Journal of Environmental Chemical Engineering 5 (2017) 5770–5776

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Research Paper

A cost effective and eco-friendly green route for fabrication of efficient graphene nanosheets photocatalyst

Sajjad Shamaila[a,*], Ahmed Khan Leghari Sajjad[b,*], Quart-ul-Ain[a], Sania Shaheen[a], Anum Iqbal[a], Saima Noor[a], Ghulam Sughra[a], Uzma Ali[a]

[a] International University, H-10, Islamabad, Pakistan
[b] Pakistan Institute of Engineering and Applied Sciences, Islamabad, Pakistan

ARTICLE INFO

Keywords:
Green reduction
Graphene sheets
Nanomaterials
Microwaves
Photocatalysis

ABSTRACT

Graphene sheets have been prepared via green route in comparison to chemical method. Azadirachta indica leaves contained phytochemicals terpenoids and flavanones which behaved as an efficient reducing and capping agents for reduction of graphene oxide into graphene. For preparation of graphene sheets via chemical method, graphene oxide was reduced to graphene through ammonium hydroxide. Furthermore, microwaves were used during the reduction process. In comparison, green route was adopted to reduce GO to graphene sheets with well-maintained morphological feature. The absorption of microwaves led to rapid heating of GO which caused desorption of oxygen functional groups as well as re-ordering of graphene basal plane. Graphene sheets prepared by green route exhibited superior photo activity as compared to chemically prepared graphene sheets, graphene oxide and graphite. This is due to the efficient adsorption of dye molecules which actually sensitized the surface of highly smooth, transparent and well intensified exfoliated graphene sheets and suppressed the electron hole pair annihilation.

1. Introduction

Nowadays graphene stimulates researchers to focus their thoughts towards its potential applications. Textile, paper, food and cosmetic industries use variety of dyes which are the biggest source of environmental pollution. Graphene based nanomaterials as photo-catalyst present one of the best possible solutions for purification of environmental pollutants [1]. Due to its suitable specific surface area, attractive hydrophobic, mechanical and good chemical stability, graphene attains a great research interest. It is a suitable candidate for photo-catalysis as postponement in electron-hole pair and augmentation of light adsorption assortment and intensity [1]. Graphene is a two dimensional allotrope of carbon which consists of single layer of sp^2-bonded carbon atom arranged in a honeycomb lattice [2,3]. In 2010, Geim et al. got Nobel prize in Physics because of their discovery of graphene in 2004 [4]. Graphene gets tremendous attention from both experimental and theoretical scientific communities because of its exceptional properties [5] such as required Young's modulus range [6], ideal fracture strength [1], attractive electric and thermal conductivities [7], effective carriers mobility [8], excellent optical transparency [9] and fascinating transport phenomena (quantum Hall effect and ambi-polar electric field effect) [10]. Depending on these remarkable properties, graphene has attractive applications in energy conversion and storage (e.g., fuel cells [11] and capacitors [12]), sensors [13], electro-catalysis [14], photocatalysis [15], reinforced composites, biomedicine and electronic devices [16].

Different methods were carried out to synthesize graphene. Initially in 1840 Schafhacutl, a German scientist introduced that both compounds graphite and graphite oxide are interposed compounds [17]. Further, in 1859, British Chemist B.C Brodie worked out graphite oxide [18]. Staud's method is applied to produce the most oxidized graphite oxide [19]. Mostly, the chemicals used in above mentioned methods were potassium chlorate and nitric acid. Most recognized oxidizing agent for the preparation of graphite oxide is nitric acid which reacts with carbon surfaces voluntarily [20]. Now a days, frequently Hummers method is used to yield the graphene [19]. In comparison to other methods, only two hours are required to accomplish Hummers method instead of a week. This method shows prominent enhancement in oxidation of graphite [21,22].

Green synthesis is environmentally out-going tactics which utilizes numerous reducing agents for the reduction of graphene oxide (GO) [6]. Some of them are ascorbic acid [23,24], reducing sugar [25], bovine serum albumin [26] and heparin [27]. But the neem leaves i.e. Azadirachta indica (A. indica) are better reducing agent for GO. A.

* Corresponding authors.
E-mail addresses: shalisajjad@yahoo.com, shamaila.sajjad@iiu.edu.pk (S. Shamaila), sajjad12320@yahoo.com (A. Khan Leghari Sajjad).

http://dx.doi.org/10.1016/j.jece.2017.11.009
Received 22 July 2017; Received in revised form 19 October 2017; Accepted 2 November 2017
Available online 03 November 2017

indica leaves have got a great attention in research. A. indica leaves abundantly prevalent in the tropical countries of the world have been reported to be anti-inflammatory, antipyretic, hypo-glycemic [28] and exhibits antimicrobial and anti-cancerous properties as well [29].

In this paper, extract of A. indica leaves is selected due to attractive features. Firstly, these are abundant plant. Secondly, these leaves are external stabilizing agent during synthesis of nanoparticles. Thirdly, these are used in anti-microbial properties [30]. Fourthly, the leaves contain phytochemicals like terpenoids and flavanones which behave like reducing as well as capping agent. Silver nanoparticles (AgNPs) are directly achieved by the reduction of silver salt using A. indica leaf extract. Fifthly, the leaves extract treated nanoparticles are enriched antibacterial activity. Green synthesis of MgO nanoparticles was carried out using Azadirachta indica leaf extract [31].

Recently, many types of hybrid materials consisting of graphene and metal oxides have been synthesized [6]. Li et al. [15] determined a microwave assisted synthesis of silver (Ag)/reduced graphene oxide (RGO) nanocomposite. This demonstrated that Ag/RGO based nanocomposite had a potential application for environmental purification. Rong et al. [32] prepared TiO_2/graphene nanocomposites by hydrothermal method and studied its photo-catalytic activity under visible light.

