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Facile synthesis of VS₄/graphene nanocomposites and their visible-light-driven photocatalytic water splitting activities

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ABSTRACT

VS₄/reduced graphene oxide (VS₄/rGO) composites are successfully synthesized via a one-step hydrothermal route. Then their photocatalytic activities are examined by water splitting reaction, and the morphology and structure are characterized by transmission electron microscopy, X-ray diffraction, Fourier transform infrared, X-ray photoelectron spectroscopy and thermo gravimetric analysis, respectively. It is shown that graphene accelerates the nucleation during the growth period of VS₄. Main product is VS₄, not VS₂. Monoclinic VS₄ particles interact with graphene through chemical action. VS₄/rGO composites show excellent photocatalytic water splitting activities under visible-light irradiation. This excellent performance is due to the formation of π -conjugated structure, which can transmit electrons from S2_p to graphene rapidly. However, composites with excess graphene show poor dispersion, which leads to the best doping ratio of graphene is 5 wt%. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

In order to fight against the worsening crisis of global warming and energy shortage, nations around the world have been searching for alternative energy sources to replace fossil fuel. Hydrogen energy, as a clean and recyclable secondary energy, is the best choice [1]. However, hydrogen is mainly reformed from fossil fuel or electric energy now. These measures can't fundamentally solve the problem. Therefore, how to transform inexhaustible solar energy into hydrogen energy is of vital importance.

Since the discovery of the Honda-Fujishima effect [2], which involves a TiO₂ semiconductor electrode for water splitting under UV radiation, considerable attention has been

paid to semiconductor photocatalysis for water treatment and splitting [3–6]. As well known, water splitting on semiconductors is initiated by the absorption of photons with energy equal to, or greater than the semiconductor band-gap. Then electrons are stimulated from the valence band (VB) to the conduction band (CB), leading to the formation of electron–hole pairs (e[−]–h⁺). The produced electrons (e[−]) and holes (h⁺) can trigger the reduction of H⁺ and the oxidation of OH[−], respectively. Therefore, strong enough reducing property of e[−] and oxidizing property of h⁺ are simultaneously required in this system. Furthermore, due to the low proportion of UV light, photocatalysts should have a sufficiently narrow band-gap to harvest visible photons. However, recombination of e[−]–h⁺ and photocorrosion of catalysts both lead to low optical efficiency [7]. Although there are many visible-light driven

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photocatalysts developed recently by techniques such as metal loading, ion doping, and dye sensitization [8–10], they have not shown satisfactory efficiency owing to these limitations. In a word, searching a kind of stable semiconductor which has a narrow band-gap and high quantum efficiency is the key to realize water splitting.

Recently, lots of similar sulfide minerals that include an S_2^{2-} dimer have been successfully synthesized. With the special layered and band structures of transition-metal dichalcogenides, lots of potential applications have been reported, including catalysis, energy storage, sensing and energy conversion [11–13]. VS_4 is one of the typical representatives. Since the discovery of the VS_4 mineral in 1906 and the specification of its crystallographic structure in 1964, lots of attempts have been made to synthesize and apply the material [14–16]. Nevertheless, due to the existence of various non-stoichiometric phases of vanadium sulfides with different oxidation states, it is very difficult to synthesize a pure form of VS_4 phase [16,17]. And there is no report about its application in photocatalysis up to now. According to density functional theory (DFT), VS_4 is found to have a bandgap of about 1.0 eV [14], which expresses a strong absorption in the visible spectrum region. However, the bandgap of VS_4 is so narrow that the e^- and h^+ pairs recombine very quickly. Therefore, its photocatalytic efficiency is still to be further improved.

In this work, graphene was introduced into the preparation process of VS_4 . A one-step synthesis of VS_4 /reduced graphene oxide (VS_4 /rGO) composites was carried out through a simple hydrothermal route. Unlike ordinary graphene composites, e.g. TiO_2 and MoS_2 [18,19], graphene not only accelerates the nucleation of VS_4 but also decreases the photo-generated e^- - h^+ recombination. The photocatalytic performances were investigated via water splitting under visible-light irradiation.

