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One-pot synthesis of cuprous oxide-reduced graphene oxide nanocomposite with enhanced photocatalytic and electrocatalytic performance

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ABSTRACT

We report on the facile one-step synthesis of porous cuprous oxide nanoparticles on reduced graphene oxide (Cu_2O–RGO) by synchronously reducing Cu^{2+} ions and GO with ethylene glycol. The basic chemical components, crystal structure and surface morphology of prepared nanocomposite was carefully characterized. The photocatalytic activities of the as-prepared nanocomposite was investigated by photodegrading methylene blue (MB) under visible light. The electrocatalytic property of the nanocomposite was investigated by electrocatalytic determination of acetaminophen. The results indicate that the corporation of RGO with Cu_2O nanoparticles could high enhance the both photocatalytic and electrocatalytic properties. Moreover, we found that the content of RGO introduced into nanocomposite could highly affect the product properties.

1. Introduction

Recent research has witnessed rapid advances in syntheses of nanostructured semiconductors of different sizes, shapes and compositions for use in photocatalysis, adsorption, solar cells, supercapacitor and chemical sensors. Cuprous oxide is a p-type semiconductor with unique optical and electrical properties, which presents itself as a promising material in the fields of solar energy conversion, photocatalytic degradation, catalysis and sensors [1–4]. Also it was reported that the copper/copper oxide nanostructures can inhibit the growth of bacteria in visible light irradiation [5]. Moreover, Cu_2O is abundant and nontoxic, and has low production cost. However, there are intrinsic drawbacks of Cu_2O, including the instability in wet air, photo-corrosion under light irradiation, particularly the fast recombination of the photogenerated electron–hole pairs, which lead to the deactivation of Cu_2O and thus limit its practical applications [6,7]. In order to better use Cu_2O, many work has been concentrated coupling Cu_2O nanoparticles with other materials, such as noble metals, semiconductor nanoparticles and carbon materials [8–10].

Graphene, a newly developed form of carbon, has attracted increasing attention recently due to its unique physical and electrochemical properties. In electrochemistry field, using graphene as modifier showed potential advantages of high surface area, ease of processing and safety [11]. Besides, graphene has a large theoretical surface area (2630 m^2/g) and superior electrical conductance (64 mS/cm) [12,13]. Moreover, graphene also exhibits a large potential window, low charge-transfer resistance and fast electron transfer rate. Many reports also pointed out that graphene could enhance the electrocatalytic and photocatalytic performance of semiconductor nanoparticles [14,15]. So far, materials produced by combining RGO with metal oxide semiconductors have emerged as promising products for a wide range of potential applications in electronic devices, drug delivery, photocatalysis, energy conversion and storage [16–19].

Herein, we report a facile and efficient route to load Cu_2O nanoparticles on RGO via a simple one-pot solvothermal method. The Cu_2O nanoparticles are uniform in diameter and are well-dispersed on the 2D graphene sheets. The as-prepared Cu_2O/RGO nanocomposites were characterized using a series techniques. The photocatalytic activities of the as-prepared nanocomposite was investigated by photodegrading MB under visible light. The electrocatalytic property of the nanocomposite was investigated by electrocatalytic determination of acetaminophen. We found the Cu_2O/RGO nanocomposites owing excellent photocatalytic and electrocatalytic properties compared to the pure Cu_2O nanoparticles and RGO. Moreover, the effect of content of RGO in the nanocomposite was also studied.

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2. Experimental

GO was synthesized by the modified Hummers method using natural graphite as precursor [20]. Briefly, 2 g of graphite powder and 1.25 g $NaNO_3$ were added to 60 mL of concentrated H_2SO_4. 7.5 g of $KMnO_4$ was added gradually with stirring and cooling to maintain the mixture below 20 °C. The mixture then stirred at 35 °C for 30 min. 120 mL of distilled water was slowly added to the mixture and the temperature increased to 98 °C, then the mixture was maintained at this temperature for 15 min. The reaction was terminated by adding 350 mL of distilled water followed by 10 mL of 30% H_2O_2 solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulfate could not be detected with $BaCl_2$, and then washed three times with ethanol and dried in vacuum at 60 °C overnight.

Cu_2O–RGO nanocomposites were synthesized by chemical reduction of copper(II) acetate in ethylene glycol solution in the presence of GO. In a typical procedure, 50 mg of GO and 100 mg of copper(II) acetate monohydrate were dispersed in 50 mL of EG. The mixture was transferred into 100 mL steel autoclave. The steel autoclave was sealed, maintained at 180 °C for 2 h and then cooled naturally to the room temperature. The mixture was filtrated and washed copiously with ethanol for several times to remove the remaining ethylene glycol and soluble byproducts, and then dried in a vacuum desiccator. The resulting product was labeled as Cu_2O–RGO. For comparison, Cu_2O and RGO samples were also achieved by the same procedure. To investigate the effect of GO content on the photocatalytic activity of the Cu_2O–RGO nanocomposites, the weight percentages of GO–Cu_2O were varied from 0 to 0.5 (0.05, 0.1, 0.2, 0.3 and 0.5 wt%) and the resulting samples were labeled as Cu_2O–RGO-1, Cu_2O–RGO-2, Cu_2O–RGO-3, Cu_2O–RGO-4 and Cu_2O–RGO-5, respectively.

