



# A facile green synthesis of amino acid boosted Ag decorated reduced graphene oxide nanocomposites and its catalytic activity towards 4-nitrophenol reduction



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## ABSTRACT

Motivated from the enormous popularity of green chemistry over chemical processes, herein, a new reduction method has been coined for preparing reduced graphene oxide (rGO). L-Arginine (L-Arg) has been used as a green reducing agent as well as superior intercalating agent. The prepared reduced graphene oxide exhibited colloidal stability up to 3 weeks. The partial reduction has been monitored and supported by UV–visible spectra, Fourier transformed infrared (FTIR) spectra and surface enhanced Raman spectroscopic (SERS) techniques. The morphological analysis by electron microscopic techniques also showed dislodged distinct nano-sheets of the prepared rGO. The conductivity has also been measured in the order of  $0.01686 \text{ S cm}^{-1}$  which is drastically improved than Hummer's graphite oxide. Besides this, *in situ* fabricated nano-silver decorated rGO can act as efficient catalyst against toxic *para*-nitrophenol (4-NP) reduction. Thus our prepared nanomaterial can be applicable for efficient low cost catalyst in future.

## 1. Introduction

*Para*-nitrophenol (4-NP) is the main organic ingredient for manufacturing products of pharmaceuticals, textile, pesticide and other chemical industries [1,2]. The presence of 4-NP in water even at very low concentration would be hazardous to amphibian life because of its toxic, malignant and poisonous nature [3,4]. So, to remove these hazards waste from water through an eco-friendly chemical route is required which use green solvents, harmless chemical to degrade their under normal reaction condition [5,6]. From environmental remediation point of view, reduction of 4-NP to *para*-aminophenol (4-AP) in presence of sodium borohydride ( $\text{NaBH}_4$ ) using catalyst is one of most suitable method [7].

Recently, noble metal nanoparticles have drawn considerable attention not only of their idiosyncratic physico-chemical behavior but also their implication as efficient catalysts for degradation of various hazards materials like dyes, phenol derivatives etc. [8]. These noble metal nanoparticles can be synthesized by various methods such as wet chemical [9], co-reduction [10], radiation [11], *in-situ* green synthesis [12] etc. Among all the methods, *in-situ* green synthesis has been recommended as most efficient and clean technology due to its environmental friendliness.

Graphene, two dimensional one atom thick  $\text{sp}^2$  bonded single layer

carbon atom arranged in hexagonal honeycomb lattice has brought to focus enormously both in scientific as well as industrial area due to its superior mechanical, thermal and electrical properties [13–16]. Up to date different stagey have been endorsed to prepare graphene beginning from graphite. These are chemical vapor deposition (CVD) [17], micromechanical exfoliation of graphite [18], epitaxial growth on electrically insulating surface [19], solvo-thermal analysis [20] and solution based chemical reduction of graphene oxide at moderate temperature (GO) [21]. Among them, last method is cost effective to prepare rGO in bulk scale and the process in short can be called as solvo-thermal chemical reduction of GO. Different reductant such as hydrazine [21], dimethyl hydrazine [22], sodium borohydride [23], hydroquinone [24] etc. have been already used to prepare solution based chemically reduced graphene oxide (rGO) from GO. But these reducing agents have the problem of either slow reaction or hazardous in nature. On the other hand strong  $\pi$ - $\pi$  interaction between reduced graphene plates and low solubility in water or in other organic solvents require capping agents (polymer or surfactant) to prevent formation of irreversible agglomerate. These capping agents may affect the properties of graphene sheets leading to limitation in its application fields [25,26]. Hence, as the days go researchers are more endeavoring to develop environment friendly, rapid and highly productive method to produce graphene under breezy condition. Chemically rGO displays

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acceptable thermal and electrical conductivity and also provides high surface area which can be utilized for illuminating metal nanoparticles [27,28].

Graphite oxide has expanded layer structure in contrast to graphite where layers are stacking over each other to make 3-dimensional structure. Due to heavily oxidation of graphite sheets, the plane of graphite oxide are not only just decorated with oxygen containing functional groups (such as hydroxyl, epoxy and carboxylic acid) but also the sheets become more thick and hydrophilic in nature [13]. By removing this oxygen containing surface functional groups using reductant, single or few layers chemically rGO with restoration of conjugated structure can be obtained [29].

L-Arginine (L-Arg) is usually categorized as one of the essential amino acid for human health. L-Arg, being a mild reducing agent and non-toxic in nature, is generally employed in living cell and now it become available as bio-molecule reducing agent in laboratory like other reactive chemicals [30]. It is active for reducing other molecules due to presence of functional groups like amino ( $-\text{NH}_2$ ), carboxyl ( $-\text{COOH}$ ) and this molecule should have also ability to stabilize as well synthesize metal nanoparticles from its precursors [31].

Herein firstly, we present eco-friendly and facile approach of preparation of chemically rGO through solvo-thermal approach employing L-Arg as reducing agent. As it has been seen that L-Arg not only reduce GO but also its oxidative products help to prevent stacking of graphene sheet i.e. acts like capping agents. Another advantage of using L-Arg is that its oxidized products are environment friendly compared to that of other reducing agents. In the next section, we prepared AgNPs decorated rGO using best combination of GO and L-Arg (at 1:1 ratio) by *in-situ* green synthesis method. Here, L-Arg acts as reducing agent both for GO and  $\text{Ag}^+$  to reduce its metallic state with dimension in the nano-range as well as provides stability to both. Finally prepared AgNPs decorated rGO catalyst was used to reduced toxic 4-NP to nonpoisonous 4-AP to determine its catalytic efficacy based on pseudo 1st order model.

