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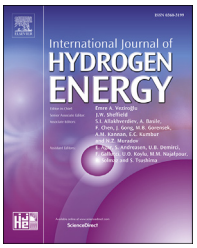

Photocatalytic hydrogen production by flower-like graphene supported ZnS composite photocatalysts

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ABSTRACT

Flower-like graphene (FG) prepared by a transformer coupled plasma enhanced chemical vapor deposition method was used as support for the preparation of composite photocatalysts. Small ZnS particles were formed on the surface of FG by a hydrothermal process with $ZnCl_2$ and Na_2S precursors. The surface morphology, surface area, surface chemistry, crystalline property, optical properties, photogenerated current and photocatalytic hydrogen production activity of the FG-ZnS photocatalysts were investigated by using the X-ray diffraction, scanning electron microscope, transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet-visible diffuse reflectance spectra, photocurrent response, photoluminescence spectra, electrochemical impedance spectra and photocatalytic hydrogen production tests. The maximum hydrogen production rate of FG-ZnS composite photocatalyst ZS-G0.02 was 11600 μmol $g^{-1}h^{-1}$ under UV light irradiation at a graphene/$ZnCl_2$ precursor weight ratio of 0.02. The flower-like structure of FG may help the light absorption, adsorption of sacrificing agents in the solution, and separation of photogenerated carriers. In comparison with pristine ZnS photocatalyst, the FG-ZnS nanocomposites exhibits enhanced photocatalytic hydrogen production activity.

Introduction

Semiconductor materials have been developed for some applications, such as H_2 production [1,2], photocatalytic degradation [3,4], and gas sensor [5]. The photocatalyst which has a more negative conduction band than the reduction potential of proton will have high photocatalytic water splitting activity [6,7]. ZnS can generate electron-hole pairs rapidly under light irradiation and exhibit a relatively high activity for photocatalytic H_2 production [8–10]. Researchers have reported some processes to improve the photocatalytic activity by hybridizing semiconducting photocatalysts with electric conductive materials which can induce the charge separation in the photocatalysts, such as fullerene C60 [11], graphene [12], conducting polyaniline (PANI) [13] and stainless steel wire mesh substrates [14]. Because of the large specific surface area and excellent electronic conductivity, graphene with 2D planar π-conjugation structure can act as a catalyst support [15,16] Graphene-semiconductor composite photocatalysts have enhanced photocatalytic H_2-production activity by

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inhibiting the recombination of photogenerated electron-hole pairs in the photocatalysts [17–19].

However, the van der Waals forces between adjacent graphene layers may result in the aggregation of graphene sheets which lead to a decrease of the specific surface area [20]. A large surface area is very important for the use of graphene in some applications such as supercapacitor, sensor and fuel cell, because it can provide more sites for adsorption and catalytic reaction [21,22]. In order to solve this problem, many researchers have devoted to synthesize three dimensional (3D) porous graphene materials with large specific surface area and interconnected pore structure by different methods [23–25].

Some surface morphology, such as nanorod array and pore array, exhibits light trapping effects [26] which may help to increase photocatalytic activity [27–31]. Yang et al. reported that the light-trapping effect by the nanowire arrays enhances light absorption and improves the photocatalytic activity of SiNW arrays [32]. Kim et al. [33] found that the surface-textured TiO_2 inverse opal maximized the photon-trapping effects and improves the photoelectrochemical hydrogen generation performance. The light-trapping effect can be confirmed by the decrease in the transmittance and reflectance spectra of the sample [34]. We believe that the flower like graphene can exhibit the light-trapping effect and help to improve the photocatalytic activity.

