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Fabrication of Graphene–CuO Nanocomposite with Improved Photocatalytic Degradation for Palladium Solution under Solar Light Irradiation

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ABSTRACT

A facile synthesis of graphene oxide-copper oxide nanocomposite (GO-CuO) was performed by using wet chemical method of graphene oxide and copper acetate precursors. The nanocomposite was characterized and intercalated with Raman spectroscopy, FE-SEM, TEM, SAED and EDAX. The crystalline nature was studied from P-XRD. Photocatalytic degradation of palladium ion was studied by using UV-VIS spectrophotometer. Significant high-performance photocatalytic activity of GO-CuO nanocomposite was exhibited on palladium ions degradation under solar light.

1. Introduction

There is great interest in the removal and recovery of precious metals such as gold, palladium, platinum and other noble metals from wastewater. The two most important reasons and motivations for precious metal removal are the economic impact of losing these metals and their environmental concerns [1]. They are common contaminants in wastewater and many of them are known to be toxic or carcinogenic. Trace amounts of these precious metals can be found in some wastewaters as a result of mining [2], electroplating industries [3], or electronic and jewellery manufacturing. However, such wastewaters contain precious metals not recovered from precipitation methods with concentrations around 10 mg/L, and other valuable metals with concentrations ranging from several mg/L to more than 10,000 mg/L. The most current, efficient and economical method to remove heavy metals by photocatalytic degradation using day-light driven in the presence of an appropriate photocatalyst that is able to promote the reduction of toxic metals to favorable by products.

Graphene has high chemical stability and versatile platform for photocatalysis due to specific surface area (2630 m2/g), excellent electrical conductivity and outstanding optical transmittance. At present major problems affecting the mankind are energy crisis and environmental problems. The potential solution of these problems is utilization of solar energy for photocatalytic degradation using suitable semiconducting photocatalysts. In the process of photocatalysis, graphene to enhancing the separation and exchange of photo-generated charge carriers from semiconductors [4, 5]. Many researchers have synthesized a number of graphene-supported semiconductors such as activated carbon-silica (SiO_2/AC), GO-CuO, GO-TiO_2 and NiO/graphene oxide for the removal of water pollutants as organic and inorganic to enhance its catalytic activity [5-9]. Therefore, researchers have tried to improve distinguishable nanocomposites/ nanoparticles for reduction of heavy metal ions to overcome this tricky. Hybridization of graphitic materials with CuO offers the efficient photocatalytic activity [10, 11]. For this purpose, CuO has been reported to be one of the best metal oxides that can be grown on graphene sheets. CuO has unique physical and chemical properties such as large specific surface area [12], excellent solar light absorbance [13], and a narrow band gap (Eg ~ 1.2 eV) [14], rendering this material useful for many practical applications. CuO has also been explored in various fields such as optoelectronics [15], electronics [16], gas sensing [17], solar cells [18], batteries [19] as well as heterogeneous catalysis [20].

In this study, we prepared and fabrication and exploration of the potential of a hybrid materials specifically graphene- CuO nanocomposites by wet chemical method for degradation of Pd(II) ion under solar light. The decomposition kinetics and mechanism of the photocatalysts were also studied.

2. Experimental Methods

2.1 Chemicals

The materials graphite flakes (+200 mesh) were commercially obtained from Sigma-Aldrich, copper acetate dihydrate [$(CH_3COO)_2Cu.2H_2O$], sodium hydroxide [NaOH], sodium nitrate [$NaNO_3$], hydrogen peroxide [H_2O_2], sulfuric acid [H_2SO_4], hydrochloric acid [HCl], and potassium permanganate [$KMnO_4$] all these chemicals procured from the Merck and used without further refinement, Ethyl alcohol [C_2H_5OH], AR,99.9% (Jiangsu Huaxi International Trade Co.Ltd., Made in china). Throughout the experiment double distilled water was used.

2.2 Synthesis of Graphite Oxide

Graphite oxide was prepared by the modified Hummers method [21]. In a typical procedure, about 5 g of graphite flakes was added to 115 mL of concentrated (98%) H_2SO_4 in an ice bath with stirring for 30 min. A 15 g of $KMnO_4$ was added slowly to the above mixture with stirring and cooling for 30 min. Subsequently, 2.5 g of $NaNO_3$ was added with continuous stirring for 1h. So that the temperature of the mixture maintained below 15 °C during that time. The temperature of mixture then raised upto 40 °C with water bath, and the mixture was continuously stirred for 30 min. After that, the mixture was diluted by 800-1000 mL of distilled water, the temperature of which then raised to 98 °C. The mixture was then added by H_2O_2 (30%) until gas evolution ceased followed by filtering. The color of the dispersion turned from black to yellow. The product was washed repeatedly with 1 M HCl (5%) and distilled water until the pH value of the product arrived at near 7. Then the product was dried in an air oven at 60 °C to obtain graphite oxide.

