

Catalytic reduction of 4-nitrophenol by gamma radiation assisted synthesized Au-rGO nanocomposite

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Received: 20 March 2016, Revised: 04 August 2016 and Accepted: 22 November 2016

DOI: 10.5185/amlett.2017.6556
www.vbripress.com/aml

Abstract

Gold-reduced graphene oxide (AG) nanocomposites were synthesized by one-step gamma radiation assisted method. UV-Visible spectroscopic results showed the disappearance of 230 nm peak and appearance of a peak around 269 nm in AG nanocomposite confirming the reduction of GO, and also a peak around 534 nm appears confirming the formation of gold nanoparticles (AuNPs). X-ray diffractogram results of AG nanocomposite showed a broad peak around 25° corresponding to reduced graphene oxide and also it showed peak corresponding to face centered cubic structured AuNPs corroborating the UV-Visible spectroscopic results. The decoration of AuNPs of size 6 nm on reduced graphene oxide sheet was revealed by Transmission electron microscopic results. X-ray photoelectron spectroscopic results confirmed the removal of oxygen functional groups from graphene oxide and formation of Au 4f in AG nanocomposite. The synthesized AG nanocomposite showed enhanced catalytic reduction of 4-Nitrophenol compared to rGO and AuNPs due to synergistic effect of individual component. Gamma radiation assisted method synthesis of Au-rGO nanocomposite may emerge as one-step synthesis that don't require high temperature or harsh reducing agent. Copyright © 2017 VBRI Press.

Keywords: Reduced graphene oxide, AuNPs, nanocomposites, reduction, 4-Nitrophenol.

Introduction

Reduced graphene oxide (rGO) is considered as analogues of graphene that has high surface area, good conductivity and chemical stability [1, 2]. The high surface area provided by rGO can be used to deposit the nanoparticles like silver [3], SnO₂ [4], ZnS [5] and gold [6] etc. The nanoparticles deposited rGO nanocomposites have got attention due to their wide range of applications such as super-capacitor [7], sensor [8], water splitting [9] and photocatalysts [10].

Among many metal nanoparticles, gold nanoparticles have got attention because of its application in various fields such as biosensors [13], biological imaging [14], pollutants degradation [15] etc. The gold and rGO based nanocomposites have attracted due to their application in various fields such as sensor [6, 10], photocatalysts [11], oxygen reduction electro-catalysts [12] etc. The properties of AuNPs can be enhanced by scaffolding on rGO sheets [10-12, 16-21]. Singh *et al.*, [16] have reported the enhancement in the electrochemical immunosensitivity of Au-rGO nanocomposite for the cardiac biomarker myoglobin. The facile synthesis of Au-rGO nanohybrid for potential use in industrial wastewater treatment has been studied by Kar *et al.*, [17]. Wang *et al.*, [18] have functionalized the Au-rGO nanocomposite for ultrasensitive electrochemical sensing of mercury ions

based on thymine–mercury–thymine structure. The nanocomposite composed of rGO and AuNPs has been synthesized by Zhang *et al.*, [19]. Turcheniuk *et al.*, [20] have reported the Au-rGO core/shell nanoparticles for plasmonic photothermal cancer therapy. Hong *et al.*, [10] have synthesized AuNPs/graphene nanocomposites by electrostatic interaction process and showed its application in biosensor application. Au/graphene hydrogel as a photocatalysts has been synthesized by Li *et al.*, [11] by hydrothermal method using triethylenetetramine as a reductant. Xu *et al.*, [12] have reported the synthesis of AuNPs/rGO nanocomposite with regenerated silk fibroin as a oxygen reduction electrocatalysts. Goncalves *et al.*, [21] have studied the synthesis of AuNPs on the surface of graphene sheets by chemical method. But, the synthesis of gold-rGO nanocomposite by gamma radiation assisted method is sparse. Gamma radiation assisted method has advantages over other methods as it is clean, avoids the use of harsh reducing agent and high temperature.

There are limited reports are available in literature for the synthesis of gold-reduced graphene oxide nanocomposite by one-step gamma radiation assisted method and its application for catalytic reduction of 4-Nitrophenol. Therefore, here in, we report the one-step gamma radiation assisted synthesis of AG nanocomposite

in the presence of isopropyl alcohol and N-hexadecyltrimethylammonium bromide. The synthesized AG nanocomposites have been characterized using UV-Visible spectroscopy, X-ray Diffractogram (XRD), Transmission electron microscopy (TEM) and X-ray Photoelectron spectroscopy (XPS). The synthesized nanocomposites have been studied for catalytic reduction of 4-Nitrophenol in the presence of sodium borohydride. The gamma radiation assisted synthesis of AG nanocomposite doesn't require high temperature or harsh reducing agent.

