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Natural saponin stabilized nano-catalyst as efficient dye-degradation catalyst

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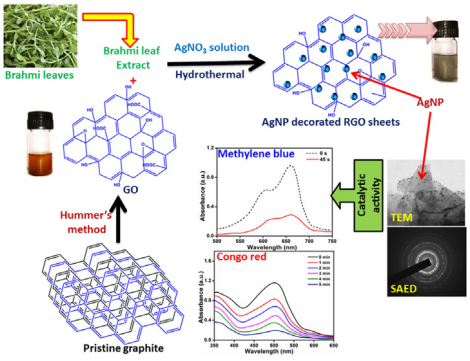
HIGHLIGHTS

- Natural saponin has been used as a green reducing agent as well as stabilizer.
- Nanoparticle exhibited catalytic activity towards to synthetic dyes.
- Nanoparticle was tested as bactericidal.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles decorated reduced graphene oxide is a well-established nanoparticle for multifunctional applications. Herein, the aim of the work is to prepare the nanoparticles in an *in situ* green reduction fashion without using any external reducing agent and stabilizing agent. Thus, a new stabilizer cum reducing agent has been introduced for the first time to prepare the silver nanoparticle decorated reduced graphene oxide. The new stabilizer cum reducing agent was naturally occurring saponin which has been extracted as Brahmi leaf (*Bacopa monniera*) sap. The as-synthesized material has been confirmed by X-ray diffraction, UV–visible spectra and Raman spectra. The surface chemical features have been confirmed by X-ray photoelectron spectroscopy. Transmission electron micrograph revealed distinct nanoparticles abound range of 12-35 nm over reduced graphene oxide basal plane. The synthesized nanoparticles have been tested for dual applications, i.e., solid state catalytic activity and bactericidal activity.

1. Introduction

Industrial effluents from various industries like paper, plastic, leather, food, textiles and cosmetics are the major concerns for environmental issues due to their direct negative impact in civic life as well aquatic animals. [1,2] Synthetic dyes are the most

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hazardous materials removed from those above-mentioned industries. These synthetic dyes are toxic and carcinogenic in nature. These can affect human life as well other biological organisms in nature. Thus scientists are looking for some specific smart materials to eradicate such pollutions. Most common methods adopted by various researchers are to degrade/reduction/separation of toxic materials from waste water. The common methods are adsorption [3], microbial degradation [4], catalytic degradation [5], electrocoagulation [6], electro-Fenton degradation and so on [7]. Among all these methods chemical reduction of organic pollutants by noble metals like Pt, Au, Ag and Cu are the most practiced technology in this field. Recently, metal nanoparticles have been used for waste water treatment. [8]

There are several carbon nanomaterials already nurtured since last decades [9–12]. Graphene is the most significant and widely uttered cousin of carbon family. Graphene, a 2D carbon material having excellent mechanical and electrical properties always offer fair possibilities to fabricate composite materials with catalytic effects [13,14]. As a matter of fact graphene sheets have also been exploited as support material to grow and stabilize various nanoparticles (Au, Pd, Pt, TiO_2, Co_3O_4, etc.) [15–19] and some high end-applications [20–22]. Au nanoparticles are already been synthesized via chemical reduction over graphene sheets. From various literatures plenty of graphene-nano metal composites have been reported. [23,24] But green reduction of graphene oxide (GO) is still a challenge. Green reduction is always welcomed because chemical reducing agents have much toxicity, non-biodegradability become a rescuing issue day by day. Various phytoextracts like carrot roots [14,25–27], green tea [28], orange peel [29], bacteria [30], cloves, cherry, roses, mango leaves, potato extracts, lactulose etc. have been used to reduce graphene oxide. Silver nanoparticles become more attracting in this field due to their dual behavior of catalytic and bactericidal activity. [31,32] The activity of the silver nanoparticles has been enhanced after preparing several nanosilver decorated graphene oxide composites. Several researchers already reported various methods to prepare nanosilver for catalytic applications, like silver mirror reaction [33], ultrasonic irradiation [34], solution based method [35], electrostatic force driven assembly [36] and microwave irradiation [37].

After a thorough study of the literatures, one major concern for the researchers is the stabilization of the prepared solid state nanoparticle catalyst. Major portion of the researches uttered about the insertion of polymers or surfactants. As nature is a great inspiration, we coined the idea of natural saponin which can be an effective non-hazardous stabilizer for nanoparticles. Saponins are natural glycosides which have an immediate foam forming ability after contact with water. These typical glycosides commonly constitutes of triterpenoids or steroids or alkaloids either in linear or branched form having hydroxyl and carboxylic acid groups. We choose *Bacopa monniera* Wettst. herb which is very popular as "Brahmi". The polar fractions of the leaf extract consist of two water soluble saponins; named bacoside A_1 and bacoside A_3 [38].