## 2. Experimental

### 2.1. Materials

Graphite powder (98% pure) was purchased from Loba Chemie, Mumbai. The crystalline form of potassium permanganate ( $\text{KMnO}_4$ ) ( $\geq 99\%$  pure), sodium nitrate ( $\text{NaNO}_3$ ) ( $\geq 97\%$  pure) L-Arginine ( $\geq 98\%$  pure), *para*-nitro phenol (4-NP), sodium borohydride ( $\text{NaBH}_4$ ) and silver nitrate ( $\text{AgNO}_3$ ) ( $\geq 99\%$  pure), were obtained from Sigma Aldrich and used as received. Sulphuric acid ( $\text{H}_2\text{SO}_4$ , 96% extra) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30% solution) were procured from Merck, Germany and used without further purification. N, N-di-methyl-formamide (DMF), ethylene glycol, toluene, and acetone using as solvent for dispersion were also brought from Loba Chemie, Mumbai.

### 2.2. Synthesis of graphene oxide (GO)

GO was prepared from graphite by renowned hummer's methods [32]. In a nutshell, 2 g of natural graphite and 1 g of  $\text{NaNO}_3$  were added into 250 mL beaker containing 100 mL of  $\text{H}_2\text{SO}_4$  and subsequently stirred for 2 hours in an ice bath. After that 6 g of  $\text{KMnO}_4$  were incorporated gradually during stirring and during incorporation temperature were maintained around 20 °C. After few minutes later, the reaction mixture was removed from ice bath and heated to constant temperature of 35 °C for 30 min. Then 100 ml of water was added to it and stirring was continuing for another 30 min. The color of the mixture changed to yellowish-brown as shown in Fig. 1. Later the mixture was treated with mixture of hot water and 30%  $\text{H}_2\text{O}_2$  (aq.) to destroy excess  $\text{KMnO}_4$ . Finally, the mixture was centrifuged with water and dilutes HCl solution at 8000 rpm until pH value around 7. The obtained powder was dispersed in water and ultra-sonicated for 1 h to obtain

exfoliated graphitic oxide i.e. graphene oxide. The sonicated mixture was filtered and dried in vacuum at 50 °C for overnight to obtain black color GO.

### 2.3. Synthesis of chemically reduced graphene oxide (rGO)

100 mg of GO powder was added in beaker containing 50 ml of water and sonicated for 1 h. Immediately after sonication, GO colloidal dispersion was immersed in oil bath at 50 °C and continued stirring. After that, L-Arg was added into the GO dispersion in different proportions. The GO:L-Arg experimented ratios were taken as 1:0.05, 1:0.4, 1:0.5, 1:0.75 and 1:1. The prepared L-Arg/GO system was named later as GOX, where X stands for the percentage of L-Arg addition. Then, the whole dispersion was stirred at a stretch for 12 hours without alteration of the bath temperature. Prior to separation of the prepared rGO from the system, the dispersion was centrifuged and washed thoroughly with distilled water to confirm the removal of loosely bounded excess L-Arg from GO surfaces. The obtained products were vacuum dried in at 50 °C for overnight to get black color rGO and its aqueous dispersion after conversion is shown in Fig. 1.

### 2.4. Synthesis of Ag NPs decorated reduced graphene oxide

After the *in situ* reduction of GO via L-Arg, AgNPs decorated rGO were synthesized by using the best combination of GO:L-Arg (at 1:1 ratio).  $\text{AgNO}_3$  was used as AgNPs precursors and L-Arg used as reductant for GO and  $\text{AgNO}_3$  as well as stabilizer for both rGO and AgNPs. In brief, GO powder (30 mg) was dispersed in 30 ml water by sonication for 1 h to form exfoliated stable suspension. After that aqueous solution of  $\text{AgNO}_3$  (10 mL, 1 mM) was added into the solution under stirring condition. Then, 30 mg of L-Arg was dissolved in 30 mL water and added to the solution. Immediately, the mixture was kept in oil bath at 50 °C and continued stirring for next 4 hours and the mixture gradually changed its color from brown to mixture of gray and black color as shown in the Fig. 1. Finally, the slurry like product was centrifuged with water to remove unreacted reagents and dried in vacuum at 50 °C to obtain rGO/AgNPs nanocomposites.

### 2.5. Catalytic activity of synthesized nano-catalyst

In a typical procedure, 1 mg of AgNPs/rGO nanocomposite was added into 20 ml aqueous solution of 4-NP (0.2 mM). After that freshly prepared 5 ml aqueous solution of  $\text{NaBH}_4$  (0.1 M) was added to the mixture and was kept under stirring condition at room temperature. The conversion of 4-NP to 4-AP was monitored by recording time-dependent UV-visible absorption data obtained from aliquot withdrawn from reaction mixture at 60 s interval. The calculation of rate constant is based on the decreasing absorbance peak at 400 nm which is characteristic peak of 4-NP in presence of  $\text{NaBH}_4$  due to formation of *p*-nitro-phenolate ion. After complete reaction, the catalyst was separated from the reaction mixture by centrifugation followed by repeatedly washed with water and ethanol and dried at room temperature for next cycle to study the reusability of catalyst.

### 2.6. Measurement and characterization

XRD data was recorded by X Pert PRO made by PANalytical B.V., The Netherlands; with Ni filter; Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and rate of scanning 0.005° (2 $\theta$ /s). Surface Enhance Resonance Raman (SERR) data was assembled with help of Trivista 555 spectrograph (Princeton Instruments) and Kr laser excitation at 647 nm (Coherent, Sabre Innova SBRC-DBWK) was used for scanning in the range of 400–2000  $\text{cm}^{-1}$  and acquisition time of 120 s was used. The morphology of the prepared samples was characterized by contact mode AFM (ACAFM, Agilent 5500 scanning probe microscopy), HRTEM (JEM-2100 high resolution transmission electron microscope (JEOL,

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