Experimental

Materials

Graphite powder, Sodium nitrate (NaNO_3 , $\geq 99.5\%$ pure), Sulfuric acid (H_2SO_4 , $\geq 98.5\%$ pure), Potassium permanganate (KMnO_4 , $\geq 99\%$ pure), Chloroauric acid (HAuCl_4 , 99.99% pure), N-hexadecyltrimethylammonium bromide (CTAB, $\geq 99\%$ pure), 4-Nitrophenol ($\geq 99.5\%$ pure) and sodium borohydride (NaBH_4 , $\geq 96\%$ pure) were procured from Sigma Aldrich Company, India. Hydrogen peroxide (29-32% w/w aqueous solution) and isopropyl alcohol (IPA, $\geq 99\%$ pure) were procured from Alfa Aesar, UK.

Synthesis of GO and AG nanocomposites

GO was synthesized by modified Hummers' method [22]. In brief, graphite powder (0.5 g), sodium nitrate (0.5 g) and sulfuric acid (23 mL) were mixed in an ice-bath under a continuous stirring. Potassium permanganate (3.0 g) was slowly added into the reaction mixture at 20°C . Flask was then transferred to water bath (35 ± 5) $^\circ\text{C}$ and solution was stirred for an hour to get thick pasty product. 100 mL water was added and temperature of the bath was raised to (90 ± 5) $^\circ\text{C}$ under constant stirring for another 15 min. The solution was diluted by adding 500 mL water and 3 mL H_2O_2 (30 % v/v) was subsequently added which led to color change from dark brown to yellow. The mixture was filtered and washed several times with hot water to eliminate the acid residue. The resultant solid was dried under vacuum and stored in a desiccator for subsequent use. Then, it was dispersed in IPA with concentration of 0.25 mg/ml by sonicating for 1 h. 2ml of 0.002M CTAB and 2 ml of 25 mM of HAuCl_4 was added to above GO solution. Then, the mixture was stirred for 30 min. 4 ml of this solution was taken in a glass bottle and exposed it to Co-60 gamma radiation to a dose of 29 kGy at a dose rate 3.6 kGy/h. After irradiation, the

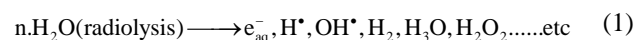
sample was centrifuged, washed with double distilled water (DDW) and named it as AG-29. Similarly, other samples were also prepared at gamma radiation dose of 58 kGy, 86 kGy and 115 kGy and named it as AG-58, AG-86 and AG-115 respectively. Also, rGO and AuNPs were synthesized at a gamma radiation dose of 115 kGy.

Characterization of nanocomposites

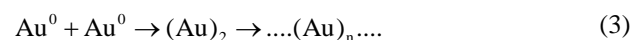
UV-Visible spectroscopy for all the samples was carried out using JASCO, V-670 at room temperature keeping DDW as reference. XRD analysis was done using a Bruker AXS D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation at ambient conditions. To study the surface morphology of nanocomposite, the centrifugation obtained was dispersed in DDW and sonicated for 30 min. Then, it was drop casted on to copper grid and TEM image of that sample was taken using TEM of model Tecnai G2 U-thin 200 kV, LaB_6 filament. XPS was carried out using Omicron EA 125 analyser at ambient conditions. To study the catalytic reduction of 4-Nitrophenol, 0.1 mg of AG-115 catalyst was added to freshly prepared mixture of 2.8 ml of 5 mM 4-Nitrophenol and 0.2 ml of 10 mM NaBH_4 . The final mixture was suddenly transferred in to quartz cuvette and UV-Visible absorption spectrum was measured for different time interval. Similarly, the experiment was also repeated for rGO and AuNPs prepared at a gamma radiation dose of 115 kGy.

