

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

# Noble metal-free cuprous oxide/reduced graphene oxide for enhanced photocatalytic hydrogen evolution from water reduction

Honglei Xu<sup>a</sup>, Xiangqing Li<sup>a,\*</sup>, Shi-zhao Kang<sup>a</sup>, Lixia Qin<sup>a</sup>, Guodong Li<sup>b</sup>, Jin Mu<sup>b,\*</sup>

<sup>a</sup> School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, China

<sup>b</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

## ARTICLE INFO

### Article history:

Received 27 April 2014  
Received in revised form  
22 May 2014  
Accepted 25 May 2014  
Available online 19 June 2014

### Keywords:

Graphene  
Co-catalyst  
Hydrogen evolution  
Visible light  
Charge separation

## ABSTRACT

Cu<sub>2</sub>O loaded reduced graphene oxide (Cu<sub>2</sub>O/RGO) was prepared via a one-step in-situ reduction method. Composition and structure of the Cu<sub>2</sub>O/RGO were characterized by X-ray diffraction, high resolution transmission electron microscope and X-ray photoelectron spectroscopy. With eosin Y (EY) and rose bengal (RB) as co-sensitizers, the activity of hydrogen evolution over the Cu<sub>2</sub>O/RGO dramatically increased and achieved a maximum when the loading amount of Cu on the RGO was about 3 wt.%. It exceeded that of RGO and Cu<sub>2</sub>O by a factor of 7.3 and 4.2 at the same conditions, respectively. It could be even comparable to that of the Pt/RGO under the same reaction conditions. This work showed a possibility of utilizing Cu<sub>2</sub>O as an alternative for noble metals (such as Pt) due to its low cost and high performance in photocatalytic hydrogen production.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

As a new, clean fuel source, hydrogen energy has attracted great attention recently. Photocatalytic hydrogen production from water splitting is an attractive and challenging issue in the conversion of solar energy into chemical energy [1,2]. Herein, it is vital to design and prepare a cheap and stable photocatalyst for photocatalytic hydrogen evolution.

Graphene, which offers an excellent electron transport property and possesses an extremely high specific surface area, is desirable for use as a two-dimensional catalyst

support to provide adsorption and reaction sites and to suppress the recombination of photogenerated electron-hole pairs [3,4]. The potential application of graphene-based photocatalysts to boost the efficiency of solar energy conversion has been explored [5,6]. Dye-sensitization is an effective route to enhance the visible response of the RGO-based catalysts [7,8]. Unfortunately, even though the electrons can transfer from excited dye to RGO sheets, they may recombine with surface oxidized dye species if the trapped electrons are not quickly transferred. Therefore, it is important to accelerate the electron transfer on the

\* Corresponding authors. Tel.: +86 21 60873061; fax: +86 21 64253317.

E-mail addresses: [xqli@sit.edu.cn](mailto:xqli@sit.edu.cn) (X. Li), [mujin@sit.edu.cn](mailto:mujin@sit.edu.cn) (J. Mu).  
<http://dx.doi.org/10.1016/j.ijhydene.2014.05.156>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

surface of RGO in order to obtain higher photocatalytic efficiency.

The graphene decorated with metal nanoparticles have been shown to exhibit enhanced electrocatalytic and photocatalytic performances [9]. The graphene matrix is found to not only increase the active surface area and stability of the catalysts for the electrocatalytic reaction but also modulate the electronic structure of support metal nanoparticles [10,11]. For example, noble metal Pt nanoparticles immobilized on graphene sheets have displayed a high activity and stability in methanol and hydrogen fuel cells [10]. In addition, as the co-catalysts, noble metals can not only promote the separation of photoexcited electrons and holes and serve as the active sites, but also improve the stability of the photocatalyst by timely consuming of the holes, which play an essential role in the production of H<sub>2</sub> and O<sub>2</sub> [12]. However, noble metals are rare and expensive, which restrain their practical application. Therefore, replacing noble metals may be a promising method in clean and renewable energy issues. It is found that cheap transition metals or their oxides such as Cu species are rarely used as the cocatalysts in photocatalytic hydrogen production even though some Cu species have demonstrated high activity in heterogeneous catalysis [13,14].

Herein, by means of a facile process, Cu<sub>2</sub>O loaded RGO nanocomposites are prepared. With EY and RB (ER) as co-sensitizers, activity of the Cu<sub>2</sub>O/RGO for photocatalytic hydrogen production from water is investigated under visible light.

## Experimental

With graphite oxide and CuCl<sub>2</sub> as the reactants, NaBH<sub>4</sub> as the reductant, various Cu<sub>2</sub>O/RGO composites were prepared via

one-step in-situ chemical reduction method. In addition, 2% Pt/RGO and 3% Pt/RGO composites were also prepared under same conditions. The experimental details were described in the Supporting Information (SI).

