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Facile synthesis of ZnO/GO nanoflowers over Si substrate for improved photocatalytic decolorization of MB dye and industrial wastewater under solar irradiation

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ABSTRACT

In this work, we report a new method for the synthesis of zinc oxide (ZnO) nanoflowers/graphene oxide (GO) composite, uniformly grown over Silicon (Si) substrate. The synthesis is performed by utilizing aqueous chemical approach where ZnO nanoseeds are obtained using zinc acetate ($C_4H_6O_4Zn$) and isopropanol (C_3H_7OH), while Graphene oxide (GO) is fabricated by using Hummer's method. The nanocomposite was fabricated by mixing of GO and ZnO nanoseed solution followed by vigorous ultra-sonication and spin-coating over the Si substrate. Finally, the nanoflowers type structures were grown from ZnO nanoseed by placing the coated Si substrate in a solution containing Zn^{+2} environment. The nanocomposite was characterized by various techniques such as Field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray diffraction (XRD) analysis. The performance of nanocomposite was analyzed for remediation of methylene blue (MB) dye by utilizing sunlight as an energy source to initiate the photoreaction. The composite (GO/ZnO) shows ~ 33% faster decolorization of 20 mg/L of MB dye in comparison with pure ZnO. The improved performance is attributed to the prevention of recombining of electron (conduction band) and holes (valence band) during the photocatalytic reaction. Moreover, GO itself provides excess electrons for enhancing the photocatalytic reaction by providing excess hydroxyl radicals. Further, the nanocomposite was successfully utilized for decolorization of an industrial dye. Hence, nanoflowers type ZnO/GO composite material grown over Si substrate provides an alternative for effective removal of real dye from industrial wastewater without any post process filtration requirement.

1. Introduction

In today's world of industrialization, environmental pollutants have been increasing day by day. Various industries use water for cleaning, heat treatment, coloring, and transportation purposes. During these processes, water is mixed with various chemicals, dyes, and harmful reagents turning into an effluent which cannot be directly discharged to the environment due to its toxicity. The industrial wastewater consists of chlorinated organic compounds, phenols, heavy metals (As, Cr, Cu, Pb, Hg, Ni, etc.), salts, pH, naphthalene, oil, pesticides etc., [1]. It also contains volatile organic compounds such as benzene, methylene chloride, and trichloroethylene and toluene etc., [2]. So, there is an utmost need to provide a solution to eliminate these pollutants from the industrial effluents for the sake of plant, animal, and human life. The development of nanotechnology offers a promising solution for filtering, adsorbing, and degrading these pollutants from the water and making it reusable for irrigation or industrial applications [3–7]. Photoreaction is one such method which utilizes a form of light energy and creates holes and electrons in water solution [8]. The photoreaction can be catalyzed by using some material with certain band gap and the reaction is called photocatalysis. Metal oxide based semiconductors (MOS) have been used to work as a catalyst in photoreactions and found to be effective in degradation of polluting dyes from water. The mechanism of dye decolorization through MOS materials (TiO_2 [9], ZnO [10], V_2O_5 [11] etc.) is well known and attributed to the formation of the electron-hole pair at the conduction and valence band after absorbing a small amount of energy from visible or Ultraviolet light. ZnO has shown excellent catalytic properties in the remediation of wastewater by removing different type of organic dyes [12–14]. Suitable band gap (~ 3.4 eV), ease of fabrication, low cost, and nontoxicity enable ZnO to perform well in photocatalysis [15,16]. ZnO can be fabricated in different shapes such as nanosheets [10], nanorods [17],

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nanowires [18], nanospheres [19] etc. Nanomaterials with higher surface area show better performance in catalytic applications due to the larger interaction of surface charge carriers with the environment. Through the studies conducted in past, it was observed that surface defects present in the ZnO play an essential role in increasing the photocatalytic performance [20]. Solvothermal method of synthesis is found to be useful in creating these type of surface defects on ZnO nanostructures [21]. In this study, we will use a solvothermal approach for synthesizing ZnO nanoflowers to utilize the surface defect phenomenon. Addition of metal nanoparticles (Au, Ag, Al, Fe etc.) has also been used to enhance the photocatalytic activity by absorbing a large amount of visible light [11,22–24]. Some recent studies have found nanocomposite of ZnO with graphene as an improved form of MOS based catalyst in photoreaction [25–28]. Graphene sheet offers several properties such as large surface area, a great electron acceptor, and high visible light optical transparency [29–31]. MOS face issue of recombination of excited electrons and holes without taking part in the photocatalytic reaction. Graphene, due to its lower work function than ZnO, scavenge the excited electron from the conduction band and hence prevents the recombination losses [32]. Most of the above-mentioned studies showed better performance by using ZnO/GO nanocomposite but there was always the issue of graphene sheet agglomeration and catalyst filtration requirement from the treated water.

In this study, we have addressed these issues by coating the solution mixture of GO and ZnO nanoseeds over Si substrate and growing ZnO nanoflowers over it in a controlled environment. The advantage and novelty of this method come from the growth of ZnO nanoflowers from ZnO nanoseed, which was mixed with GO and pre-coated over the Si substrate. It is very difficult to grow the good quality and uniformly distributed ZnO nanostructures over GO sheet by other methods. The Si substrate based ZnO/GO nanocomposite was used for efficient photocatalytic decolorization of MB and industrial dye.