Results and discussion

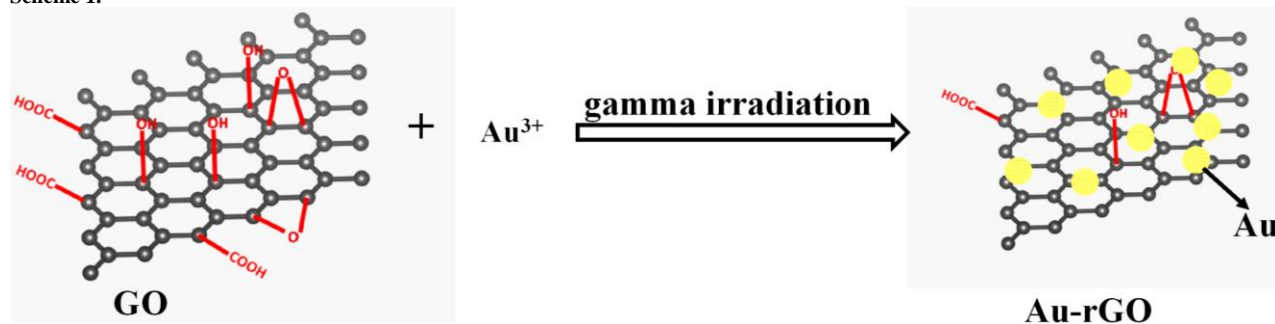
The mechanism of formation of AG nanocomposites by gamma radiation assisted method can be explained as follows. The primary radicals produced during radiolysis of water are e_{aq}^- , $\bullet\text{H}$ and $\bullet\text{OH}$ [22].



These produced hydrated electrons are strong reducing in nature and they will reduce the gold ions (Au^{3+}) into zero valent state (Au^0). These zero valent state gold (Au^0) nucleates with each other and form gold nanoparticles. These formed gold nanoparticles will scaffold on the surface of rGO.



Scheme 1.



Moreover, the cationic CTAB used in the reaction prevents the agglomeration and precipitation of Au^{+3} ions and form mono-dispersed AuNPs on rGO. At the same time, gamma radiation also detaches oxygen functional groups from GO forming rGO [22] which is confirmed by XPS analysis explained in later section. In addition to this, the IPA used in the reaction system acts as scavenger for $\bullet\text{OH}$ radical. The reaction product of isopropyl alcohol and $\bullet\text{OH}$ namely isopropyl radical is also reducing in nature and helps in the reduction of metal ions to their respective nanoparticles [23].

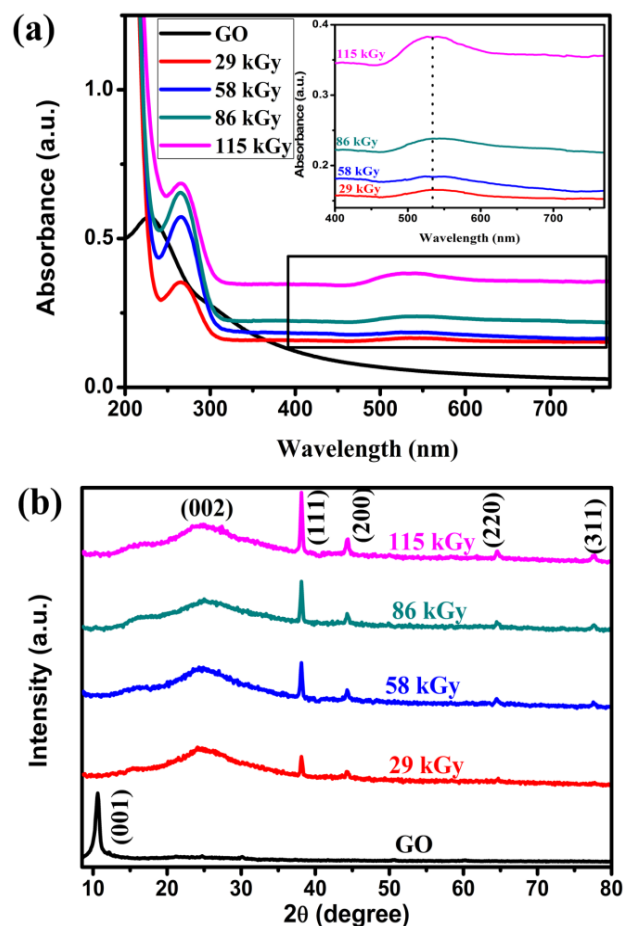


Fig. 1. (a) UV-Visible spectrum and (b) XRD of GO and AG nanocomposites prepared at different doses.

Fig. 1(a) shows UV-Visible absorbance spectrum of GO and AG nanocomposites prepared at different doses. The peaks around 230 nm and 296 nm in GO corresponds to surface plasmon resonance of AuNPs [11]. The absorbance of both these peaks (269 nm and 540 nm) increases with increase in dose indicating the more formation of rGO and AuNPs. In addition to this, the AuNPs peak shift towards lower wavelength side (blue shift) i.e. 534 nm for AG-115 nanocomposite indicating the decrease in the particles size [22]. to $\pi\text{-}\pi^*$ transition of aromatic C-C bond and $n\text{-}\pi^*$ transition of C=O bond [3]. These peaks disappear for AG-29 nanocomposite and a peak around 269 nm appears corresponding to rGO. Also, one more peak around 540

