



One-pot hydrothermal synthesis of SrTiO₃-reduced graphene oxide composites with enhanced photocatalytic activity for hydrogen production



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ABSTRACT

SrTiO₃-reduced graphene oxide (SrTiO₃-RGO) composites were synthesized via a facile one pot hydrothermal process. This was achieved by decorating graphene oxide (GO) layers with Ti(OBu)₄ and Sr(NO₃)₂ as starting materials followed by hydrothermal synthesis, which converts the SrTiO₃ particles with a diameter of 87–200 nm on the RGO surface, without using strong reducing agents. The as-prepared samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), diffuse reflectance spectra (DRS), photoluminescence spectra (PL), electrochemical impedance spectra (EIS), and photocurrent analysis. SrTiO₃ particles were shown to be grown homogeneously on the RGO sheets with close interfacial contacts. The photocatalytic hydrogen evolution activities of the SrTiO₃ and SrTiO₃-RGO composites were contrasted. Compared to SrTiO₃, SrTiO₃-RGO composites showed much higher photocatalytic hydrogen production activity under UV light irradiation. The SrTiO₃-0.8%RGO composite showed the highest photocatalytic H₂ evolution activity. PL, EIS and photocurrent analysis were used to elucidate the mechanism that the enhancement of photocatalytic hydrogen evolution activity over the SrTiO₃-RGO composites is attributed to the reduction of the photogenerated electron-hole recombination.

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1. Introduction

Photocatalytic hydrogen production from water has recently become a rapidly expanding focus of research [1–3]. Many photocatalysts, which have shown high photocatalytic rates and quantum efficiencies for hydrogen production from water, have been explored, such as oxides [4–6], oxynitrides [7,8] and sulfides [9–12], and so on. The perovskite strontium titanate (SrTiO₃) has been regarded as one of the efficient photocatalysts for water splitting and photocatalytic degradation of organic pollution. However, as it has a large energy gap of about 3.2 eV [13], the photoabsorption range of SrTiO₃ is restricted to UV light and hinders the efficiency of solar-energy conversion. Besides, the high recombination rate of photogenerated electron-hole pairs of SrTiO₃ under UV light irradiation [14] greatly limits the photocatalytic activity of catalysts. In view of the above two points, the photocatalytic activity of SrTiO₃ was enhanced by doping or combining with noble metal [15,16], non-metal [17–19], transition metal oxide [19,20] and other photocatalysts [21,22].

Graphene as an allotrope of carbon has many extraordinary properties because of its special structure. Graphene has large surface area, exciting electronic and photonic properties [23,24], so it has attracted researchers' significant attention for various applications, such as energy storage, photovoltaics, photoelectrochemical and catalysis. As graphene is a two-dimensional planar structure material, and this structure should be maintained in the resulting composite, which affects significantly the unique properties of the graphene. In addition, the intimate interfacial contact between photocatalyst and graphene favors the transfer of the electrons from the conduction band of the semiconductor to graphene. Therefore, many graphene-based photocatalysts, such as graphene-TiO₂ [25], graphene-CdS [26], reduced graphene oxide-WO₃ [27], reduced graphene-MoS₂ [28,29], ZnS/graphene [30], have been prepared by different approaches to keep graphene as individual sheets and to provide the good interfacial contact between photocatalyst and graphene in composite photocatalysts. The common ways include hydrothermal synthesis [25–27], photoreduction method [28], pyrolysis [29], and low-temperature solid-state synthesis [30]; Various reducing agents such as ethanol [25], N₂H₄ [26], NaBH₄ [30], glucose [31] and photoreduction [28] have been used to reduce GO, and they all reported highlighting the improvements in photocatalytic activity of graphene-based com-

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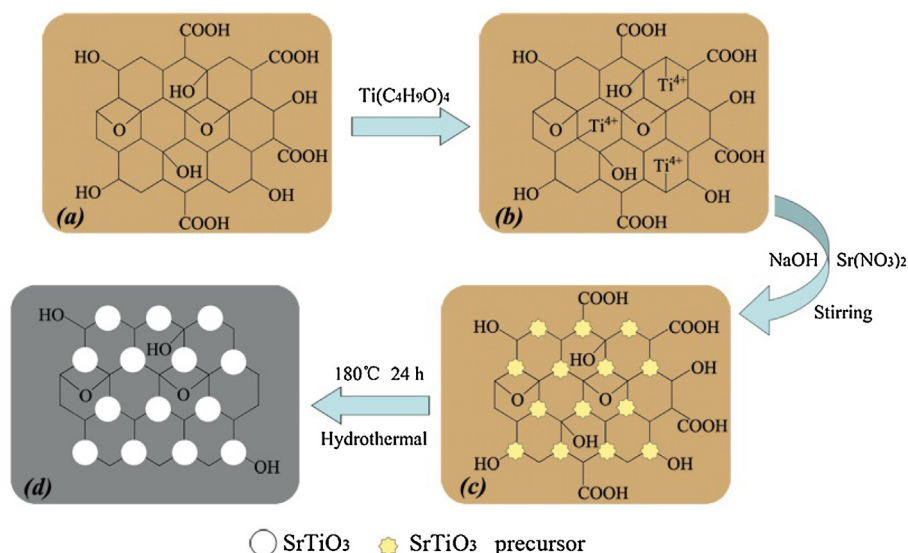


Fig. 1. Flowchart of the synthesis process and growth mechanism of SrTiO₃-RGO.

posite photocatalysts for the degradation of organic molecules or photocatalytic splitting of water.

