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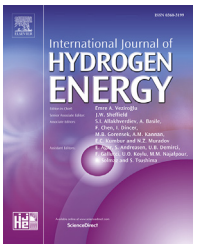

Enhanced photoelectrochemical water splitting in hierarchical porous ZnO/Reduced graphene oxide nanocomposite synthesized by sol-gel method

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ARTICLE INFO

Article history:
Received 18 December 2017
Received in revised form
2 March 2018
Accepted 8 March 2018
Available online xxx

Keywords:
ZnO
Reduced graphene oxide
Photoelectrochemical water splitting
Sol-gel dip coating
ZnO/rGO composite

ABSTRACT

Today the utilization of solar energy to split water and its conversion to hydrogen and oxygen has been considered as a powerful way to solve the environmental crisis. Hierarchical porous nanostructured ZnO and ZnO/reduced graphene oxide (rGO) composite photoanodes are synthesized by innovated sol-gel method using triethylenetetramine (TETA) as a stabilizer. The hierarchical porous ZnO structure containing large agglomerates each consisting of tiny nanoparticles are formed. The X-ray diffraction analysis and Raman spectroscopy confirm the in-situ reduction of graphene oxide sheets during synthesis and formation of ZnO/rGO nanocomposite. Although the band gap and transmittance of the porous nanocomposites do not dramatically change by rGO addition, the main photoluminescence peak quenches entirely showing prolonging exciton lifetime. The ZnO/rGO porous structure achieved remarkably improved current density (1.02 mA cm^{-2} at 1.5 V vs. Ag/AgCl) in 1 wt% rGO, up to 12 times higher compared to the bare ZnO (0.09 mA cm^{-2} at 1.5 V vs. Ag/AgCl), which attributes to positive role of ZnO hierarchical porous structure and rGO electron separation/transportation. These findings provide new insights into the broad applicability of this methodology for promising future semiconductor/graphene composite in the field of photoelectrochemical water splitting.

Introduction

Photoelectrochemical (PEC) water splitting, a highly-efficient and eco-friendly approach, has been emerged as an ideal candidate for reducing the consumption of fossil fuels to solve the world energy crisis and environmental problems [1,2]. Since Fujishima and Honda [3] reported the H_2 evolution on a TiO_2 photoanode under UV-light irradiation in a photoelectrochemical cell for the first time, much attention has been paid on the development of metal oxide semiconductor materials applying in this field [4–8]. In comparison with a TiO_2

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https://doi.org/10.1016/j.ijhydene.2018.03.052
0360-3199/

electrode, ZnO has two major advantages: (i) it exhibits about 10–100 times higher electron mobility and a lower rate of carrier recombination [9] and (ii) it can be easily synthesized with different morphologies such as nanoparticles [10], nanorods [11], nanowires [12], and nanosheets [13]. Among the wide range of different structures, spherical particles are of great significance. The large specific surface area, high level of symmetry, and strong light absorption ability give them excellent performance to harvest solar light for PEC water splitting [14,15].

However, zinc oxide is a semiconductor with a wide band gap (3.37 eV), the photoactivity of which is observed only when it is irradiated with UV light, thereby corresponding to only approximately 4% of solar spectrum [6]. Moreover, the photogenerated electrons and holes recombine easily on the surface of ZnO, resulting in the poor utilization of photogenerated carriers [16]. In order to alleviate these limitations and enhance the solar harvesting performance of ZnO based photoelectrodes, many strategies have been pursued such as elemental doping of metal [17–20] or non-metal atoms [21–24] to change its band gap and sensitizing with narrow band-gap particles [2,25–28]. Tailoring of zinc oxide nanostructures is another strategy to improve the PEC performance, e.g. nanorods [29], nanotubes [30], nanodisks [31], nanoflowers [32], nanotree and nanocluster structures [33], nanopencil arrays [34], nanoforests [35], and caterpillar-like structures [36]. Another effective way to enhance the efficiency of PEC water splitting is incorporation of ZnO nanostructures with electron conducting scaffolds to improve the charge separation and/or transport efficiency. Reduced graphene oxide (rGO) and graphene oxide (GO) are widely recognized as a conducting scaffold that can hinder the charge carrier recombination by excellent electron collection and transportation [37]. In previous reports, a few approaches have been demonstrated for preparing ZnO/GO (rGO) composite photoanodes for PEC water splitting. Chandrasekaran et al. [38] reported that triangular shaped ZnO on GO can be formed at a proper pH condition, which results in the enhancement of photoelectrochemical activity. Similarly, Lin et al. [39] reported fabrication of a rGO/ZnO nanocomposite for photoelectrochemical water splitting by the electrophoresis technique. Khan et al. [40] successfully engineered ZnO NWAs/rGO heterostructures on FTO substrate by sonochemical assisted approach to show amoleriated photoelectrochemical hydrogen production. Additionally, Thangaraj et al. [41] prepared rGO/ZnO hybrid with ZnO star like morphology decorated on rGO by using low frequency (42 kHz) ultrasound, which showed enhanced photocatalytic efficiency. Upadhyay et al. [42] used electrodeposition method to fabricate rGO/ZnO nanocomposites both with and without Ag-doping to suggest improved photoelectrochemical response. However, simultaneous existing of both large and small pores in the composite cannot be achieved by these methods, which can seriously affect the special surface area or proper media diffusion. Therefore, the formation of hierarchical porosity and the effective integration of rGO and ZnO porous nanostructure would lead to a photoanode with enhanced photoelectrochemical activity and long-term durability.

