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Synthesis of AuNPs@RGO nanosheets for sustainable catalysis toward nitrophenols reduction

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ABSTRACT

A facile, green and one-pot synthesis strategy for the convenient preparation of well-dispersed gold nanoparticles (AuNPs) decorated reduced graphene oxide (RGO) without using any other toxic chemicals and reductants is reported herein. The synthesized AuNPs@RGO hybrid nanomaterials were characterized by UV–visible absorption spectroscopy, FT-IR, XRD, Raman, SEM, TEM and EDX analysis. The AuNPs@RGO acts as an efficient catalyst for the reduction of organic nitroaromatics (2- & 4-nitro phenols) in the presence of $NaBH_4$. This newly synthesized hybrid AuNPs@RGO has superior catalytic activity over any other Au-nanomaterials ever reported. The rate of nitro aromatics reduction is found to be dependent on concentrations of substrate, reductant and catalyst. The mechanisms for the synthesis and catalytic reduction have been studied and discussed.

1. Introduction

Today, water pollution by organic contaminants has become a serious environmental issue and received significant attention [1,2]. Nitroaromatics are toxic and mutagenic organic pollutants which are widely used in the manufacturing of pharmaceuticals, pigments, dyes, plastics, insecticides, fungicides, drugs and explosives [3]. These nitroaromatic compounds are highly hazardous on release in the environment. In particular, 4-nitrophenol (4-NP) and 2-nitrophenol (2-NP) have been listed as "priority pollutant" by US Environmental Protection Agency (EPA) because of its higher solubility and stability in water. Hence wastewater from these industries creates an alarming situation that requires immediate attention due to the adverse effects of the pollutants on human and aquatic life [4,5]. Up to now, a variety of technologies have been exploited to remove these contaminants including adsorption, photocatalytic degradation, chemical oxidation, membrane filtration, flocculation and electrooxidation [3–6]. However, these technologies have not been widely applied in wastewater treatments because of the fact that there always exist some drawbacks in their applications. Therefore, exploring simpler, low cost and safer technologies is still needed for practical applications. Catalytic reduction is one of the most effective approaches for the treatment of nitroaromatics.

The size, shape and surface morphology of the particles are very crucial in tuning the catalytic properties of nano-sized metal particles. A development of nanoscale gold nanoparticles (AuNPs) has attracted considerable interest because of their high surface area and excellent surface reactivity [7]. The aggregation of metal nanoparticles (MNPs), however, may result in the decrease in the surface area and thus their efficiency. Therefore, it has always been a hot issue to develop highly dispersed heterogeneous metal nanocatalysts. As one of the most important carbon based materials, graphene has been used widely as support materials in the field of heterogeneous catalysis [8], because of its fascinating physicochemical properties such as extraordinary mechanical strength [9], tunable optical properties [10], quantum hall effect [11], high electron mobility [12], and fast heterogeneous electron transfer rate [13]. Thus, it is of great interest to prepare reduced graphene oxide (rGO) based metallic nanoparticles with excellent catalytic activity, stability, high surface area, tunable pore size, and robust surface chemistry. The preparation of gold supported catalysts has involved various physical, chemical and biological methods. Among these, physical and chemical methods suffer from few drawbacks such as high cost, high pressure, energy, temperature and use of environmentally hazardous chemicals [14]. For this reason, one of the most essential needs in nanotechnology is to develop environmentally friendly and green approaches in nanomaterials synthesis. Ultrasonication has been successfully used for the synthesis of nanomaterials in recent years [2,3]. In comparison to conventional methods, ultrasonicated preparation is efficient and facile for rapid preparation of nanostructured materials.

In this work, the AuNPs-decorated RGO was synthesized by the reduction of gold ions on the GO surface using *Simarouba glauca* leaf

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extract (SGLE) without the addition of any other chemical surfactants and stabilizing agents. The synthesized AuNPs@RGO was characterized by various instrumental techniques such as UV–visible absorption spectroscopy, FT-IR, XRD, Raman, SEM, TEM and EDX analysis. The results show that AuNPs are well dispersed on RGO with relatively uniform particle shape and size. The AuNPs@RGO acts as an efficient catalyst for the reduction of organic nitroaromatics (2- & 4-nitro phenols) in the presence of $NaBH_4$. The utilization of high intensity ultrasound offers a facile, versatile synthetic tool for nanostructured materials that are often unavailable by conventional methods. In this work, the ultrasonic synthesis has facilitated the control over size, morphology and nanostructure. Also, the ultrasonically synthesized AuNPs@RGO is found to be superior over any other nanomaterials prepared by other conventional methods ever reported for the reduction of nitro phenols in the waste water treatment.

