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Supercritical fluid mediated synthesis of highly exfoliated graphene/ZnO composite for photocatalytic hydrogen production

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ABSTRACT

Reduced graphene oxide (RGO)/zinc oxide (ZnO) composite was synthesized via a simple and environmentally-friendly route using supercritical carbon dioxide. The structure and morphology of the resulting composite was characterized by transmission electron microscopy, X-ray diffraction and Raman spectroscopy. The nanocomposite exhibited enhanced photocatalytic activity for hydrogen (H_2) production from water photo-splitting because the ZnO nanoparticles on the RGO sheets can capture light energy and facilitate excited electron transfer for photocatalytic H_2 production via RGO, which acts as an efficient electron mediator.

1. Introduction

Hydrogen (H_2) is considered an ideal fuel for the future because it can be produced from clean and renewable energy sources [1]. Since the discovery of the photocatalytic splitting of water on TiO_2, semiconductor-based photocatalysis for H_2 production has attracted considerable attention [2]. Zinc oxide (ZnO) is a promising semiconductor photocatalyst on account of its wide band gap of 3.37 eV, low cost, non-toxicity, and good oxidizing power. On the other hand, electron-hole recombination is a major impediment to the widespread applications of its photocatalytic activity. Recent studies have shown that carbon nanomaterials, particularly carbon nanotubes (CNTs), are promising cost effective cocatalysts [3]. CNTs are believed to be capable of accepting, transporting and storing electrons, and hence reducing the recombination of the photoinduced electrons and holes [3]. Similar to CNTs, graphene-related materials can also act as an outstanding source of acceptors and electron transport because of their conductivity, high electron mobility and large theoretical specific surface area [4,5]. In addition, graphene-related compounds have great adsorption ability and are expected to be a good choice for adsorbent materials with a photocatalyst [6]. Owing to its remarkable electron storage and shuttling properties, graphene facilitates photoinduced charge separation and inhibits electron-hole recombination when semiconductors are immobilized on its surface in photocatalytic processes [4]. Therefore, considerable effort has been made to use graphene as a co-catalyst with semiconductor oxide-based hybrid materials for superior photocatalytic activity [7,8]. Although there are some reports of semiconductor/graphene composites for photocatalytic H_2 production, there are no accounts of H_2 production using reduced graphene oxide (RGO)/ZnO nanocomposite as a photocatalyst.

In this article, RGO/ZnO nanocomposite was synthesized using supercritical carbon dioxide ($scCO_2$) and evaluated as a photocatalyst for H_2 production. The advantages of this $scCO_2$ chemical deposition technique lay in its flexibility, simplicity, green properties, and efficiency in material science and chemical processing. The nanocomposite was characterized by Raman spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The photocatalytic activity was evaluated by measuring the level of H_2 production from water photo-splitting under UV-irradiation.

2. Experimental

Synthesis of RGO/ZnO nanocomposite: All chemicals used in this study were purchased from Sigma-Aldrich and used as received. Ultra high purity CO_2 (99.999%) was obtained from Deokyang Energy Co. GO was prepared from natural graphite using a modification of Hummers method [9]. The RGO/ZnO composite was synthesized using a previously reported procedure [10]. In a typical experiment, GO was dispersed in ethanol (5 mg/mL) under sonication for 2 h at room temperature to form a homogeneous suspension. A precursor solution was prepared by dissolving 100 mg of $Zn(NO_3)_2 \cdot 6H_2O$ in 1 mL of ethanol. The precursor

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solution was added to the above solution, and the resulting mixture was transferred to a 20 mL stainless steel reactor. CO_2 was then charged into the reactor. The temperature and pressure of the reactor were adjusted to 300 °C and 9 MPa, respectively. The $scCO_2$ conditions were maintained for 6 h with magnetic stirring. The CO_2 was then vented slowly, and the product was collected. Pure ZnO and RGO were also prepared in a similar manner in $scCO_2$. The weight ratio of RGO to TiO_2 in composite was found to be 1:20.

Photocalytic H_2 production: The photocatalytic H_2 production experiment was performed in a 100 mL double walled quartz flask with a water inlet and outlet to maintain the temperature of the photoreactor [11]. The photocatalytic reaction was carried out at room temperature and atmospheric pressure. In a typical experiment, 0.1 g of the sample was dispersed in 60 mL of an aqueous solution containing Na_2S (0.1 mol/L) and Na_2SO_3 (0.05 mol/L) as the sacrificial reagents. The solution containing the photocatalyst was ultrasonicated for 20 min, degassed for 30 min, and irradiated with UV-light with stirring to ensure uniform exposure of the suspension throughout the process. To avoid the photo-corrosion of ZnO, the experiment was performed under a N_2 atmosphere. The amount of H_2 produced was analyzed by gas chromatography (Agilent Technologies: 6890N) using a thermal conductivity detector (TCD), molecular sieve 5A and N_2 carrier gas.

Characterization: TEM (Technai G2 F20) was performed at an accelerating voltage of 200 kV. The phase and crystallinity were examined by XRD (Brooker) using Cu Kα radiation over the range, 10 to 80° 2θ. The Raman spectra were recorded on a confocal micro-Raman spectrometer (LabRAM ARAMIS, HoribaJobin Yvon) with 532 nm laser excitation.