Experimental

Preparation of graphene oxide (GO) and its solution

GO was prepared from natural graphite using a modified Hummers' method [20]. Briefly, 1.0 g of graphite powder and 0.5 g of $NaNO_3$ were mixed with 23 mL of concentrated H_2SO_4 (98 wt%) at 273 K. Then 3.0 g of $KMnO_4$ was added gradually. The mushy mixture was stirred at 308 K for 3 h. Next 46 mL of deionized water was added drop by drop, then reacted for 3 h at 371 K. 10 mL of H_2O_2 (30 wt%) was added to remove the extra $KMnO_4$. The product was then washed and centrifuged with dilute HCl and deionized water several times. Finally, the precipitate was dried at 333 K.

0.5 g of GO was dispersed in 100 mL of deionized water, using ultrasonic irradiation to gain single layer of GO. The supernatant (volume coded as V) was poured into a reagent bottle. And the remaining solid was dried and weighed (coded as m). So the concentration (coded as C_0) of GO solution was: $C_0 = (0.5 - m)/V$.

Synthesis of VS_4 /rGO nanocomposites

VS_4 particles were incorporated with reduced graphene oxide (rGO) through a simple one-step solvothermal route, in which

VS_4 was formed on GO, and GO was transformed to rGO simultaneously. In a typical process, a specific amount of GO solution was diluted to 60 mL by deionized water. Then, 1.8 g of $Na_3VO_4 \cdot 12H_2O$ and 1.65 g of CH_3CSNH_2 were added and stirred for 1 h at room temperature by a magnetic stirrer. Na_3VO_4 was anchored on the GO surface via chemisorption with the oxygen-containing functional groups of GO at the molecular level [21]. Afterward, the solution was transferred into a 100 mL Teflonlined autoclave and maintained at 433 K for 24 h. The nanocomposite product was isolated by centrifugation (4000 rpm), and then washed 3–5 times with deionized water and anhydrous ethanol, followed by drying in a vacuum oven at 333 K for 6 h. The as-synthesized samples with 1, 3, 5 and 7 wt % rGO, which are defined as the weight ratio of graphene to VS_4 , were named as VG1, VG2, VG3 and VG4, respectively. In addition, a similar process was used to prepare pure rGO.

Characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-R diffractometer with a copper target at 40 kV and 30 mA from 10° to 70° . The crystalline phases were identified by reference to powder diffraction data (JCPDS-ICDD). The morphology of the samples was characterized by transmission electron microscopy (TEM) with a Hitachi H-600 microscope operating at 120 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI5700 ESCA system (Physical Electronics) with Al $K\alpha$ X-ray source. Fourier transform infrared (FT-IR) spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer at room temperature using KBr pellets. Thermo gravimetric analysis (TGA) was performed in dry air using a TA Q-600 from 323 K to 873 K at a heating rate of 10 K min^{-1} .

Photocatalytic test

The photocatalytic performances of the samples were evaluated by water splitting reaction under visible light. The light source was a 500 W Xe lamp (Shanghai Special Lighting Factory). Visible light irradiation was obtained by a 400 nm long pass glass filter to remove UV. A 500 mL bottle was chosen as photocatalytic reactor, and a quartz cold hydrazine was used to cool the light. Water was boiled in advance to remove dissolved oxygen. $0.35\text{ mol L}^{-1} Na_2S$ and $0.25\text{ mol L}^{-1} Na_2SO_3$ was dissolved in water as electron donor. Solution was decentralized by a magnetic stirrer. In a typical process, 500 mL of solution was added into the reactor, and a certain amount of photocatalysts (0.1, 0.2, 0.3, 0.4 or 0.5 g) were dispersed. After 30 min ultrasonic treatment in dark, N_2 was passed into the system to remove air. Then reaction started and lasted for 1–50 h. The produced gas was collected periodically and then analyzed by a GC4000A gas chromatograph.

Results and discussion

Phase and morphology

Fig. 1 gives the XRD patterns of graphite, GO and rGO. The diffraction peak of graphite at 26.5° and peak of GO at 11.4° , are

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