Synthesis of Ag-reduced graphene oxide nanocomposite by gamma radiation assisted method and its photocatalytic activity

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Abstract

Silver-reduced graphene oxide (Ag-rGO) nanocomposite was prepared in the presence of Isopropyl alcohol (IPA) and polyvinyl pyrrolidone (PVP) by gamma irradiation assisted method. UV–Visible spectroscopic results showed the peak of rGO and surface plasmon resonance of Ag nanoparticles. X-ray powder Diffraction (XRD) results revealed the formation of face centered cubic structured Ag nanoparticles along with rGO signature after irradiation. Transmission electron microscopy (TEM) results showed the decoration of Ag nanoparticles of size 10 nm on rGO sheet corroborating the UV–Visible spectroscopic and XRD results. Raman spectroscopic results of Ag-rGO showed the increase in the ratio of D to G band (I_D/I_G) after gamma irradiation. The prepared Ag-rGO nanocomposite was tested for the degradation of methylene blue (MB) and results distinctly enhanced photocatalytic degradation compared to bare Ag nanoparticles and graphene oxide. The prepared Ag-rGO nanocomposites act as photo-catalysts that utilize visible light as an energy source.

1. Introduction

Graphene is a two dimensional material which has received an extensive attention due to its high surface area, excellent electrical and thermal properties, extended charge carrier mobility. Graphene oxide (GO) is considered as a precursor of graphene which is composed of nearly flat rigid of carbon atoms in which oxygen containing groups are covalently linked [1]. GO exhibits large surface area which can be used to decorate metal nanoparticles like silver. Silver nanoparticles can be synthesized by many methods like chemical reduction, photo reduction, electrochemical method, atom beam sputtering and radiation assisted method [2]. Among all these methods, gamma radiation assisted in situ synthesis of AgNPs has been termed as a simple, clean and efficient method [3]. Recently, some of the researchers have reported the reduction of graphene oxide by gamma, microwave and UV–radiation [4–8].

Ag-reduced graphene oxide nanocomposites can be synthesized by different method. Hsu and Chen [9] have synthesized Ag nanoparticles of size (10.3 ± 4.6), (21.4 ± 10.5) and (41.1 ± 12.6) nm by varying the microwave irradiation cycle number and deposited on rGO which showed increased surface enhanced raman scattering (SERS) with 4-aminothiophenol. The decoration of Ag nanoparticles of size (5–10) nm on rGO in the presence of ethanol synthesized by rapid microwave assisted method has been reported by Li and Hai [10] and it showed enhanced photocatalytic degradation of Rhodamine B. Chook et al. [11], have synthesized the Ag nanoparticles of size ~38 nm by modified Tollens’ process using glucose as a reducing agent by microwave irradiation assisted method and simultaneously deposited on graphene oxide sheet. The Ag nanoparticles deposited graphene oxide showed enhanced antibacterial performance than of the bare nanoparticles. The ionic liquid facile synthesis of Ag nanoparticles of size 20 nm on rGO in the presence of 1-ethyl-3-methylimidazolium acetate by gamma radiation method at a dose of 160 kGy has been reported by Wang et al., [12]. The gamma radiation assisted synthesized Ag-rGO nanocomposite showed enhanced SERS effect. Hung et al. [13], have decorated the Ag nanoparticles of size (10–30) nm on rGO in the presence of ethylene glycol by solvothermal method and found the enhancement in the electroconductibility of the Ag–rGO film. One-pot synthesis of Ag nanoparticles decorated rGO has been synthesized by Tian et al. [14], by chemical method and its application for photocurrent generation in the visible spectral region. However, to the best of our knowledge, no one has synthesized the Ag–rGO nanocomposite in the presence of IPA and PVP by gamma radiation assisted method.

Therefore in the present work, we have synthesized the Ag...
nanoparticles-reduced graphene oxide nanocomposite in the presence of isopropyl alcohol and polyvinyl pyrrolidone by gamma radiation assisted method. The prepared Ag-rGO nanocomposites were characterized by UV—Visible spectroscopy, XRD, TEM and Raman spectroscopy. The prepared Ag-rGO nanocomposites were checked for the photocatalytic degradation of MB dye.