2. Experimental section

2.1. Synthesis of graphene oxide

Graphene oxide was fabricated by using hummers' process with slight modifications. The fabrication method is reported elsewhere in details [33]. Briefly, 1 g of graphite powder (M/s S D fine-chem limited) is ground with 60 g NaCl (M/s MERCK) in a mortar and dissolved in 1 l of DI water. The ground graphite powder is filtered and dried overnight at 90 °C. After that, the powder was dissolved in 23 ml of H_2SO_4 (M/s Fisher Scientific) under magnetic stirring for 8 h and 3 g of $KMnO_4$ (M/s MERCK) was added slowly while the solution was kept in ice bath to maintain the temperature below 20 °C. After that, the solution is heated to 40 °C for 30 min and then to 70 °C for 45 min (to avoid a sudden increase in temperature). Finally, the reaction is terminated by slowly adding 200 ml of DI water and 10 ml H_2O_2 (30% vol/vol, M/s Fisher). The final solution is washed several times with DI water and HCl (M/s Fisher). The final product is dried at 60 °C for 24 h and obtained in form of a black powder of GO.

2.2. Synthesis of ZnO nanoseed

For growing ZnO nanoflowers, ZnO nanoseeds were fabricated by following our previously reported work [21]. Briefly, 0.1 M solution of zinc acetate dihydrate is mixed with Isopropyl alcohol followed by ultra-sonication to get a homogeneous solution. This solution is then dropwise coated over a pre-cleaned Si substrate. The substrate is heated to 200 °C to get ZnO nanoseeds by decomposition of zinc acetate dihydrate. The nanoseeds layer is scratched out from the silicon substrate using a surgical blade and stored.

2.3. Synthesis of ZnO/GO nanocomposite

A solution mixture of ZnO nanoseeds and GO sheet was prepared by adding the ZnO nanoseed powder with PGMEA (Propylene glycol methyl ether acetate, $C_6H_{12}O_6$, M/s Sigma Aldrich), PPG (polypropylene glycol, $(CH(CH_3)CH_2O)_n$, molecular weight: 20,000 g-mol^{-1}, M/s Sigma Aldrich) and PMSSQ (Polymethylsilsesquioxane, $(CH_3SiO_{1.5})_n$, M/s GRANT Industries) in a manner reported earlier [34]. These polymeric materials have been useful to form a porous bed of ZnO nanoseed over Si wafer for growing porous networks of pinned ZnO in our earlier studies [20]. Later 20 ml of this solution is mixed with a 3 ml aqueous solution of GO (1 mg/ml) and ultrasonicated for 6 h to achieve a homogeneous mixing of ZnO nanoseed and GO sheet. The prepared solution (1 ml) is then spin-coated over a pre-cleaned Si wafer at 2500 rpm for 30 s. The wafer is then heated to 200 °C to cause the evaporation of PPG resulting into formation of a porous bed of ZnO/GO nanocomposite. The wafer containing ZnO nanoseeds with GO is then placed upside down in a solution mixture of $Zn(NO_3)_2$ (0.01 M) and hexamethylene tetraamine (HMTA) (0.05 M) at 90 °C for 24 h. $Zn(NO_3)_2$ and HMTA undergo a chemical reaction which creates Zn^{+2} and OH^- environment which further leads to the formation of $Zn(OH)_2$. The dehydration of $Zn(OH)_2$ under heated environment results into formation of ZnO nanoparticles which later self-assemble into nanoflowers type structure. Uniformly distributed ZnO nanoseed over GO sheet forms homogeneously distributed ZnO nanoflowers attached with GO sheet on Si substrate. The same process is repeated without adding GO sheet to fabricate the pure ZnO nanoflowers for comparative studies. The steps of the synthesis process are described schematically in Fig. 1 for better understanding.

2.4. Characterization methods

To characterize the synthesized ZnO/GO nanocomposite various techniques such as: field emission scanning electron microscope (FESEM) (Zeiss Supra 40 V, Germany), X-ray diffraction technique (XRD) (PANalytical, Cu Kα, wavelength = 1.5418 Å), Transmission electron microscopy (TEM) (FEI Titan G2 60-300), RAMAN spectroscopy (WITec alpha 300, Helium-Neon laser, and wavelength 532 nm), and X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versa Probe II, FEI Inc.) were used. While the absorbance spectra of the dye was analyzed at regular intervals of time by UV–vis spectrophotometer (Thermo Scientific™ Evolution 300).

2.5. Photocatalytic study

ZnO/GO nanocomposite is used for the photocatalytic remediation of methylene blue (MB) dye using sunlight. A Si wafer (1 in. × 1 in.) with grown ZnO/GO nanocomposite thin film (~ 10 mg), is placed in a 50 ml aqueous solution of MB dye (20 mg/L) (M/s Sigma Aldrich). The solution was placed under sunlight to start the photoreaction. A fixed amount of aliquot is taken from the dye solution and added back after analyzing the absorbance through UV–vis spectrophotometer in a regular interval of time. To evaluate the effect of GO, decolorization results of MB dye by using pure ZnO and ZnO/GO nanocomposite were compared. The effectiveness of photo-catalysts was evaluated by percentage decolorization of dye with respect to time by using the following equation:

$$\text{Dye decolorization}(\%) = [(C - C_o)/C_o]\ X\ 100 \tag{1}$$

Where, 'C' and 'C_o' are instantaneous and initial dye concentrations, respectively. Photocatalytic dye decolorization reactions follow the Langmuir-Hinshelwood mechanism [35], given as:

$$dC/dt = K_{app} X\ C \tag{2}$$

Where, 'dC/dt' represents, the rate of change of dye decolorization with light irradiation time 't' and K_{app} (min^{-1}) represents apparent first-