure for the fabrication of S- and C-codoped TiO_2 was described. Firstly, 0.5 g $K_2S_2O_8$ (the S source) was added into 20 mL of absolute acetone and stirred for 5 min. Then the suspension was added drop-wisely into 100 mL DI water (60 °C) under vigorous stirring. The mixed solution was continuously stirred for 30 min before cooling down to room temperature (solution A) [6]. Secondly, 10 mL $Ti(OC_4H_9)_4$ (Merck, Germany) was added into 20 mL of absolute ethanol and stirred for 5 min to ensure the formation of clear and homogeneous solution (solution B). This solution B was added drop-wisely into 40 mL of above prepared solution A under vigorous stirring. The subsequently formed white suspension was continuously stirred for 120 min to allow sufficient hydrolysis and reaction. The suspension was withdrawn and centrifuged at 6000 rpm for 5 min to discard the supernatant. The precipitates were thoroughly washed with DI water before calcination at different temperatures from 200 °C to 800 °C in air for 180 min. The S- and C-codoped TiO_2 calcined at different temperatures was designated as TSC-*T*, where -*T* indicates the calcination temperatures (°C), for example TSC-200, TSC-400, TSC-500, TSC-600 and TSC-800 indicate the S- and C-codoped TiO_2 calcined at 200 °C, 400 °C, 500 °C, 600 °C and 800 °C, respectively. Particularly, the uncaclined S- and C-codoped TiO_2 was designated as TSC-0.

As Pt loading on the surface of TiO_2 is widely reported to be a useful technique to enhance the photocatalytic activity of pure TiO_2, therefore we also prepared 0.5% Pt/TiO_2 catalyst via loading Pt on the surface of previously synthesized hierarchically meso/nanoporuos TSC-600 by using a photodeposition method [31,41]. In brief, a mixed solution of H_2PtCl_6 and TSC-600 was prepared under sonication. Afterwards, the suspension was illuminated under UV light (UVP Lamp, UK) overnight at room temperature [37]. Finally, the precipitate was filtrated, washed by DI water and dried at 120 °C for 8 h in an electronic oven. The light gray color of the prepared 0.5% Pt/TiO_2 catalyst indicates that the Pt was successfully deposited on the surface of TiO_2 [31].

2.2. Characterization

The morphology of the prepared samples was observed by field emission scanning electron microscopy (FESEM) (Jeol, JSM 7600F) and transmission electron microscope (TEM) (Jeol, JEM-2010) with an accelerating voltage of 200 kV. An energy dispersive X-ray spectrometer (EDS) detector (Oxford, 80 mm^2) attached to the FESEM was used to measure the element composition and distribution of the prepared samples. The chemical composition and electron structure of the prepared samples were measured by a Kratos axis ultra X-ray photoelectron spectrometer (XPS) with a monochromic Al Kα source at 1486.7 eV, at a voltage of 15 kV and an emission current of 10 mA. The carbonaceous C 1s line of 284.6 eV was applied as the reference to calibrate the binding energies (eV). The structure and crystal phase of the prepared samples were analyzed by powder X-ray diffractometer (XRD, Bruker AXS D8 advance) with monochromated high-intensity Cu Kα radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 30 mA. Ultraviolet–visible (UV–vis) diffuse reflection spectra of the prepared samples were recorded by a Thermo Scientific Evolution 300 UV-vis spectrometer (Thermo Fisher Scientific, Massachusetts, USA) equipped with an integrating sphere assembly and a Xenon lamp source. The porous structures of the prepared samples were characterized by N_2 adsorption/desorption isotherms using a Micromeritics ASAP 2040 system at liquid nitrogen temperature (77 K). Before the measurement, 0.1 g sample was out-gassed under vacuum for 6 h at 250 °C. Pore volume and diameter distributions were derived from the desorption branches of the isotherms by the Barrett–Joyner–Halenda (BJH) model, and the Brunauer–Emmett–Teller (BET) specific surface areas were calculated from the linear parts of the BET plots.

Table 1
Binding energy (eV), fwhm of the TSC-600.

Position (fwhm)			Position (fwhm)		Position (fwhm)	Position (fwhm)	
C 1s			O 1s		S 2p	Ti 2p3/2	Ti 2p1/2
284.6 (1.31)	286.06 (1.03)	288.49 (0.84)	528.95 (1.14)	531.74 (2.98)	168.91 (3.86)	457.84 (1.06)	463.52 (1.72)

2.3. Evaluation of photocatalytic H_2 generation activity

The photocatalytic H_2 generation test of the prepared samples was carried out in an inner irradiation type Pyrex reactor with a volume of 270 mL with a 400 W high pressure Hg lamp (Riko, UVL-400HA) as the light source. The reactor was wrapped by a cooling water jacket with re-circulating tap water to maintain a constant reactor temperature of 298 K. The prepared sample at a dosage of 0.5 g/L was suspended into the mixed methanol/water solution on a magnetic stirrer to form homogeneous reaction solution. Prior to irradiation, the reactor was purged thoroughly with nitrogen gas for 30 min to de-aerate the reactor. The H_2 gas generated from the photocatalytic reaction was collected by a water replacement trap and was analyzed using a TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A) [42,43]. The photocatalytic H_2 generation activity of the well prepared 0.5% Pt/TSC-600 was also evaluated using the same method as above.

3. Results and discussion

The chemical composition, electronic structure and the presence of elements in the prepared TSC-T was measured by XPS. Here, the TSC-600 was taken as a typical example to do the detailed analysis about its XPS survey spectra (Fig. 1a) and high resolution spectrum of Ti 2p (Fig. 1b), S 2p (Fig. 1c), C 1s (Fig. 1d) and O 1s (Fig. 1e). The detailed binding energies and full width at half maximum (fwhm) of those elements were listed in Table 1. The XPS survey spectra in Fig. 1a reveal that the TSC-600 contains Ti, O, S and C. The high resolution Ti 2p spectra (Fig. 1b) exhibits two typical