Normally, an important method to enhance water splitting activity is enlarging interfacial area between the electrolyte and ZnO/rGO composite due to the exposition of more catalytic active sites, which facilitate charge collection by reducing the diffusion length of photoexcited holes [43]. Based on such key scientific method, focus on the research of porous ZnO/rGO composite is a solution for enhancing water splitting. The template-assisted method is a common way to synthesize porous materials, while it is complicated, expensive, and hard to grow porous composite nanostructures [44].

In this context, this article aims to combine 3D sphere-like ZnO hierarchical porous nanostructures with rGO sheets using sol-gel synthesis approach to use it as an efficient water splitting photoanode for the first time. In other words, this type of porous structure has not been synthesized by this method yet. Besides, unlike conventional porous material formation in which different templates and binders serve to form porous ZnO matrix, an innovative strategy is introduced for obtaining hierarchical porous ZnO based on the utilization of a new stabilizer during sol-gel process. The ZnO/rGO hierarchical porous thin films are synthesized by a simple template-free method that allows direct utilization of the resulted photoanodes with proper interface in the device due to occurrence of in-situ reduction of rGO and two-step calcination process. Additionally, the effect of rGO addition in different amounts as a conducting scaffold to the nanocomposite is investigated using different characterization methods.

Experimental section

Materials

Graphite powder (Sinchem, 150–200 mesh, 95%), sulfuric acid (H_2SO_4, Merck, 98%), potassium permanganate ($KMnO_4$, Merck, 99%), hydrogen peroxide (H_2O_2, Merck), and hydrochloric acid (HCl, Merck, 32%) were utilized for synthesis of rGO papers without further purification. In order to prepare the ZnO sol, different materials were employed including zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$ - ZAD) as a zinc source, absolute ethanol (EtOH, Merck, 99%) as a solvent, and triethylenetetramine (TETA, Merck) as a stabilizer reagent. All chemicals used were of analytical reagent grade.

Synthesis of GO

GO was synthesized by a modified Hummer's method according to previous report [45]. Briefly, 0.5 g of natural graphite was mixed with 11.5 mL concentrated H_2SO_4 in a flask and stirred for 2 h. Then, 1.5 g $KMnO_4$ was added to the solution very slowly. The temperature of the colloid should not exceed 30 °C to avoid explosive reactions. After addition of $KMnO_4$, the mixture was heated at 35 °C and stirred for 1 h. Excess deionized water (DIW) of about 23 mL was added to the flask and the mixture was heated at 95 °C and stirred for 1 h. At the end, in order to terminate the oxidation reactions, 70 mL DIW and 2.5 mL H_2O_2 was added to the mixture. The final suspension was centrifuged and washed with HCl two times and DIW six times and dried in air.

Synthesis of ZnO/rGO nanocomposites

The method of preparing sols and thin films of ZnO is the same as procedure carried out in our previous work [46].

Please cite this article in press as: Ghorbani M, et al., Enhanced photoelectrochemical water splitting in hierarchical porous ZnO/Reduced graphene oxide nanocomposite synthesized by sol-gel method, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.03.052