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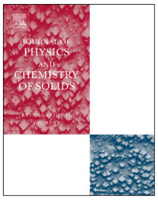

Copper and Graphene activated ZnO nanopowders for enhanced photocatalytic and antibacterial activities

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ABSTRACT

ZnO, ZnO:Cu and ZnO:Cu:Graphene nanopowders were synthesized via a facile wet chemical method. The XRD studies show that the synthesized samples have hexagonal wurtzite structure. It is found that graphene addition induces a decrease in crystallite size. UV–vis absorption spectra of the samples show sharp absorption edges around 380 nm. Photoluminescence studies reveal that the incorporation of copper and graphene in ZnO facilitates the efficient photo generated electron–hole pair separation. It is found that the ZnO:Cu and ZnO:Cu:Graphene nanopowder exhibit improved photocatalytic efficiency for the photodegradation of Methylene Blue (MB) under visible light irradiation. Moreover, improved antibacterial activity of ZnO:Cu:Graphene nanopowder against *Escherichia coli* and *Staphylococcus aureus* bacteria is observed.

1. Introduction

Degradation of pollutants in aquatic systems is a challenging task. Photocatalytic treatment is one of the best ways to degrade the toxic pollutants. Off the various photocatalysts, ZnO is one of the desirable inorganic material having superior properties like low cost, abundancy and non toxicity. However, because of its large band gap, it can absorb only the ultraviolet region of the solar spectrum which confines its photocatalytic activity to the UV region only. Moreover, fast recombination of electron–hole pair in ZnO is also a limiting factor in the photocatalytic process. In order to utilize visible light energy and effective charge carrier separation, ZnO can be suitably hybridized with transition metal ions [1], noble metals [2], graphene [3] and graphdyine [4]. Doping of transition metals in ZnO lattice may form new energy levels between the valence band and conduction band, extending the light absorption to the visible region. Among the transition metals, Cu offer several advantages as a dopant with ZnO, as reported by several researchers [5]. Therefore in the present work, Cu is added with ZnO expecting a reasonable enhancement in the photocatalytic activity.

Graphene is a unique two dimensional layer structure of sp^2 hybridized carbon atoms having excellent properties such as zero band gap, large specific surface area ($2630\ m^2\ g^{-1}$), high mobility of charge carriers ($>200\ 000\ cm^2\ V^{-1}\ s^{-1}$ at electron densities of $2\times10^{11}\ cm^{-2}$) and excellent thermal conductivity ($\sim5000\ Wm^{-1}K^{-1}$) [6,7]. It has high capacity of storing and transporting electrons [8]. Many researchers attempted to improve the photocatalytic activity via the combination of ZnO with graphene. The inclusion of graphene with semiconductor can boost the lifetime and transfer of charge carriers in the graphene-semiconductor photocatalysts [9]. Further, ZnO with graphene can enhance the photoactivity and anti-photocorrosion of semiconductor ZnO [10]. The combination of graphene-single semiconductor with metal (additional functional component) yields photocatalytic composite with multilevel/route electron transfer [11]. Improved photocatalytic performance can be expected from multi-component hybrid nanomaterials because of their extraordinary composite properties due to an integrative combination of individual components [12].

Considering the above mentioned points, in the present work, we have attempted to synthesize Cu and graphene involved nanopowder system to obtain a novel photocatalytic material with enhanced efficiency. We have synthesized ZnO, ZnO:Cu and ZnO:Cu:Graphene nanopowders using a facile wet chemical method. The photocatalytic performance of the synthesized samples was investigated by measuring the degradation of Methylene Blue (MB) dye under visible light irradiation. In addition, the application of the synthesized samples extended for inhibition of bacterial growth, since a very few work is done on graphene-semiconductor with

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metal system. The antibacterial activity of the samples against *Escherichia coli* and *Staphylococcus aureus* bacteria was reported.

2. Experimental

2.1. Preparation of Graphene Oxide (GO)

Graphene Oxide (GO) was prepared by the modified Hummer's method [13]. 2 g of graphite and 2 g of $NaNO_3$ were mixed together followed by the addition of 150 mL of concentrated H_2SO_4 in an ice bath under continuous stirring for 1 h. Then, 8 g of $KMnO_4$ was added pinch by pinch to the solution and the ice bath was removed after 30 min. Stirring was continued for 8 h at room temperature and 150 mL of deionized water was added gradually to the above mixture solution. For the completion of reaction 5 mL of 30% H_2O_2 was added. The resultant mixture was centrifuged and washed with 1 M HCl and deionized water. Finally the precipitate was dried at 60 °C for 24 h. The graphene oxide sheets were thus obtained.

2.2. Preparation of ZnO, ZnO:Cu and ZnO:Cu:Graphene nanopowders

ZnO nanopowder was prepared by adding 100 mL of 0.4 M NaOH solution into 100 mL of 0.2 M $ZnSO_4$ solution at an approximate rate of 10 mL/min under magnetic stirring. Then the mixture was kept at 60 °C for 2 h. For Cu source, 0.005 M of Cu NO_3 in 100 mL of DI water has been prepared and used as stock solution. The ZnO:Cu sample was prepared by adding 50 mL of 0.005 M $CuNO_3$ (taken from the above stock solution) into $ZnSO_4$ solution as prepared above followed by NaOH addition and kept at 60 °C for 2 h. For the ZnO:Cu:Graphene sample, 50 mg of Graphene Oxide was dispersed in 50 mL of deionized water and ultrasonicated for 30 min. 100 mL of 0.2 M $ZnSO_4$, 50 mL of 0.005 M $CuNO_3$ and 4 mL of 0.0008 M $NaBH_4$ were added slowly into the beaker containing GO under stirring followed by NaOH addition and kept at 60 °C for 2 h.. All the products were centrifuged and washed by deionized water and calcined at 400 °C for 4 h.