In this work, microwaves assisted green approach has been used for the synthesis of graphene nanosheets (GNs). GO was prepared by modified Hummer's method. In chemically prepared graphene sheets, the GO was reduced through ammonium hydroxide. In comparison, green route was adopted to reduce GO to graphene sheets with well-maintained morphological feature using plant extract. The microwaves were used during this reduction process. The graphene was treated under microwaves to allow more oxygen elimination due to the thermal effects. Energy absorbed from microwave irradiation was not strong enough to break numerous chemical bond interactions that exist between graphene sheets. Therefore, absorption of microwaves led to rapid heating of graphene sheets which caused de-sorption of oxygen functional groups as well as re-order of graphene basal plane. After microwave heat treatment, thinner layers with irregular edges are formed. Graphene sheets synthesized by green route exhibited superior photo-catalytic activity in comparison to chemically prepared graphene sheets, GO, graphite and P-25 due to the efficient adsorption of dye molecules on highly smooth and transparent surface of graphene sheets. Dye molecules actually sensitized the surface and suppressed electron hole pair recombination. Green synthesis is the most effective method instead of chemical reduction for large-scale production of graphene due to its cost effectiveness [19]. Since the huge abundance of Neem leaves in nature, elimination of the elaborate process of cell culture, involvement of the convenient and speedy synthetic routes and its easy separation from the final product make the present study highly cost effective in comparison to conventional chemical reduction of GO using ammonium hydroxide.

2. Experimental

2.1. Chemicals and materials

Natural graphite, sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), ammonium hydroxide (NH_4OH) and ethanol (C_2H_6O) were used. All these chemicals were purchased from Sigma-Aldrich. Deionized water (H_2O) was used throughout the experimental procedure.

2.2. Synthesis of graphene oxide

Firstly, Graphite Oxide (GtO) was synthesized by modified conventional Hummers method [33]. 23 mL of H_2SO_4 was poured into beaker in an ice bath to set the operational temperature at 0 °C. 1.5 g of natural graphite was added and stirred for 5 min to attain the dispersion of graphite powder in sulfuric acid. Then 0.5 g of sodium nitrate ($NaNO_3$) was mixed into graphite dispersion and stirred for 30 min to homogenize it. The solution was removed from the ice bath and 3.0 g of potassium permanganate ($KMnO_4$) was slowly added with light stirring. Solution was allowed to react at 35 °C for another 1 h. At this stage, solution becomes viscous with brown color. Then 40 mL of deionized water was gradually added to the mixture and stirred for 30 min. Another addition of 100 mL of water was done for further dilution and kept solution at 70 °C for 1 h. Reaction was terminated with addition of deionized water and 30 mL of H_2O_2 to reduce the residual $KMnO_4$ and MnO_2 to convert into soluble $MnSO_4$. After this treatment, solution becomes bubbly. Its color was changed to brilliant yellow which indicated that graphite was oxidized into GtO. GtO particles were separated from the solution and washed with the 5.0% HCl solution to remove metal ions. At the end washed the synthesized particles with deionized water to remove unwanted HCl. Final product was dried at 60 °C to obtain the GtO powder. Exfoliation of GtO was done to convert the graphite oxide in GO. GtO powder was re-dispersed into deionized water to obtain yellow-brown dispersion for exfoliation. Then this solution was ultra-sonicated for 2 h. GO powder was obtained after centrifugation and drying at 60 °C.

2.3. Reduction of graphene oxide

2.3.1. By using ammonium hydroxide as reducing agent

25 mL of ammonia was mixed into 25 mL of deionized water in beaker. Then the solution was stirred for 30 min at 25 °C to get homogenized ammonia solution. 1.0 g of synthesized GO was then added into ammonia water and stirred. This solution was kept directly into the microwave frequency system for 60 min. The reduced graphene sheets were settled at the bottom of the beaker and easily be separated after cool down the solution at room temperature. The graphene sheets were obtained finally after washing with deionized water and drying at 60 °C. Graphene sample product was labeled as GA.

2.3.2. By using plant extract as reducing agent

1.0 g prepared GO was suspended into 90 mL of deionized water to obtain brown dispersion and stirred until homogenize. Then 10 mL of plant extract was gradually added into the solution while stirring. This dispersion was directly placed into the microwave generated system for 60 min by setting microwave oven at low power. Graphene product was settled at the bottom of the solution and separated after cooling at room temperature. Finally, graphene sheets were obtained after three times washing with deionized water. The product was dried at 60 °C and labeled as GP.

2.4. Catalyst characterization

The crystal phase composition and crystallinity of the obtained samples were determined by a Rigaku D/MAX 2550 X-ray diffractometer. X-ray diffraction patterns of all samples were collected in the range of 20–80° (2θ) for wide angle XRD using (Cu $K_{\alpha 1}$ radiation, λ = 1.5406 Å), operated at 40 kV and 100 mA. FT-IR spectrometer of manufacturing model Nicolet 740 equipped with beam splitter of KBr along with TGS detector was used for obtaining spectra of the samples. The morphology was studied using scanning electron microscopy and transmission electron microscopy. A JEOL-JAD-2300 instrument was used for obtaining SEM images and energy dispersive X-ray spectra (EDX) of the samples. Transmission electron microscopy (TEM) was performed on a JEOL JEM 2010 instrument at an acceleration voltage of 120 kV. The samples usually were prepared by dispersing a small amount of powder in ethanol. Next, one drop of the dispersion was put on a carbon-coated copper grid (400 mesh) and left to dry under ambient conditions before insertion into the device.