## Results and discussion

Fig. 1A shows the XRD patterns of the RGO and the composite. Compared to that of the RGO (Fig. 1A(a)), some new peaks (Fig. 1A(b)) at  $2\theta = 36.3^\circ$ ,  $42.3^\circ$ ,  $61.3^\circ$  and  $73.4^\circ$  are observed and indexed to (111), (200), (220) and (311) crystalline planes of the cubic phase Cu<sub>2</sub>O (JCPDS No. 05-0667), respectively [15]. The sharp and strong peaks suggest high crystallization of the Cu<sub>2</sub>O in the composite. The peaks assigned to C, O and Cu elements are observed in the EDX spectrum of the composite (Fig. S1). The C peak is resulted from RGO, Cu peak is from Cu<sub>2</sub>O species, and O peak comes from Cu<sub>2</sub>O and RGO. The results of XRD and EDX confirm the existence of Cu<sub>2</sub>O on the RGO. Further, the intensity ratio of D band ( $1346.6\text{ cm}^{-1}$ ) to G band ( $1587\text{ cm}^{-1}$ ) (Fig. S2) enhances, which indicates the presence of unrepaired defects after reduction of graphene oxide. It is consistent with the literature reported [16,17]. The TEM image shows some nanoparticles evenly loaded onto the RGO sheets (Fig. 1B). The size of the nanoparticles ranges from 4 to 24 nm, and is mostly 10 nm, as illustrated in Fig. 1D. The absence of isolation and apparent aggregation of Cu species in the image reveals a strong interaction between RGO and Cu<sub>2</sub>O. In addition, the obvious lattice fringe assigned to (111) and (200) crystalline planes of cubic Cu<sub>2</sub>O can be observed in the HRTEM image of the Cu<sub>2</sub>O/RGO (Fig. 1C). It is in good agreement with the result of XRD (Fig. 1A).

To further identify the surface chemical composition and the valence state of copper species in the composite, the

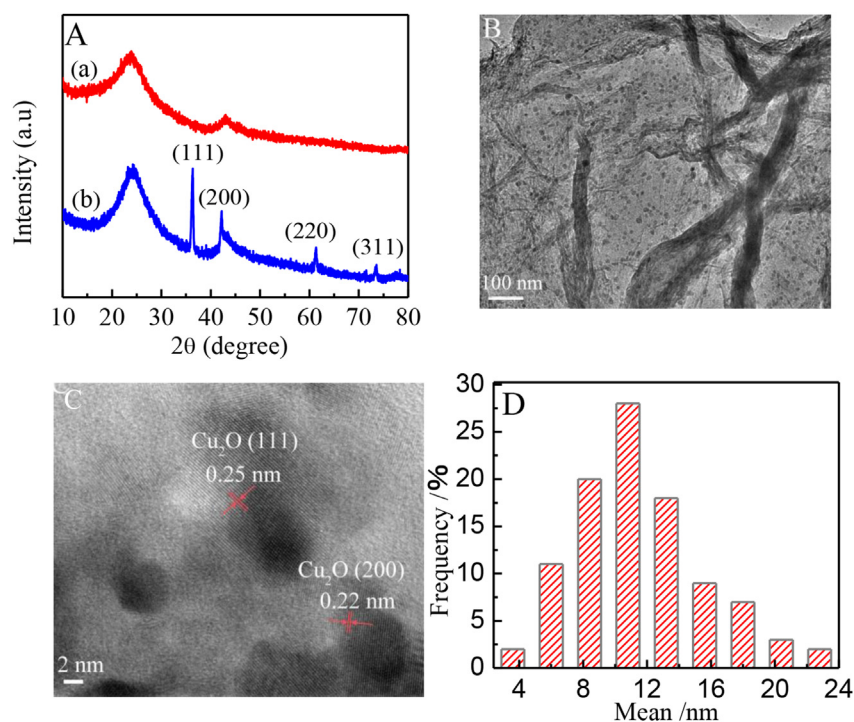


Fig. 1 – (A) XRD patterns of the RGO (a) and Cu<sub>2</sub>O/RGO composite (b); TEM image (B), HRTEM image (C) and size distribution histograms (D) for the Cu<sub>2</sub>O/RGO. The loading amount of Cu in the RGO was 3 wt.%.

Download English Version:

<https://daneshyari.com/en/article/1273176>

Download Persian Version:

<https://daneshyari.com/article/1273176>

[Daneshyari.com](https://daneshyari.com)