Motivated from the recent applications of green synthesis and waste water treatment, we prepared silver nanoparticles decorated reduced graphene oxide via solvothermal green method by using Brahmi leaf extract. There was no requirement of additional stabilizing agent for the preparation of this catalyst; thus the method can be named as 'green'. Brahmi leaf extract itself can acts as a reducing agent and colloid stabilizer. The catalytic activity towards hazardous dyestuffs (cationic and anionic dye) was experimented.

2. Materials and methods

2.1. Materials

Graphite powder (<20 μm) was procured from Sigma-Aldrich, Germany and used as received. $AgNO_3$ (99.8% Sigma-Aldrich), HCl (37%, Merck; India), $NaNO_3$ (Loba Chemie, India), $KMnO_4$ (Merck, Germany), H_2SO_4 (Merck, India) and H_2O_2 (30% w/v, Merck, India) were used as received. Others chemicals used here were all of analytical grade. Fresh Brahmi leaf was collected from local market place.

2.2. Preparation of graphene oxide (GO)

GO was prepared from graphite powder by modified Hummer's method [39]. Graphite powder and $NaNO_3$ (1 g each) were taken into 60 ml 98% H_2SO_4 and vigorously stirred in a conical flask positioned in an ice bath. After slurry formation, 6 g of $KMnO_4$ was slowly added into the black slurry for 30 min keeping the reaction bath temperature below 20 °C. After 4 h, the whole system was moved out from the ice bath and diluted with 130 mL of double distilled water with continuous stirring for 2 h. To terminate the reaction, 100 mL water followed by 25 mL 30% w/v H_2O_2 were poured into the reaction vessel which resulting the color change from brownish black to bright yellowish brown. Then the reaction mixture was washed several times until neutral pH condition. To obtain pure GO powder, the slurry was gathered in a glass petridish and dried at 60 °C for 24 h.

2.3. Biosynthesis of reduced graphene oxide-silver (RGO-Ag) nanocomposites

RGO-Ag nanocomposites were synthesized by green reduction method by reducing GO and $AgNO_3$ in single step. The synthesis procedure is documented as follows and the procedure has been showed in Scheme 1;

1. 1 g of Brahmi leaf powder was boiled in 50 mL of deionized water and filtered through a 25 μL Teflon filter.
2. The prepared GO taken 30 mg in 60 mL deionized water and ultra-sonicated at 40 kHz for 2 h at room temperature (28 °C).
3. Silver nitrate aqueous solution was prepared by solubilizing desired amount of $AgNO_3$ into deionized water. The $AgNO_3$ solutions' concentrations were 0.01, 0.03, 0.05, 0.07 and 0.1 M.
4. 200 mg GO powder, Brahmi leaf extract (13 mL) and $AgNO_3$ solution (with above mentioned concentration, 2 mL) were mixed homogeneously and subsequently transferred into a 50 mL Teflon-lined steel autoclave for hydrothermal treatment. The autoclave was then sealed with a steel gasket and maintained at 200 °C for 8 h in a drying oven. The time was also varied i.e. 8 h, 10 h and 12 h.
5. When the aforesaid time was over for the hydrothermal treatment, the autoclave was cooled to room temperature. The mixture was then centrifuged and washed thoroughly with water and dried in a vacuum oven.

2.4. Method for determine catalytic activity of RGO-Ag

20 mL of CR aqueous solution having concentration of 1.57×10^{-5} M was mixed with 5 mg of RGO-Ag catalyst and stirred mildly. Then 15 mL of freshly prepared borohydride aqueous solution (5×10^{-3} M) was added into the aforementioned dispersion followed by stirring. The red color was vanished gradually of the system which impels the progression of reaction. The discoloration was monitored by UV–visible spectrophotometer at specific intervals. The characteristic wavelength for CR was fixed at 493 nm. After complete discoloration the system was washed thoroughly, centrifuged with deionized water and ethanol followed by vacuum drying and stored for further use.

Typically for MB reduction, 5 mg of RGO-Ag catalyst was taken with 20 mL 2.8×10^{-5} M aqueous solution of MB was stirred as the above mentioned procedure followed by borohydride addition. The catalytic behavior was monitored by UV–visible spectrophotometer at λ_{max} of 663 nm. The catalyst purification was done in the previous method.