Solar Energy 161 (2018) 226–234

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

# ZnS nanospheres/reduced graphene oxide photoanode for highly efficient solar water oxidation

Tahereh Mahvelati-Shamsabadi[a], Elaheh K. Goharshadi[a,b,*]

[a] Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran
[b] Center of Nano Research, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran

## ARTICLE INFO

*Keywords:*
RGO-ZnS nanocomposites
Photowater splitting
Oxygen evolution reaction
Surface plasmons

## ABSTRACT

One of the most important challenges in renewable energy conversion is construction of an earth-abundant, active, and stable water splitting photoelectrocatalyst operating at all pH values. In this work, ZnS nanoparticles (NPs) were embedded on different amounts of reduced graphene oxide (RGO) nanosheets with the help of ultrasonic waves. The role of the RGO-ZnS nanocomposites as an efficient photoanode for oxygen evolution reaction was evaluated. The RGO-ZnS nanocomposite with 10% RGO (RGO10-ZnS) exhibits outstanding photoelectrocatalytic activity compared with ZnS, RGO, and other prepared nanocomposites. It shows a negative onset potential of −200 mV with a maximum photocurrent density of 1.1 mA cm$^{-2}$ at 1.23 V (vs RHE) in $Na_2SO_4$ (0.5 M) solution which is five times higher than that of ZnS NPs. The solar-simulated light power is saved 1 V from the external power source or produced power of 0.9 mW cm$^{-2}$. RGO10-ZnS showed −400 mV increase in the photovoltage than that of ZnS nanoparticles. The excellent conductivity and high surface area of RGO provide an outstanding ability to the nanocomposite to harvest and localize the light near ZnS NPs through its plasmonic structure which causes a negative shift in the onset potential compared with both ZnS and RGO. In other words, RGO has the ability to trap light in modes so-called surface plasmons. The light surface plasmon resonances can efficiently enhance the optical absorption at resonant frequency to slow down the photons.

## 1. Introduction

Searching for novel renewable and abundant energy sources is essential to respond to the continually growing energy demands (Kang et al., 2016; Moniz et al., 2015; Rojas et al., 2016). Among the investigated sources, much attention has been paid to solar light. Although the market for photovoltaics is growing approximately 40% per year, the intermittent and diurnal nature of solar power requires the development of an efficient method for energy storage. With the goal of achieving energy conversion using a simple single device, the photoelectrochemical (PEC) water-splitting cells combine the processes of solar light collection and water electrolysis to produce hydrogen and oxygen which can recombine in fuel cells to efficiently exploit their stored energy (Dias et al., 2015; Rojas et al., 2016). Since the first demonstration of this idea in 1972, a great deal of attention has paid to semiconductor materials as photoelectrodes (Fujishima, 1972).

At least 1.23 V of applied voltage is needed to overcome the thermodynamic barrier energy of water-splitting. A considerably larger voltage than 1.23 V is usually required because of the practical overpotentials. The commercial electrolysers operate normally at a voltage of 1.8 to 2.0 V (Luo et al., 2014). In general, for overall water-splitting into $H_2$ and $O_2$ simultaneously, it is necessary to have a semiconductor with a band gap larger than 1.23 eV along with suitable band edge positions which cover well the water-splitting potential region (Brillet et al., 2012).

The key aspect of electrochemical energy conversion system is choosing a suitable electrocatalyst (Jiao et al., 2016; Luo et al., 2014). Up to now, few studies investigated metal sulfides in comparison with metal oxides for $H_2$ and $O_2$ generation. Some metal sulfides are visible light active (VLA) photocatalysts because their band gaps are generally narrower than those of corresponding metal oxides (Iwase et al., 2016, 2015). Therefore, we are interested in construction of a VLA photocatalyst system using a metal sulfide for water splitting. ZnS is an efficient n-type semiconductor for PEC due to its suitable band gap and high conduction band (Mahvelati-Shamsabadi and Goharshadi, 2017). Meanwhile, there are three main challenges preventing its application as an efficient photocatalyst for water-splitting. The first issue is its thermodynamic instability (photocorrosion through self-oxidization or self-reduction by photoinduced charges during the photocatalytic process) (Iwashina et al., 2015). To