The photocatalytic activity of the samples were compared by monitoring the decolouration of heterocyclic dye MB under visible light irradiation. In a typical process, 20 mg of smaple were added into a quartz tube containing a MB solution (50 mL, 20 mg/L), which was placed with a 15 cm distance from the lamp. Prior to the illumination, the suspension was magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrium. At given time intervals, 2 mL of suspension was sampled and centrifuged, the supernatant was collected for absorption analysis on a UV–vis spectrophotometer. The absorbance of MB at 664 nm was used for measure the residual dye concentration.

For electrocatalytic activity test, a glassy carbon electrode (GCE) was polished by 0.3 and 0.05 μm alumina slurry followed by thoroughly rinsing with ethanol and water. For the electrode surface modification, 5 μL of as-prepared Cu_2O–RGO nanocomposites dispersion (0.5 mg/mL) was dropped onto the GCE surface and dried at room temperature. All electrochemical measurements were performed on a CHI430a electrochemical workstation (USA) at room temperature. A conventional three electrode system containing a modified GCE as working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl (3 M KCl) electrode as reference electrode was used throughout the electrochemical experiments.

3. Results and discussion

SEM was used for observing the morphology of synthesized Cu_2O/RGO nanocomposite. As shown in Fig. 1A, it can be clearly seen that the Cu_2O/RGO nanocomposite was successfully synthesized. The RGO sheets show a corrugated structure. The Cu_2O nanoparticles are decorated on the both sides of RGO sheet, which could effectively prevent the stacking of RGO sheets. The average size of Cu_2O nanoparticle formed via galvanic displacement is calculated as 40 nm.

The crystal information of GO and Cu_2O/RGO nanocomposite are shown in Fig. 1B. As shown in the figure, the XRD pattern of GO has a characteristic diffraction peak (002) at around 10°, corresponding to a d-spacing of 0.772 nm, which is larger than the interlayer distance of the (002) peak for graphite. This pheromone could be ascribed to the introduction of oxygenated functional groups, such as epoxy, hydroxyl (–OH), carboxyl (–COOH) and carbonyl (–C=O) groups attached on both sides and edges of carbon sheets. The XRD pattern of Cu_2O/RGO nanocomposite shows diffraction peaks correspond to (110), (111), (200), (220) and (311) crystal planes of cubic Cu_2O (JCPDS 78-2076). Moreover, there is no peaks of impurities are detected, indicating that the formed nanocomposites are pure and well crystallized.

Fig. 2A shows the Raman spectrum of the Cu_2O–RGO nanocomposite. The Raman bands at 218, 401 and 624 cm^{-1} are assigned to $2\Gamma_{12}^{-}$, $4\Gamma_{12}^{-}$ and $\Gamma_{12}^{-(2)}$ vibration modes of Cu_2O, respectively [21]. The bands at 1572 and 1335 cm^{-1}, which was assigned to the graphite (G band, first-order scattering of E_{2g} phonons by sp^2 carbon atoms) and diamondoid (D band, breathing mode of κ-point photons of A_{1g} symmetry) bands, respectively [22]. The 2-D peak of Cu_2O–RGO nanocomposites appears at 2707 cm^{-1}, shifts to the higher wave number value of, and becomes broader for an increasing number of layers with respect to single-layer graphene (2-D, 2680 cm^{-1}). The peak at 2938 cm^{-1} (D+D′) is attributed to defects, due to the combination of two phonons with different momentum [23]. The data suggest the formation of Cu_2O–RGO composites.

Fig. 2B displays the FTIR spectra of GO and Cu_2O/RGO nanocomposite. GO showed a series of oxygen containing groups, the strong band at around 3397 cm^{-1} is due to the stretching vibration of O–H, the band at 1722 cm^{-1} reflects the C=O vibration of –COOH located at edge of GO sheets, the features of O–H, epoxide groups and skeletal bending vibration can be seen at 1618 cm^{-1}, the peak at 1392 cm^{-1} is attributed to the tertiary C–OH groups stretching vibration, the band at 1225 cm^{-1} is the C–O stretching

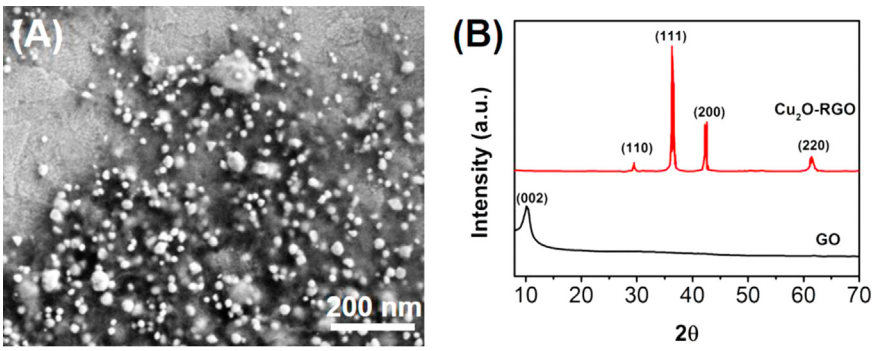

Fig. 1. (A) SEM image and (B) XRD pattern of Cu_2O/RGO nanocomposite.