2.3. Characterization techniques

The crystal structure of the synthesized samples was studied using X-ray diffractometer (PANalytical-PW 340/60 X' pert PRO) with Cu-K_α radiation ($\lambda = 1.5406$ Å). The absorption spectra were measured by the UV–vis Spectrophotometer (Systronics, 2202). Photoluminescence (PL) spectra were obtained using spectroflurometer (ELICO, SL174). Fourier transform infrared (FTIR) spectra were observed using spectrophotometer (Bruker, Alpha T, Germany). The surface morphology was examined by Scanning Electron Microscope (SEM) (PHILIPS XL30 combined with EDX) and HR-TEM images were obtained by JEOL-2010 field emission transmission electron microscope. XPS analysis was carried out with Thermo Scientific-MULTILAB2000.

2.4. Photocatalytic test

The photocatalytic activity of the samples was evaluated by photo degradation of Methylene Blue (MB) dye in aqueous medium under visible light irradiation. A 300 W Xe arc lamp with an ultra violet cut off filter was used as the visible light source located 15 cm above the top surface of the MB solution. 50 mg of each synthesized sample was dispersed in 150 mL of MB aqueous solution (1×10^{-5} M) separately. The mixed solution was sonicated for 30 min in dark to reach an adsorption-desorption equilibrium. Under ambient conditions, the photocatalyst mixed MB solution was exposed to visible light irradiation for 60 min. The reaction solution was sampled at intervals of 15 min, centrifuged and filtered to remove the photocatalyst. The degradation was observed by measuring the absorbance of MB at 664 nm using a UV–vis Spectrophotometer (Systronics, 2202).

2.5. Antibacterial activity test

The antibacterial activity of the synthesized samples was tested for *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive) bacteria by disc diffusion method. In this work, Mueller-Hinton agar was used as a nutrient agar medium. The prepared medium was poured into Petri plates and using sterile cotton swab, fresh bacterial culture was spread over the plates by spread plate technique. The discs containing samples were dispensed on to the plates and pressed gently in order to ensure the discs were attached to the agar. The plates were incubated at 38 °C for 24 h. The diameter of inhibitory zones was measured in millimeter (mm).

3. Results and discussion

3.1. Structural studies

The structural features of the synthesized nanopowders were studied using X-ray diffraction technique. Fig. 1. shows the XRD patterns of ZnO, ZnO:Cu and ZnO:Cu:Graphene nanopowders. The sharp and intense diffraction peaks of the samples indicate that the samples are of good crystalline nature. All of the diffraction peaks can be indexed according to the JCPDS card no. 36-1451 affirming that all the synthesized samples have hexagonal wurtzite structure of ZnO. No diffraction peaks related to copper are observed for ZnO:Cu and ZnO:Cu:Graphene samples. This may be because of the substitution of Cu^{2+} ions (ionic radius 0.72 Å) into the regular sites of Zn^{2+} (ionic radius 0.74 Å) or interstitial incorporations of Cu^{2+} ions into the ZnO lattice. This finding is in agreement with the previous study of Mohan et al. [14]. Similarly, the is no diffraction peak related to graphene in the XRD pattern of the ZnO:Cu:Graphene sample which might be due to the disruption in the stacking regularity caused by the insertion of nanoparticles between the adjacent sheets of graphene [15,16]. However, the presence of copper and carbon in the synthesized powders was confirmed by the EDX results of the samples (Fig. 5(c)). The crystallite size (D) of the synthesized powders was calculated by measuring the full width half maximum of the strongest diffraction peak corresponding to (101) facet in all the cases, using the Scherrer's formula,

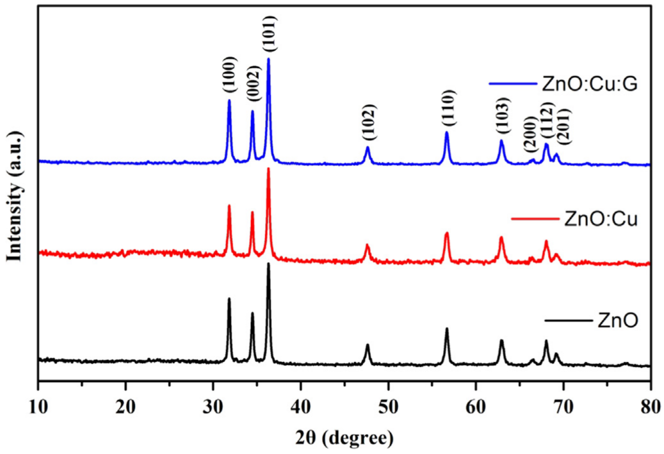

Fig. 1. XRD patterns of ZnO, ZnO:Cu and ZnO:Cu:Graphene nanopowders.