2.3 Synthesis of GO-CuO Nanocomposite

To prepare a colloidal suspension of GO [22], about 60 mg of as-prepared graphite oxide was dispersed in 60 mL of ethanol by sonication for 1 h. Consequently copper acetate 0.25 M was added in to the dispersion and then add drop wise 1 M of NaOH solution up to pH=10, which was

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calculated by pH meter. The total mixture was maintained at 140 °C for 12 hours under N_2 atmosphere. The product was washed several times with first by ethanol and thereafter distilled water. After that GO-CuO dried at 80 °C overnight in hot air oven. The synthesis procedure was shown in below (Fig. 1).

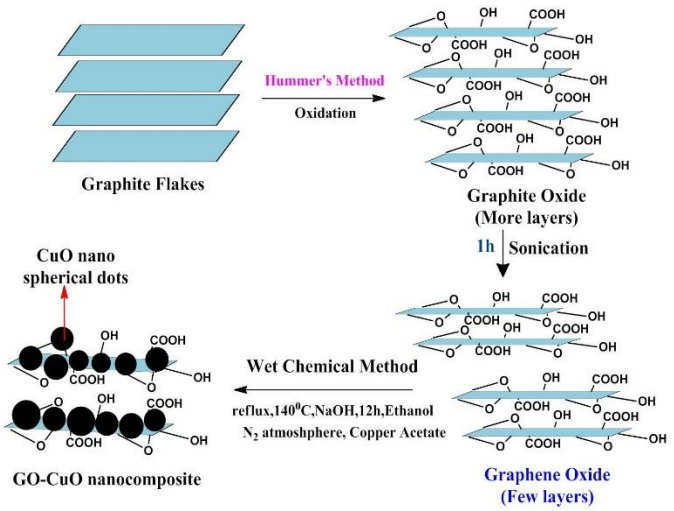

Fig. 1 Chemical route synthesis of GO-CuO nanocomposites

2.4 Instrumentation

The structure and morphology of the samples were characterized by X-ray diffractometry (XRD) Bruker D8 using CuKα1 (1.5406 Å) and Kα2 (1.54439 Å) radiations, Morphologies of as-obtained products were studied by scanning electron microscope (SEM) imaging with energy dispersive Absorption X-ray spectroscopy (EDAX) or Energy dispersive spectrum (EDS) using a Carl Zeiss model Ultra 55 microscope operating at 5 and 20 kV, Structure analysis were conducted by a transmission electron microscope (TEM) measurements were performed on a Tecnai G2FEI F12 I at 200 kV, Carbon coated TEM grids were used before taking the images of the compounds. Raman spectra were recorded using a WiTec alpha 200 SNOM system. The pH of the solution was checked by using Elico pH meter.

2.5 Photocatalytic Activity Studies

To evaluate the application activity of the GO-CuO nanocomposites, degradation experiments on the palladium solution were done under the presence of solar light condition. In our frame work GO-CuO nanocomposites were show very good photocatalytic activity test. In this case 10 ppm of palladium solution in 50 mL distilled water and 50 mg of catalyst were taken in round battle flask. First, CR solution with catalyst were maintained under magnetic stirring in darkness for one hour because to reach CR solution adsorption–desorption equilibrium position. Then this solution kept under the sun light continuously stirred on magnetic stirrer after each 10 min equal interval of time 2 mL of solution was collected in the test tube. The concentration of the clean transparent zinc solution was analyzed by checking the absorbance at 400 to 600 nm with the UV-vis spectrophotometer, which denoted as C_t. In this case dried GO-CuO nanocomposites shown the good photocatalytic activity compared with the 300 and 600 °C calcination compound in the presence of sun light.

