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MoS_3 loaded TiO_2 nanoplates for photocatalytic water and carbon dioxide reduction

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ABSTRACT

Photocatalytic water splitting and carbon dioxide reduction provide us clean and sustainable energy resources. The carbon dioxide reduction is also the redemption of the greenhouse effect. MoS_3/TiO_2 photocatalysts based on TiO_2 nanoplates have been synthesized via a hydrothermal acidification route for water and carbon dioxide reduction reactions. This facile approach generates well dispersed MoS_3 with low crystallinity on the surface of TiO_2 nanoplates. The as-synthesized MoS_3/TiO_2 photocatalyst showed considerable activity for both water reduction and carbon dioxide reduction. The thermal treatment effects of TiO_2, the loading percentage of MoS_3 and the crystalline phase of TiO_2 have been investigated towards the photocatalytic performance. TiO_2 nanoplate synthesized through hydrothermal reaction with the presence of HF acid is an ideal semiconductor material for the loading of MoS_3 for photocatalytic water and carbon dioxide reduction simultaneously in EDTA sacrificial solution.

1. Introduction

With the burning of fossil fuels for centuries, our planet is facing great climate pressure due to the rising concentration of carbon dioxide in the atmosphere. Photocatalytic water splitting and carbon dioxide reduction may provide us clean and sustainable energy resources if the solar conversion efficiency is substantially improved in the future [1–12]. The CO_2 reduction is also the redemption of the greenhouse effect. In a typical heterogeneous photocatalytic process initiated by solar irradiation, a semiconductor material is employed to absorb the photons. After the photon absorption, excited electrons and holes will be created in the semiconductor material. The excited electrons were transferred into water or carbon dioxide molecules to generate hydrogen or value added fuels, respectively. By completing a photocatalytic process, the energy from sun light can thus be converted and stored in terms of chemical energy. To conceive a successful photocatalytic system, a good light absorber material is required in the first place. Several materials including titania [8,13–19], titanates [20–22], zinc germanate/gallate [23–29], metal organic frameworks [30–34], layer double hydroxides [35–38], noble metal complexes [39–44] and other semiconductors [45–53] have been investigated as light absorbers. The challenges for currently studied systems lie in the low solar energy conversion efficiency and the employment of unsustainable noble metals [1,2,9,10].

Among those well examined semiconductor materials, TiO_2 is a cost-effective and eco-friendly candidate. It has attracted extensive attention due to its light absorption efficiency, catalytic active surface, and the sufficient conduction band potential to reduce both water and carbon dioxide. Current researches of TiO_2 for photocatalytic reduction of CO_2 include the doping of other transition metals [54–56], the formation of titanates [20–22], the loading of noble metal co-catalysts [15,17,57], and its composites with polymers or silica [13,22,54,58–61]. To generate a co-catalyst on TiO_2 surface, noble metals such as Pt and Pd are generally considered to be able to enhance the activity greatly. With economical concerns, there is great necessity to investigate other noble metal free co-catalysts on TiO_2 for efficient and cost-effective carbon dioxide reduction.

Molybdenum sulphide is both experimentally and theoretically confirmed as a promising hydrogen evolution catalyst in electrocatalytic and electrophotocatalytic water splitting processes [62–65]. Although it has been widely studied for the water reduction, there is no relevant study for MoS_x as CO_2 photocatalytic reduction catalysts. A few reports have studied the electrocatalytic

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and photoelectrocatalytic CO_2 reduction based on MoS_2 catalyst [66–69]. On the other hand, TiO_2 nanoplates with large percentage of reactive facets have been synthesized via hydrothermal method in literature reports [70–73]. The nanoplate structure showed excellent performance for both photocatalytic organic dye degradation [70] and dye sensitized solar cells [71]. In this study, we introduce a facile and novel method for uniform loading of molybdenum trisulfide onto the surface of TiO_2 nanoplate via a hydrothermal acidification route. The loaded MoS_3/TiO_2 photocatalyst can efficiently reduce both water and carbon dioxide simultaneously in an aqueous sacrificial solution of ethylenediaminetetraacetic acid disodium salt (EDTA). The physicochemical properties of the photocatalysts are characterized and their photocatalytic performances are systematically investigated.

2. Experimental

2.1. Preparation of catalysts

TiO_2 with nanoplate morphology was obtained from hydrothermal reaction of titanium but oxide ($Ti(OCH_2CH_2CH_2CH_3)_4$) and hydrogen fluoride acid (HF) under 180 °C for 24 h according to literature reports [72,73]. In a typical synthesis of loaded MoS_3/TiO_2 photocatalyst, ammonium tetrathiomolybdate (NH_4MoS_4, 0.1 mmol) was dissolved in 75 mL of deionized water mixed with 0.3 g of TiO_2 powder. The mixture was ultrasonicated for half an hour and added with 0.5 mL of thioacetic acid (TAA) before being transferred into an autoclave with a capacity of 120 mL. The mixture was subjected to hydrothermal treatment under 200 °C for 12 h. After cooling to room temperature, the obtained brown color solids were washed and centrifuged thoroughly using DI water.