---

* Corresponding author at: Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran.
*E-mail address:* gohari@um.ac.ir (E.K. Goharshadi).

https://doi.org/10.1016/j.solener.2017.12.048
Received 12 August 2017; Received in revised form 21 December 2017; Accepted 26 December 2017

prevent photocorrosion, the sacrificial reagents are used to consume the photogenerated holes (Zhang et al., 2015). In the absence of a sacrificial reagent, the photogenerated holes oxidize the zinc sulfide instead of water (Iwase et al., 2016). The second issue is the unfavorable of sunlight absorption and the third is $e^-/h^+$ recombination rate. Thus, zinc sulfide cannot split water into $H_2$ and $O_2$ as a single particulate photocatalyst. The problems can be solved by doping (Muruganandham and Kusumoto, 2009; Wan et al., 2014) or combining ZnS with a suitable semiconductor (Yu et al., 2015). The reduced graphene oxide (RGO), a delocalized conjugated π system, has been extensively studied in the electron transfer processes due to its rapid photoinduced charge separation and a relatively slow charge recombination (Xie et al., 2013). It usually shows p-type semiconducting behavior (Wei et al., 2009). RGO has risen as a promising candidate for optoelectronic applications (Hadadian et al., 2016) due to its exceptional electrical, optical, and physical properties as well as its low-cost solution-phase production techniques. Meanwhile, finding new ways to control and slow down the group velocity of light in media remains a major challenge in the field of optics. Potential applications of slow light are numerous and include optical data processing and communications, nonlinear optical enhancement and temporary storage of light (Lu et al., 2015). Slow light in plasmonic structures has also attracted significant attention in the scientific community. For the design of plasmonic slow light structures, graphene represents an attractive alternative to metals due to its strong field confinement, comparably low ohmic loss, and versatile tunability. Plasmons in graphene may have an exceptionally slow phase velocity down to a few hundred times slower than the speed of light (Kaminer et al., 2016). The combination of ZnS nanoparticles (NPs) and RGO may be an ideal n-p hetrojunction system to enhance charge separation in electron-transfer processes and may be suppress the photocorrosion. Particularly, 2D n-p heterojunction photocatalysts have aroused great interest because of their high surface areas and remarkable and directional transport characteristics of electrons and holes (Xie et al., 2013). In addition, RGO can act as a cocatalyst to tune the band gap position of ZnS (Zhang et al., 2012) and as a photosensitizer to enhance visible light harvesting (Zhang et al., 2012). Meanwhile, formation of ZnS NPs on the RGO prevents particle growth and agglomeration (Xie et al., 2013). On the other hand, the hybridization of electrode materials with highly conductive graphene nanosheets leads to a significant improvement of electrode performance at high current density via the increase of electrical conductivity (Xiong et al., 2016).

Here, we report the fabrication of RGO-ZnS nanocomposites as a VLA photoelectrocatalyst. Interestingly, these nanocomposites show outstanding oxygen evolution at all pH values. The influence of RGO amount on the rate of photoelectrochemical water-splitting under visible-light irradiation was discussed. In addition, the key role of RGO in the enhancement of photoelectrochemical activity of ZnS was investigated. This study can open a new insight for the applications of photostable metal sulfides embedded on graphene in photoelectrochemical oxygen and hydrogen evolution reactions.

## 2. Experimental section

### 2.1. Chemicals

Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 98%), thioacetamide ($CH_3CSNH_2$, 99%), ethanol (96%), sodium sulfate ($Na_2SO_4$, 98%), sulfuric acid ($H_2SO_4$, 95%) and sodium hydroxide (NaOH, 98%), potassium hydroxide (KOH, 99.1%) sodium nitrate ($NaNO_3$, 99%), potassium permanganate ($KMnO_4$, 99%), hydrogen peroxide ($H_2O_2$, 30%), hydrogen chloride (HCl, 37%) were purchased from Merck without further purification. The deionized water was used for the sample preparation.