XRD of GO and AG nanocomposites are shown in Fig. 1(b). GO showed its characteristic peak around

10.71° corresponding to (001) plane [3]. For AG-29, this peak vanishes and a broad peak around 25° appears corresponding to (002) plane of rGO [3]. In addition to this, AG-29 nanocomposite also showed peaks at 38.02° , 44.22° , 65.61° and 78.41° respectively corresponds to (111), (200), (220) and (311) planes of face centered cubic (FCC) structured AuNPs which is in agreement with JCPDS (File no. 04-0784) [24]. Interlayer spacing (d-spacing) for the peak 38.02° is found to be 2.54 Å. The intensity of all these peaks increased with increase in dose due to formation of more rGO and AuNPs supporting UV-Visible spectroscopic results.

Fig. 2 (a and b) shows the TEM image of AG-115 nanocomposite. As can be seen from Fig. 2 (a) AuNPs scaffolded on rGO sheet. The average size of AuNPs is found to be around 6 nm. It can also be seen from Fig. 2 (b) that the interlayer spacing is found to be 2.54 Å corresponding to (111) plane of AuNPs corroborating XRD results. The inset of Fig. 2(b) shows the selected area diffraction (SAED) pattern of decorated AuNPs and confirmed the decorated AuNPs have good crystallinity.

Fig. 2 (c) shows survey scan XPS of GO and AG-115 nanocomposite. In survey scan GO showed two peaks at 285 eV and 546 eV corresponding to C1s and O1s respectively. In addition to above peaks, AG-115 nanocomposite also showed one more peak at 85 eV corresponding to Au 4f confirming the presence of AuNPs in AG nanocomposite. Fig. 2 (d) shows the high resolution XPS spectra of C1s of GO.

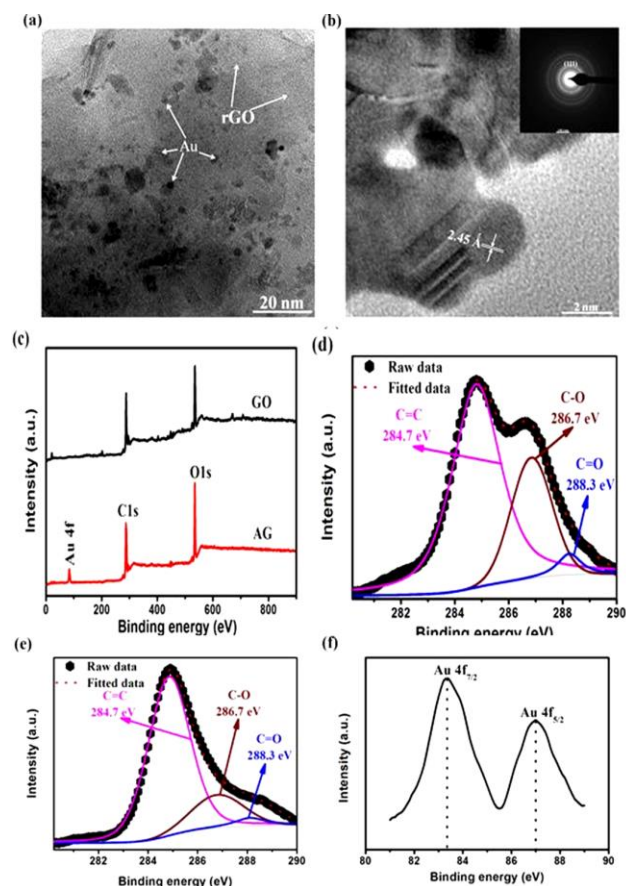


Fig. 2. (a & b) TEM images of AG-115 nanocomposite, (c) survey scan XPS of GO and AG-115, high resolution XPS of (d) C1s of GO, (e) C1s of AG-115 and (f) Au 4f of AG-115.

It was deconvoluted in to three peaks around 284.7 eV, 286.7 eV and 288.3 eV corresponding to C=C, C-O and C=O respectively [24]. The intensity of these oxygen functional groups decreased for AG-115 nanocomposite as can be seen from Fig. 2 (e) indicating the reduction of GO [24]. Fig. 2 (f) shows the high resolution Au 4f spectra. The 4f spectral region of Au showed two main peaks at 83.3 eV and 87.0 eV corresponding to Au4f_{7/2} and Au4f_{5/2} respectively which is in agreement with XPS spectra of metallic Au⁰ at 84.0 and 87.7 eV [11]. The slight blue shift of Au 4f compared to metallic Au⁰ may be due to the electron transfer from rGO sheet to AuNPs [11].