3. Results and discussion

The RGO/ZnO composite was synthesized via a facile approach using $scCO_2$. In this study, $scCO_2$ played a key role in coating the RGO surface with ZnO nanoparticles. First, $scCO_2$ is miscible with ethanol under suitable conditions. When ethanol acts as a solvent for the precursor, the zero surface tension of $scCO_2$ allows ethanol to wet the GO surface during the entire experimental process. Consequently, $scCO_2$ helps the precursor adsorb easily on the surface of GO and enhances the physical attraction of the two substances. When the temperature of the reactor reaches 300 °C, both thermal reduction of GO and thermal decomposition of precursor occurs simultaneously. Second, $scCO_2$ might act as an antisolvent for the ZnO nanoparticles in the expanded ethanol system. As the dissolution of CO_2 increased, the solvent power of the liquid phase on ZnO decreased, which led to phase separation, and the ZnO nanoparticles precipitated from the supersaturated solution. In addition, $scCO_2$ diffuses between the RGO layers because of its liquid like density, gas like diffusivity and zero surface tension. The CO_2-intercalated RGO is forced to delaminate by the expansion of $scCO_2$. The inherent properties of GO as a substrate are the key factors affecting the size and morphology of the ZnO formed [10].

Fig. 1a shows the Raman spectra of the RGO and RGO/ZnO composite. In the RGO spectrum, the two prominent peaks at approximately 1358 cm^{-1} and 1600 cm^{-1} were assigned to the D and G bands, respectively. The D band corresponds to the breathing modes of the rings or the K point phonons with A_{1g} symmetry, whereas the G band represents the in-plane bond-stretching motion of pairs of C sp^2 atoms (the E_{2g} phonons) [12]. On the other hand, the D and G bands of RGO in the composite were shifted. The D band in the composite was shifted to a lower wavenumber by 8 cm^{-1}, whereas the G band showed a blue shift of 21 cm^{-1}. In addition, the intensity ratio of the D and G bands (I_D/I_G) of the composite was much lower than that of RGO, which was attributed to interactions between the ZnO nanoparticles and RGO sheets. Furthermore, the peak at 2720 cm^{-1} was assigned to an overtone of the D band, indicating increased disorder in the RGO [10,13].

Fig. 1b shows a typical XRD pattern of the as-synthesized RGO/ZnO composite. The diffraction peaks were indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of ZnO with a wurtzite structure (JCPDS no. 396-1451). The additional peak at 26.5° was assigned to the (002) plane of graphite. No other peaks for impurities were detected, indicating the high purity of the composite.

Fig. 2a shows a representative TEM image of the RGO/ZnO composite. An analysis of the image revealed a homogeneous distribution of ZnO nanoparticles at the RGO surface with a mean particle size of ≤ 8 nm. Nevertheless, few large aggregated particles were also observed by TEM. According to these observations, the in-situ method is a simple and effective strategy for fabricating RGO/ZnO composites. High-resolution TEM (HR-TEM, Fig. 2b) showed that the lattice spacing of ZnO was approximately 0.28 nm, corresponding to the (100) plane. This confirmed that the black dots in the TEM image were ZnO nanoparticles. The corresponding selected area electron diffraction pattern (Fig. 2c) also confirmed the wurtzite crystal structure of ZnO, which is consistent with the XRD pattern.

Fig. 3a presents the photocatalytic H_2 production activities of the as-synthesized ZnO, RGO and composite under UV-light. No appreciable H_2 was detected by RGO under UV-irradiation. In contrast, ZnO showed low levels of photocatalytic H_2 production because of the rapid recombination of the conduction band

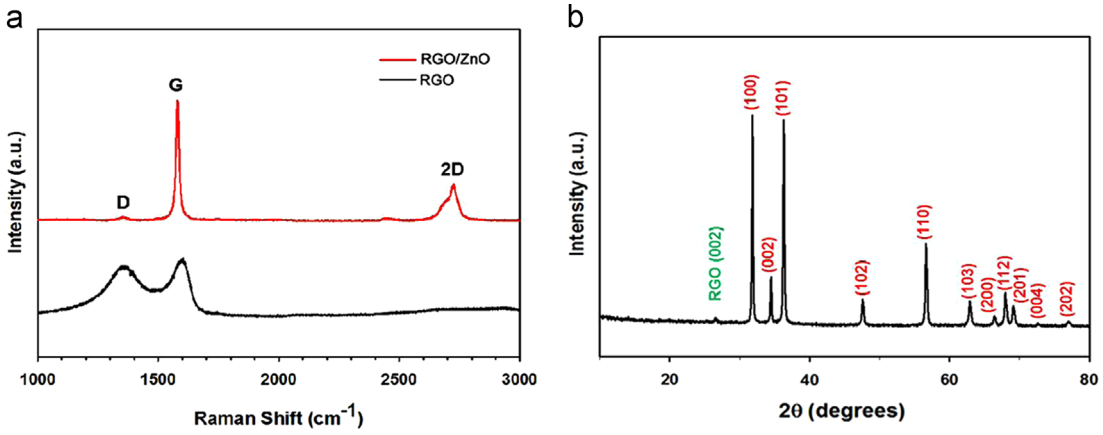

Fig. 1. (a) Raman spectra and (b) XRD pattern of the RGO/ZnO composite.