2.2. Photocatalytic reactions

The as-synthesized MoS_3/TiO_2 photocatalyst was dispersed in a reaction vessel containing 100 mL of 0.02 M EDTA aqueous solution. The vessel was connected to a closed system. The system was degassed and refilled with CO_2 gas for several times to remove the air inside. Carbon dioxide gas (200 torr) was finally charged into the closed system, and photocatalytic reaction was conducted under a 500 W Xenon-mercury lamp. Before turn on the light for each photocatalytic reaction, the system was equilibrated from vigorous stirring under dark for half an hour. Analysis showed that negligible CO and CH_4 gases were produced without irradiation. The gas products were analyzed using an on line gas chromatography (GC) with both thermal conductivity detector (TCD) and flame ionization detector (FID) equipped with series connected Hayesep Q column and Molecule Sieve 5A column [5].

2.3. Physical characterizations

Powder X-ray diffraction (XRD) patterns of the solids were recorded on a X-ray diffractometer (Bruker AXS D8, Cu $K\alpha$, $\lambda = 1.5406$ Å, 40 kV and 20 mA). The morphology, particle size, lattice fringes and Energy-filtered transmission electron microscope (EF-TEM) images were observed on a TEM (JEOL 2010) equipped with a Gatan imaging filter at an accelerating voltage of 300 kV. The UV-visible diffuse reflectance spectra (UV–vis DRS) were obtained from an UV–visible spectrophotometer (UV-2450, Shimadzu).

3. Results and discussions

3.1. Catalyst properties

The XRD patterns of the as-synthesized TiO_2 nanoplate in Fig. 1(a) display a dominant diffraction peak from the (101) plane, which is consistent with the result in literature for the anatase TiO_2 nanoplate with a highly exposed (001) facets [70–73]. A broad peak at 13.09° from separately synthesized pure MoS_3 corresponding to a lattice spacing of 0.68 nm can be referred to XRD reports of amorphous MoS_3 with weak broad diffraction peak around 14° [62]. The UV–vis DRS of the TiO_2 nanoplate before and after loading of MoS_3 are shown in Fig. 1(b). The enhancement of the visible light absorption is brought by the surface loading of MoS_3, which naturally has a deep brown colour. The insert images demonstrate the color change of the TiO_2 powder after the surface loading of MoS_3. TEM images from Fig. 2(a–c) demonstrate the nanoplate structure of the prepared TiO_2, and elucidate the well dispersion of MoS_3 on the TiO_2 nanoplate surface since no obvious aggregates are observed after the loading of MoS_3 (Fig. 2d). From high resolution TEM images (Fig. 2e–f), MoS_3 was confined into limited layers, which is essential to facilitate charge transfer and to increase surface exposed catalytic sites [74]. Element mapping of the as-synthesized MoS_3/TiO_2 photocatalyst was conducted via an EF-TEM technique. From the Ti, Mo and S element mapping images shown in Fig. 3, it can be concluded that the MoS_3 has been well dispersed onto the surface of TiO_2. Collectively, loaded MoS_3/TiO_2 photocatalyst comprise of TiO_2 nanoplate with exposed (001) facets and well dispersed MoS_3 with limited layers has been successfully synthesized through facile hydrothermal acidification process.

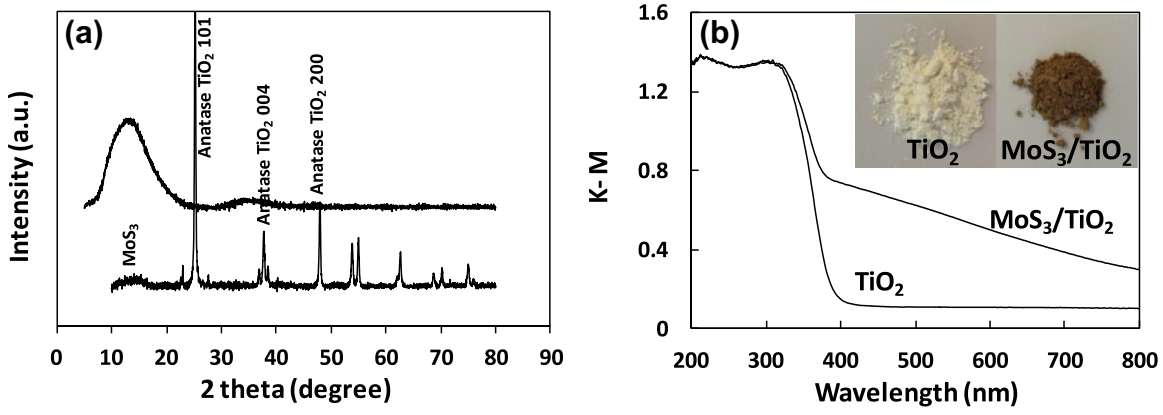

Fig. 1. (**a**) XRD patterns of the 5 wt% loaded MoS_3/TiO_2 photocatalyst (bottom), and pure MoS_3 (top) synthesized without TiO_2 via the same hydrothermal method; (**b**) UV-vis DRS of TiO_2 and MoS_3/TiO_2 (insert: images of TiO_2 before and after loading of MoS_3).