The catalytic reduction of 4-nitrophenol in the presence of NaBH₄ has been used as model reaction to evaluate the catalytic performance of metal nanoparticles [9, 11]. The mixture of 4-Nitrophenol and NaBH₄ showed peak around 400 nm (Fig. 3 (a)) due to nitro compound [11]. This absorbance was decreased in the presence of AG-115 catalyst indicating the reduction of 4-Nitrophenol. The catalytic reduction may start from AuNPs by relaying electrons from the donar BH₄⁻ to the acceptor 4-Nitrophenol. With increase in time, the absorbance around 400 nm decreased and it stopped at 420s confirming the complete degradation of 4-Nitrophenol. Also, a peak around 296 nm was slowly grown due to 4-aminophenol which is a reductant product of 4-Nitrophenol.

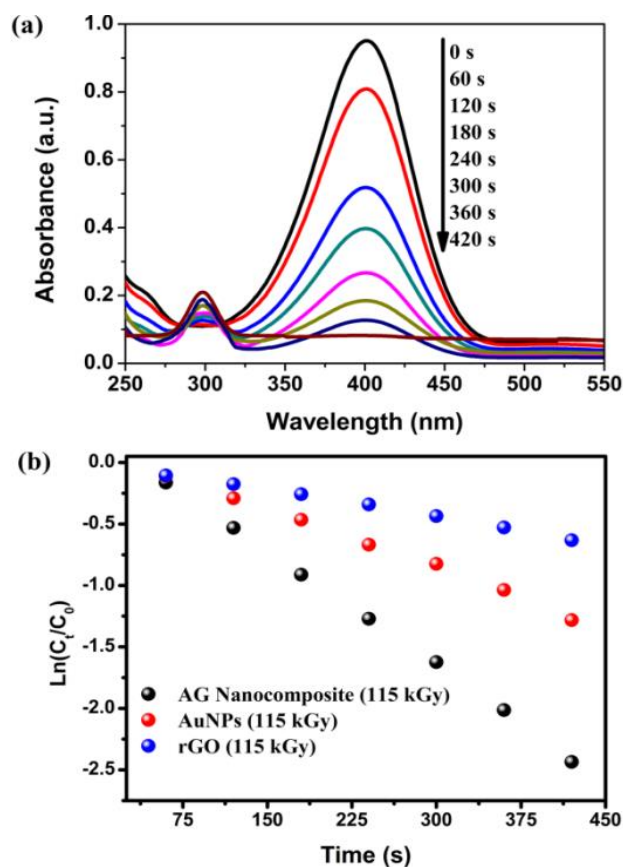


Fig. 3. (a) Absorbance spectrum reduction of 4-Nitrophenol in the presence of AG-115 nanocomposite, (b) Plot of $\ln(C_t/C_0)$ versus time.

The graph of $\ln(C_t/C_0)$ (C_t is the absorbance (at 400 nm) at time 't' and C_0 is the absorbance at '0' sec) versus

time (Fig. 3 (b)) showed linear relation indicating that the reduction of 4-Nitrophenol follows pseudo-first order reaction type [11]. The reaction constant (K) for AG-115 is found to be $6.24 \times 10^{-3} \text{ s}^{-1}$. Similarly, the reaction constant for AuNPs and rGO were calculated and found to be $3.21 \times 10^{-3} \text{ s}^{-1}$ and $1.47 \times 10^{-3} \text{ s}^{-1}$ respectively. The enhanced catalytic reduction of 4-Nitrophenol by AG-115 nanocomposite is due to the high adsorption ability of rGO towards 4-Nitrophenol that provides high concentration of 4-Nitrophenol to AuNPs and easy electron transfer from high conducting rGO and AuNPs.

Conclusion

UV-visible spectroscopic results showed the reduction of GO and formation of AuNPs. XRD results revealed that the formed AuNPs are having FCC structured and concentration increased with increase in dose. The AuNPs scaffolded on rGO sheet were having average particle size of 6 nm as studied from TEM. XPS results confirmed the removal of oxygen functional groups in AG nanocomposites indicating the reduction of GO and formation of AuNPs on it. The synthesized AG nanocomposite showed enhanced catalytic degradation of 4-Nitrophenol compared to rGO and AuNPs due to synergistic effect of individual components. Gamma radiation assisted method is a promising method for the synthesis of metal nanoparticles-rGO based nanocomposites.

Acknowledgements

The author KH is thankful to University Grant Commission, Govt. of India for awarding Dr. D. S. Kothari Post Doctoral Fellowship.


Author's contributions

Conceived the plan: KH, VNB, SDD; Performed the experiments: KH, RPJ; Data analysis: KH; Wrote the paper: KH, SDD. Authors have no competing financial interests.

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