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3D crumpled RGO-Co_3O_4 photocatalysts for UV-induced hydrogen evolution reaction

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ABSTRACT

Three dimensional (3D) crumpled reduced graphene oxide (RGO)-Co_3O_4 nanohybrids were synthesized via a novel and facile solution method for use in UV-induced hydrogen evolution reaction (HER). The synthesized RGO-Co_3O_4 was calcined at a temperature from 300 °C to 500 °C to examine the effect of calcination on its HER activity. The 500 °C-calcined 3D-crumpled RGO-Co_3O_4 exhibited the highest photocurrent density under UV illumination due to the improved interfacial hole transfer and suppressed electron recombination. In addition, it also showed excellent durability even after 1000 cycles in acidic solution.

1. Introduction

Nano sized materials have attracted significant attention in photocatalytic and photoelectrochemical (PEC) water splitting, because of their potential (large surface area, short diffusion length, enhanced electron transport, and nano confinement effect) to produce H_2 from H_2O by using the abundant solar energy [1]. Usually, in an electrolytic cell, the equilibrium or reversible potential needed for H_2 production through water electrolysis is 1.23 V at 25 °C in order to achieve a desired current density. A range of materials have been examined for use in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in both acidic [2] and alkaline environments [3], including various combinations of metals, modest oxides, and some complex materials [3,4]. Even though these materials have shown interesting variations in their catalytic behavior, they are usually not cost-effective and operate at high overpotentials. Currently, it still remains a great challenge to design with the merits of high activity, low-cost, and excellent stability.

Graphene has stimulated enormous curiosity in various research fields [5], due to its unique characteristic properties arising from its 2D structure. In specific, the deposition of nanoparticles onto the surface of graphene or between the graphene layers, has been proposed as an appealing strategy for improving the device performance in energy research [6]. It is reported that calcined CoO and Co_3O_4 on graphene sheets display an excellent photocatalytic performance [7–9]. Most of graphene-based composites have been prepared from reduced graphene oxide (RGO) and pseudocapacitive nanomaterials. However, the excellent surface and electric properties of graphene sheets have been partially exploited due to the agglomeration of graphene sheets. Thus, an effective strategy to synthesize well-dispersed graphene-based metal oxide composites for photo electrodes remains a chief theme of interest. In this work we propose a novel and facile solution method to produce crumpled RGO/Co_3O_4 nanohybrids. The samples calcined at elevated temperatures exhibited an enhanced photocatalytic performance under UV illumination (~360 nm).

2. Experimental details

Graphene oxide was prepared from graphite powder using modified Hummers' method [10]. RGO-Co_3O_4 was synthesized via a facile solution method and the detailed synthesis of GO and RGO-Co_3O_4 is provided in Supplementary Information.

3. Results and discussion

Fig. 1a shows the XRD patterns of prepared 3D crumpled RGO-Co_3O_4 nanohybrids, confirming the cubic phase of the RGO-Co_3O_4, which is consistent with the previous observation [11]. The diffraction peak from crumpled graphene (CG) is also evidenced, indicating that the d-spacing of the CG is smaller than that of GO but larger than graphite [8,12]. The XRD results indicate that the

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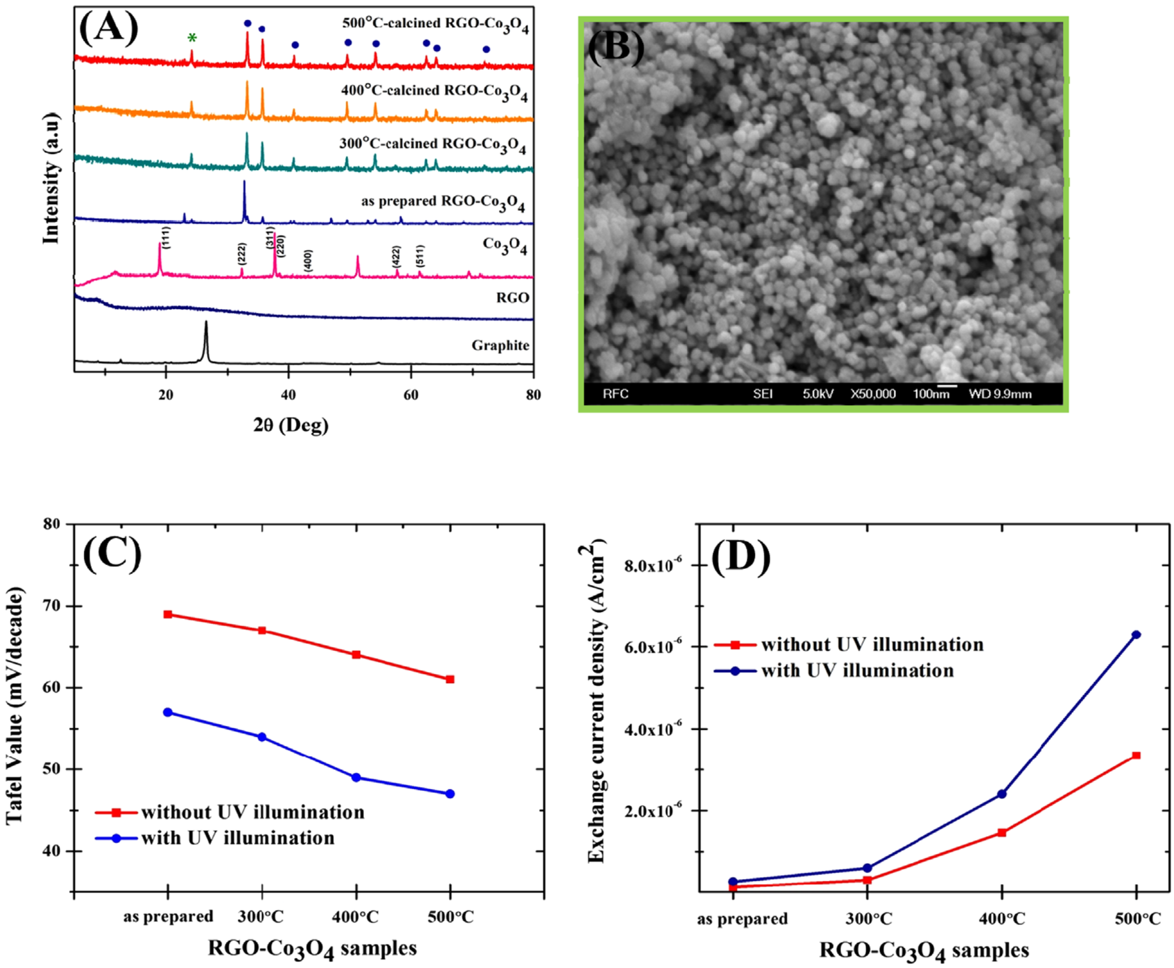