3. Results and Discussion

The crystalline nature and orientation of the as-synthesized Graphite oxide, CuO and GO-CuO nanocomposite was analyzed by powder X-ray diffraction (PXRD) as shown in (Fig. 2). For graphite oxide an intense crystalline peak around 9.92°. All the samples exhibit analogous diffraction peaks in terms of CuO framework. The dominant peaks located at ca. 35.55, 46.26, 48.70, 53.54, 58.33, 61.55, 66.22 and 66.14° are indexed to (1̄11), (111), (202), (020), (202), (113), (311) and (202) crystallographic planes of monoclinic CuO (JCPDS File Card No. 89-5899) consistent with GO-CuO composite. Where the diffraction peaks can be readily indexed to CuO with (1̄11) and (111) planes confirm the presence of CuO in the composite catalyst [23]. The XRD pattern demonstrate the presence of a monoclinic phase of CuO with no indication of Cu_2O and $Cu(OH)_2$ phase. No characteristic diffraction peaks for GO are observed in the pattern because of the low amount and the relatively low diffraction intensity of GO.

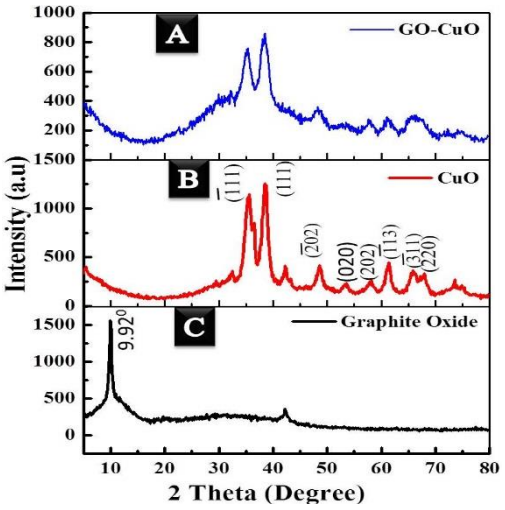

Fig. 2 P-XRD pattern of the (A) GO-CuO and (B) CuO and (C) Graphite oxide

The Raman spectra of GO and GO-CuO composites are shown in (Fig. 3). The D and G bands were observed in the range of 1000-2000 cm^{-1}. Generally in GO based samples, the disorder-induced D bands arise from the tangential stretch and sp3-hybridized carbon and the G band represents the crystalline graphite with E_{2g} zone center mode; moreover, the I_D/I_G ratio depends strongly on the amount of disorder in the graphitic material [24]. The I_D/I_G ratio should increase when more defects are introduced into GO. According to Fig. 3, the I_D/I_G ratio of GO-CuO composite is 0.998 which is higher than the 0.990 calculated from GO. That is to say, CuO modification can be effective in bringing an amount of defects into the structure of GO.

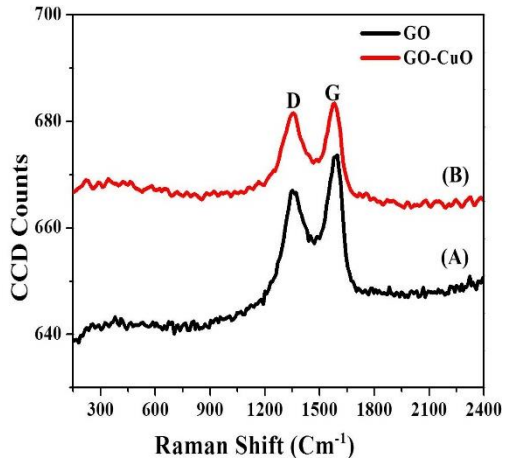

Fig. 3 Raman measurements of (A) GO and (B) GO-CuO

The SEM of nanocomposite was taken as powder synthesized, images were taken on carbon tape. Fig. 4A shows the SEM images it is unambiguous that the morphology of intercalated nanocomposite particles are really in nanosize and it shows the clumsy morphology due to the aggregation of particles in the solution while synthesis. Fig. 4B shows the Energy dispersive spectrum (EDS) results of the GO-CuO nanocomposite. Cu, O, C and Cu elements are observed.

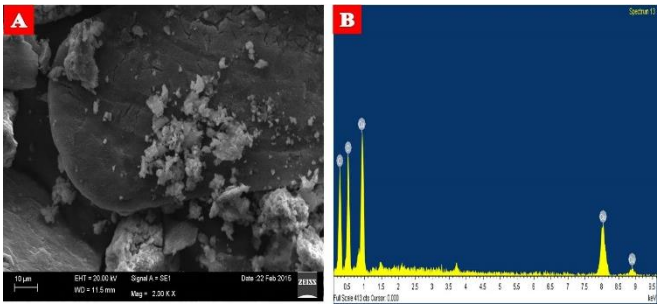

Fig. 4 (A) SEM image and (B) EDS of GO-CuO composite

Fig. 5 illustrates the typical TEM images of GO-CuO nanocomposite. It can be clearly seen that the exfoliated GO sheet was decorated by spherical dot CuO, with size <10 nm. Fig. 5(D) displays selective area electron

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diffraction (SAED) pattern of hybrid material shows the fusion of super lattices which are characteristic nature of the layer structure of any kind of materials.