It is known that tetra-*n*-butyl titanate (Ti(OBu)₄) is very easy to hydrolyze when water is added. However, Ti(OBu)₄ can be caught by the functional groups, such as COOH⁻ or OH⁻ of the graphene, so the hydrolysis rate of Ti(OBu)₄ would decrease [32]. In this paper, we present a simple and direct synthesis of SrTiO₃ on reduced graphene oxide (RGO) by a one-pot hydrothermal method using Ti(OBu)₄ and Sr(NO₃)₂ as starting materials. The hydrothermal conditions simultaneously convert GO to black RGO during hydrothermal process, and it did not require toxic solvents or chemicals. Their photocatalytic activity is demonstrated for the hydrogen production under UV light irradiation. Besides, we tested the photocatalytic stability and discussed the possible mechanism for photocatalytic hydrogen production of SrTiO₃-RGO composites.

2. Experimental

2.1. Synthesis of graphite oxide

Graphite oxide was synthesized by a modified Hummers' method [33]. 3 g of graphite was added into the mixed solution of 40 ml of H₃PO₄ and 360 ml of H₂SO₄ under stirring in an ice bath for 10 min. Then 18 g of KMnO₄ was added into the above solution and stirred for 20 min. The homogeneous solution was transferred to a 35 °C water bath and magnetically stirred for 25 min, and then continuously stirred in a 50 °C water bath for 24 h. The resultant dark brown paste was diluted with the slow addition of 300 ml of deionized water and magnetically stirred for 1 h. And then, 20 ml of H₂O₂ (30 wt%) was slowly added into the solution to produce a golden-yellow solution. The resulting product was centrifuged and washed with 500 ml of HCl (5 wt%) repeatedly to adjust the pH to neutral. Finally, the brown graphite oxide was dried via a freeze-drying process to obtain a brown powder.

2.2. Preparation of SrTiO₃

5 mmol of Ti(OBu)₄ was dissolved in 25 ml of ethylene glycol while stirring. Then 10 ml of 0.5 M Sr(NO₃)₂ solution was dropped in the above solution, and then 5 ml of 5 M NaOH solution was added. After stirring for 10 min, the mixture was transferred into a 50 ml Teflon-lined stainless autoclave and heated at 180 °C for 24 h. The solid product was centrifuged and washed three times with

deionized water and ethanol, respectively. Finally, white SrTiO₃ nanocomposite was dried at 70 °C.

2.3. Preparation of SrTiO₃-reduced graphene oxide nanocomposites

The preparation process of SrTiO₃-reduced graphene oxide (SrTiO₃-RGO) composites is illustrated in Fig. 1. Graphite oxide was sonicated in deionized water for 2 h to achieve uniform dispersions of graphene oxide (GO). In a typical experiment, 5 mmol of Ti(OBu)₄ was dissolved in 25 ml of ethylene glycol while stirring. Then 3.68 ml of the GO solution (1 mg/ml) was added dropwise to the above solution under stirring for 1 h to form a homogeneous solution. Subsequently, 10 ml of 0.5 M Sr(NO₃)₂ solution was dropped in the resultant solution, and then 5 ml of 5 M NaOH solution was added. After stirring for 10 min, the mixture was transferred into a 50 ml Teflon-lined stainless autoclave and heated at 180 °C for 24 h. The black solid product was centrifuged and washed three times with deionized water and ethanol, respectively. Finally, black SrTiO₃-0.4 wt%RGO nanocomposite was dried at 70 °C.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained using a MSAL XD-2 diffractometer with Cu K α radiation ($\lambda=0.15418$ nm) at a scan rate (2θ) of 8° min⁻¹. The accelerating voltage and the applied current were 36 kV and 30 mA, respectively. Transmission electron microscope (TEM) images were captured on a FEI-Tecnaï 12 transmission electron microscopy. A Hitachi U-2550 UV-vis spectrophotometer was used to measure diffuse reflectance spectra (DRS), which were referenced to BaSO₄. Photoluminescence spectra (PL) was acquired by a Shimadzu RF-5301PC spectrofluorometer with an excitation wavelength of 345 nm. Photocurrent was measured on an electrochemical workstation (BAS100 Instruments) in a standard three-electrode system with a working electrode, a Pt wire counter electrode, and a standard Ag/AgCl (saturated KCl) reference electrode. 0.5 M Na₂SO₄ solution was used as the electrolyte, and a Xe lamp (300 W) was used as a light source. Electrochemical impedance spectra (EIS) was recorded via a computer controlled IM6e impedance measurement unit (Zahner Elektrik, Germany) over a frequency range of 0.01–105 Hz with an ac amplitude of 5 mV, under UV light. The mixture of 0.1 M Na₂S and 0.02 M Na₂SO₃ solution was used as the electrolyte.

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