2. Experimental section

2.1. Chemicals

The chloroauric acid ($HAuCl_4$) was purchased from Sigma–Aldrich, India and used as received. The fresh *Simarouba glauca* (SG) leaf was collected in Thiagarajar College campus, Madurai, India. Raw graphite with average diameter about > 20 μm was obtained from Sigma Aldrich. 2-NP, 4-NP and $NaBH_4$ were purchased from Merck, India and used as received. All other chemicals were of analytical grade and used as such.

2.2. Bio-inspired synthesis of AuNPs@RGO

Graphene oxide (GO) was synthesized using graphite powders by the modified Hummers method [15]. 0.02 mg GO powder was dispersed in 5 ml double distilled water and subjected to ultra-sonication (irradiation power 100 W) for 30 min to give a stable light brown suspension of GO. Then 10 ml of SGLE and 5 ml of $HAuCl_4^-$ (0.01 mM) were added to the above solution and mixed by ultra-sonication for 4 h. The resulting AuNPs@RGO hybrid nano suspension was filtered and washed several times with deionized water. Similar procedure was adopted to synthesize RGO without adding $HAuCl_4$.

2.3. Catalytic reduction

In a typical reaction, 1.8 ml of (0.2 mM) 2- & 4-nitrophenols (2-NP and 4-NP) was mixed individually with 0.05 mg of AuNPs@RGO at room temperature in a 3 ml quartz cell. A freshly prepared aqueous solution of 0.1 ml $NaBH_4$ (1.0 M) was then added to the above solution. The color changes in the reaction mixture at room temperature were monitored by UV–visible absorption spectra with respect to time and the photographs were also taken with a digital camera.

The reduction percentage of nitro phenols were calculated using the following Eq. (1).

$$\text{Reduction percentage}(\%) = ((C_0 - C_t)/C_0) \times 100 \quad (1)$$

2.4. Instrumental characterization

Ultrasound vibration using TOPSONICS ultrasonic liquid processor with a wave of frequency 20 ± 1 kHz and power of 100 W was involved. UV–visible spectra were recorded on a Jasco (V-560) double beam spectrophotometer with 1 cm quartz cells. Fourier transform infrared (FT-IR) spectra were collected with a (JASCO FT-IR 460 Plus) spectrophotometer in the transmittance mode in the range

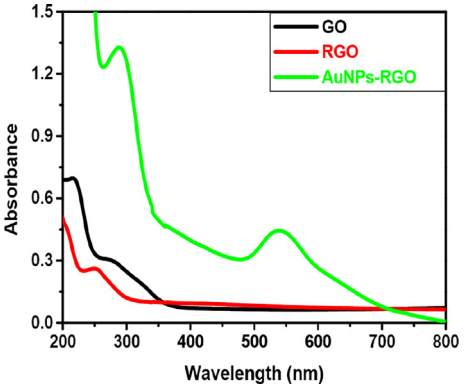

Fig. 1. UV–visible absorption spectra of GO (black line), RGO (red line) and AuNPs@RGO (green line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Scheme 1. The mechanism for the biogenic synthesis of AuNPs@RGO hybrid nanomaterials.

400–4000 cm^{-1}. XRD analysis was carried out in X-ray diffraction unit, Cu Kα radiation (λ = 1.5418° A) on JEOL JDX 8030 X- ray diffractometer. Raman spectra were recorded on a (LabRam HR800) Raman microscope with laser excitation wavelength of 532 nm. The size and morphology of the RGO and AuNPs@RGO were examined by scanning electron microscopy (Model: VEGA3 TESCAN) and high resolution transmission electron microscopy (HR-TEM- Model: FEI TECNAI T20 G2). Energy dispersive X-ray (EDX) spectrometer attached to the scanning electron microscope was used for elemental analysis.

3. Results and discussion

3.1. UV–vis spectroscopy

UV–vis spectroscopy is used in the characterization of metallic nanoparticles because of surface plasmon resonance (SPR) phenomenon and it also gives preliminary information about the size, structure and composition of nanoparticles. As shown in Fig. 1, the UV–vis spectrum of GO shows the peaks appearing at 217 and 273 nm (black line) which may be attributed to π-π* and n-π* transition respectively. The absorption peak at 217 nm is red shifted to 263 nm (red line), indicating that the electronic conjugation within the reduced graphene sheet is revived upon reduction of graphene oxide [16,17]. After the formation of AuNPs@RGO hybrid nanomaterials, it is observed that the absorbance bands appear at 270 nm and 540 nm (green line) which is characteristic of RGO and AuNPs surface plasmon resonance band, suggesting the formation of AuNPs on the RGO sheets. Scheme 1. shows the mechanism for the biogenic synthesis of AuNPs@RGO hybrid nanomaterials.