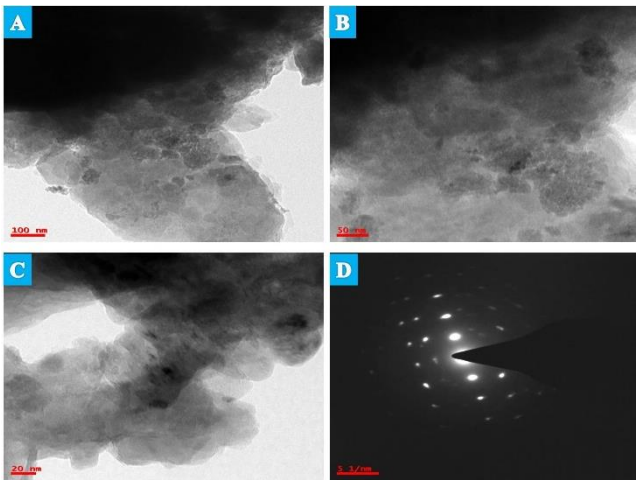

Fig. 5 (A, B, C) TEM micrographs at different magnification and (D) SAED pattern of GO-CuO composite

To illustrate the synergetic enhance of photocatalytic performance of GO-CuO Nanocomposites toward a heavy metal Pd(II) ions, the daylight driven photocatalytic reduction of Pd(II) in water was carried out at regular time intervals. The adsorption of these solutions decreased gradually with irradiation time. The characteristic adsorption of palladium almost disappeared after 70 min (Fig. 6(A)). The dried compound was 81.9% degraded in 70 min time (Fig. 6(B)), 300 °C calcinations compound was degraded 72.6 % in 70 min (Fig. 6(C)) and finally 600 °C calcinations compound was degraded 63.5% 70 min time taken (Fig. 6(D)). Because increase the calcinations temperature the particle size also increase that means the particle agglomeration was formed. This reason 600 °C compound was less degradation% compared with the dried and 300 °C calcination compounds.

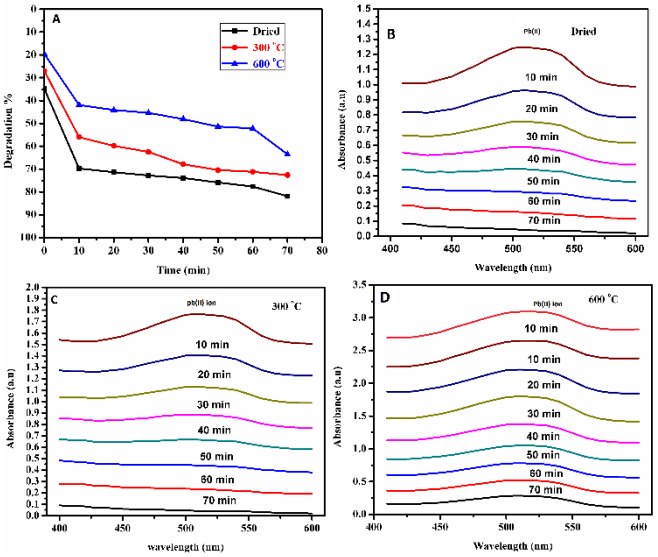

Fig. 6 Photocatalytic degradation of Pd(II) with GO-CuO nanocomposite as catalyst and comparison of different temperature

4. Conclusion

A simple and effective method was established to prepare GO-CuO photocatalyst by using graphene and CuO. Excellent circulated CuO nanocubes with an average size ranged between 5-10 nm were deposited on graphene via the wet chemical method under N_2 atmosphere. GO-CuO nanocomposite effectively reduces mutagenic aqueous solution of Pd(II) under natural daylight driven. The 300 °C calcination of GO-CuO photocatalyst have been showed high photocatalyst activity with 600 °C calcination of GO-CuO photocatalyst. Graphene based composite materials indication good-looking environmental applications such as toxic pollutants removal in terms of their cheap cost, simple handling and high degradation performance. Hence, photocatalytic reduction using GO-CuO nanocomposite is a most suitable, suitable and low cost effective technique for further treatment of industrial wastewater.

Acknowledgements

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