Fig. 1. (A) XRD patterns of graphite, thermally reduced graphene oxide (RGO), Co_3O_4 and 3D crumpled RGO-Co_3O_4 nanohybrids (* represents RGO and ● represents Co_3O_4)). (B) FE-SEM image of 3D crumpled RGO-Co_3O_4 calcined at 500 °C. (C) Tafel values of RGO-Co_3O_4 samples (D) Exchange current density of RGO-Co_3O_4 photoelectrodes.

RGO-Co_3O_4 nanocrystals are successfully produced, and that GO is crumpled and thermally reduced. The FE-SEM (Fig. 1b and Fig. S1) images confirm the 3D crumpled RGO–Co_3O_4 hybrid structure. It is evidently seen that the formation of crumpled RGO with large amounts of Co_3O_4 nano spheres (diameter of ~20 nm) that are homogeneously grown on the surface of the crumpled and ball-shaped folded RGO, giving rise to the 3D structure [8]. Some cracks on the surface were formed due to water vapor released from the precursor. The complex morphology of graphene sheets consist of wrinkles, crumples, folds, creases and blisters [13]. Hunter et al. ascribed the wrinkles and crumples to distinct symmetry breaking instabilities of elastic films on liquid drop and the folded type may be due to the superimposition of wrinkled graphene sheets [8,13–15].

The hydrogen evolution activity of the RGO-Co_3O_4 samples have been investigated using three electrode setups with and without UV light illumination. Fig. 2 shows the linear sweep voltammograms (LSV) of the as-prepared and calcined RGO-Co_3O_4. The HER process of the as-prepared RGO-Co_3O_4 started at ~ -0.18 V(reduction potential of Co^{3+}) and the current density was saturated at -0.53 V (corresponding to 1.23 V). In 0.1 M H_2SO_4 at -0.35 VS RHE, the samples exhibited a maximum current density of 0.0989 mA cm^{-2} (pure Co_3O_4, Fig.S4), 0.310 mA cm^{-2} (as-prepared RGO-Co_3O_4), 0.360 mA cm^{-2} (300 °C-calcined), 0.375 $mAcm^{-2}$ (400 °C-calcined) and 0.751 $mAcm^{-2}$ (500 °C-calcined) under UV light illumination. All the electrodes showed a decreased dark current with a negative shift, suggesting an enlarged accumulation of electrons on the surface of the electrodes and decreased charge recombination. The current density of the RGO-Co_3O_4 increased significantly upon UV illumination. In this process, hydrogen is produced by the reaction between the electrons transferred to the electrode and protons adsorbed on empty active site of the electrode. Generally, the hydronium cation is formed in acidic media and widely used as proton a source in the HER process [16–19]. The HER mechanism in aqueous acid media involves the following three steps:

$$\text{Volmer: } H^+ + e^- \rightarrow H_{ads} \quad (1)$$

$$\text{Heyrovsky: } H_{ads} + H^+ + e^- \rightarrow H_2 \quad (2)$$

$$\text{Tafel: } H_{ads} + H_{ads} \rightarrow H_2 \quad (3)$$

The HER mechanism is reflected by the Tafel slope (Fig. 1c and Fig. 3) and the compared Tafel values are provided in Table S1. Fig. 1d and Table S2 represent the exchange current densities of the RGO-Co_3O_4 samples. Tafel equation establishes a simple correlation between the current density and over potential (V) for the HER. If the Tafel constant is high the electrochemical reaction is slow (a slow reaction leads to a higher overvoltage) and vice versa. Compared with pure Co_3O_4 and other RGO-Co_3O_4 samples, the 500 °C-calcined RGO-Co_3O_4 had the smallest slope, which can be attributed to the highest electrical conductivity of RGO after high temperature annealing, nanostructure of Co_3O_4 and calcination effect. It is found that the 500 °C-calcined RGO-Co_3O_4 shows the highest current density of 0.751 $mAcm^{-2}$ (under UV light) at a small over potential of ~ -0.35 V and a reasonably small