### 2.2. Preparation of photocatalysts

#### 2.2.1. Graphite oxide

Graphite oxide (GtO) was prepared from purified natural graphite according to the modified Hummers method (Hadadian et al., 2014). Typically, graphite powder (2 g) was mixed with 70 ml concentrated $H_2SO_4$ and 0.024 mol $NaNO_3$ for 15 min and was cooled in an ice water bath. Then, 0.038 mol potassium permanganate was gradually added into the mixture. The suspension was stirred for 15 min at 0 °C. The mixture was allowed to stand for 48 h at room temperature with gentle stirring. Subsequently, 92 ml deionized water was slowly added to the obtained brown pasty mixture for 10 min. Then, the suspension was diluted by 200 ml of warm water (35 °C) and treated with 70 ml of $H_2O_2$ for 30 min. The resulting solid was centrifuged and washed several times with HCl and deionized water. Finally, it was dried at 60 °C in vacuum oven overnight.

#### 2.2.2. RGO-ZnS nanocomposites

A certain amount of prepared GtO was dispersed in 50 ml of deionized water and ultrasonicated for 30 min at 25 °C to obtain graphene oxide (GO). After that, 13.6 mmol zinc acetate was added to a flask and sonicated for 30 min. Then, 13.3 mmol of thioacetamide was added to the suspension and sonicated for 1 h at 70 °C. The suspension was transferred to an autoclave and heated at 180 °C for 12 h. The resulting grayish precipitate was centrifuged (10,000 rpm), washed with ethanol, and deionized water several times. The product was dried in a vacuum oven at 60 °C for 12 h. The same procedure was used to prepare different amounts of RGO (1, 3, 5, 10, and 20%) in the nanocomposite which named RGO1-ZnS, RGO3-ZnS, RGO5-ZnS, RGO10-ZnS, and RGO20-ZnS. Also, the similar procedure was used to prepare RGO and ZnS in the absence of zinc sulfide and GtO, respectively.

### 2.3. Characterization

The powder X-ray diffraction (PXRD) patterns of prepared nanomaterials were obtained by means of a Bruker/D8 Advanced diffractometer (2θ from 20° to 70°, by step of 0.04°) with graphite monochromatic Cu Kα radiation (λ = 1.541 Å). The standard used for PXRD instrument calibration was silicon powder. The transmission electron microscope (TEM) used for analysis of the sample was a Philip CM120 TEM with a maximum acceleration voltage of 120 kV. The field emission scanning electron microscopy (FESEM) analysis of the samples was taken by TESCAN-XMU. The UV–vis absorbance spectra of the samples were taken using an Agilent photodiode-array Model 8453 equipped with glass of 1 cm path length. The spectra were recorded at room temperature in air within the range 200–800 nm. The photoluminescence (PL) spectra of the photocatalysts were obtained using spectroflourophotometer Shimadzu RF-1501. The Fourier transform infrared (FTIR) spectra of fabricated samples were recorded at room temperature with a KBr pellet on a Thermo Nicolet-Avatar 370 Spectrometer ranging from 400 to 4000 $cm^{-1}$. Raman spectra were recorded using HANDHELD Raman analyzer in the range of 200–2000 $cm^{-1}$. The specific surface area of the degassed samples was measured by the multipoint Brunauer–Emmett–Teller (BET) method by Belsorp mini II BEL system.

Sonicator 4000 (20 kHz) with total power of 70 W was used for preparation of the prepared nanocatalysts. The photoelectrochemical analysis were performed using PG AUTOLAB model 302 N.

### 2.4. Photoelectrochemical performance measurements

Photoelectrochemical measurements were performed under acidic ($H_2SO_4$ 0.5 M, pH = 1.0), neutral ($Na_2SO_4$ 0.5 M, pH = 6.2), and basic (NaOH 1 M, pH = 13.5) conditions in a three-electrode electrochemical setup using a computer-controlled electrochemistry potentiostat under illumination of 110 W xenon lamp equipped with UV-400 cut off filter