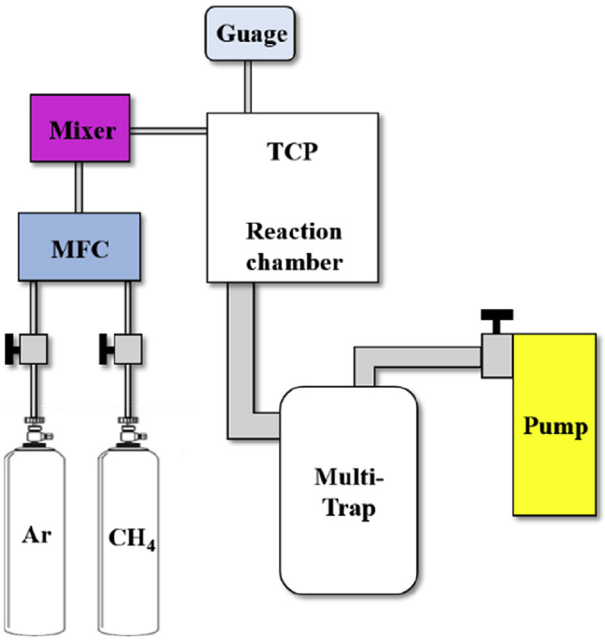
Recently, some researchers reported the use of flower-like graphene or carbon for application in supercapacitors [35,36], and methanol oxidation [37]. Inspired by the previous works, the flower-like graphene (FG) with 3D porous structure was used as conductive photocatalyst support which can enhance the separation of photogenerated electron-hole pairs in this study. The FG remarkably enhances the photocatalytic H_2 production activity of ZnS nanoparticles compared to the ZnS catalysts. This work demonstrates the feasibility of using 3D porous FG supports for the development of highly efficient ZnS-FG photocatalysts.

Experimental

Preparation of ZnS-FG composites

The flower-like graphene (FG) was synthesized by means of the transformer coupled plasma enhanced chemical vapor deposition (TCP CVD) in the reaction chamber [38]. A schematic diagram of the TCP CVD system for the present experiment is illustrated in Scheme 1. Methane was introduced and mixed with argon to grow FG in the reaction chamber. The gas was excited with plasma (medium frequency 250 kHz) in the TCP system. The flow rates of argon and methane gases were kept at 3 and 0.2 slm (standard liter per minute) by the mass flow controller (MFC), respectively. The medium frequency power was set 6000 W for 30 min. The gas pressure was kept at 7 Torr during the process.

Then, 0.2 g $ZnCl_2$ and FG were dispersed in the distilled water (50 ml), and this solution was heated to 70 °C in an oil bath with continuous stirring for 2 h. Subsequently, 0.1 M Na_2SÞ$9H_2O$ (20 ml) solution was added dropwisely and kept stirring for 4 h. Then, the suspension was transferred to a



Scheme 1 – Schematic diagram of the TCP CVD system.

100 mL Teflon-lined autoclave and maintained at 130 °C for 12 h. The final products with different weight ratios of FG were washed several times by distilled water and ethanol, and dried at 60 °C for 10 h.

Photocatalytic H_2 production

The photocatalytic hydrogen production reaction was carried out in a 100 mL Quartz cell. A 300 W high-pressure mercury lamp was used as the UV light source. The photocatalysts is placed into the quartz cell filled with 100 mL sacrificial aqueous solution. The sacrificial aqueous solution was made up of 0.1 M $Na_2S{\cdot}9H_2O$, 0.040 M Na_2SO_3 and 3 M NaCl. The solution was continuously stirred throughout the UV light irradiation procedures. A gas chromatography (TCD, Argon as carrier gas, Stainless Steel packed column with 5 mm inner diameter, Molecular Sieve 5 A as stationary phase) was used to measure the amount of hydrogen production in order to determine the photocatalytic activity.

Nomenclature

The ZnS-FG photocatalysts were denoted as ZS-Gx photocatalysts. x means the weight ratio of graphene/$ZnCl_2$. For example, the graphene/$ZnCl_2$ weight ratio of ZS-G0.02 is 0.02.

Characterization

X-ray Diffraction (XRD) patterns were measured by a MAC SCIENCE MXP3 diffractometer to investigate the crystal phase of the photocatalysts. The surface morphologies and energy dispersive X-ray (EDX) were analyzed by a field-emission scanning electron microscope (FE-SEM, HITACHI S-4800). The microstructures were monitored by transmission electron microscopy (TEM, JEOLJEM-2100). X-ray photoelectron spectroscopy (XPS) was measured by a VG ESCA scientific

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