2. Experimental details

Graphite powder, NaNO₃, H₂SO₄, KMnO₄, H₂O₂, AgNO₃, PVP, Isopropyl alcohol were procured from Sigma Aldrich Company.

2.1. Synthesis of GO and Ag-rGO nanocomposite

GO was synthesized by modified Hummers’ method [15]. 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) °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) °C under constant stirring for another 15 min. The solution was diluted by adding 500 mL water and 3 mL H₂O₂ (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. This prepared GO was dispersed in Isopropyl alcohol (0.5 mg/ml) and sonicated for 1 h.

25 mM of AgNO₃ solution was prepared. 10% PVP was added to it and stirred it for 30 min. 2 ml of AgNO₃-PVP solution was added to
20 ml of GO dispersed in isopropyl alcohol. 4 ml of this solution was taken in a glass bottle and exposed it to Co-60 gamma source to a dose of 29 kGy. Similarly other three samples were exposed to 58 kGy, 86 kGy and 115 kGy respectively. The radionuclide Co-60 ($^{60}\text{Co}_{27}$) is most commonly used source of gamma radiation with half life 5.27 years. Co-60 radioactive source can be produced by exposing Co-59 to neutrons in nuclear reactor. Co-60 decays into a Ni-60 ($^{60}\text{Ni}_{28}$) principally emitting one negative beta particle (maximum energy is 0.318 MeV). Thus, produced Ni-60 is in excited state, and it immediately emits two photons of energy 1.173 MeV and 1.333 MeV in succession to reach its stable state. These two gamma rays are responsible for radiation processing in the Co-60 gamma irradiators. Therefore, the average energy of gamma rays is considered as 1.25 MeV. The schematic representation of decay scheme of Co-60 is shown in Fig. S1 (ESI). The gamma constant for Co-60 at a distance of 30 cm will be 15.2 mR/h per 1 mCi (1 kGy = 10$^5$ R = 1 J/gm = 1000 sievert). The maximum range of beta particle emitted in air is 74 cm and that of in water is 0.1 cm. After irradiation, the sample was removed from gamma chamber, centrifuged, washed with double distilled water several times and redispersed in water for characterization. Similarly, Ag nanoparticles were prepared (at a dose of 115 kGy) without GO to compare their photocatalytic activity with Ag-rGO nanocomposite.

2.2. Characterization of the Ag-rGO nanocomposite

UV–Visible spectroscopy for Ag-rGO nanocomposites was carried out using JASCO, V-670 UV–Visible spectrophotometer. XRD diffractograms were recorded in the 2θ range (8–80°) using a Bruker AXS D8 Advance X-ray diffractometer with CuKα radiation at a wavelength of 1.5406 Å. The surface morphology was studied using TEM of model Tecnai G2 U-thin 200 kV, LaB6 filament. Raman measurements were carried out using Renishaw Invia laser Raman microscope with laser excitation wavelength of 532 nm.

2.3. Photocatalytic activity of Ag-rGO nanocomposite

The visible light catalytic activity of Ag-rGO nanocomposites was estimated by the degradation of MB. Methylene blue is a cationic dye which is commonly used for coloring paper, temporary hair colorant, dyeing cotton wools and so on. Although, MB is not considered to be a very toxic dye it can reveal very harmful effects on the living things. After inhale, symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans. Therefore, it is important to degrade the methylene blue. 1 mg of MB was dissolved in 100 ml of double distilled water. 5 mg of Ag-rGO nanocomposite was added to 20 ml of MB solution and firstly stirred in dark for 10 min. Then, the solution was exposed to a 250 W voltage mercury lamp for different time spans, namely 0–240 min. After that, the absorbance spectrum of the solution was measured. Similar type of experiment was repeated for GO and Ag nanoparticles (prepared at a dose i.e. 115 kGy).

3. Results and discussion

3.1. UV–visible spectroscopic result

The UV–Visible absorption spectrum of Ag-rGO nanocomposites are shown in Fig. 1. As shown in Fig. 1, GO showed two peaks around 230 nm and 296 nm corresponding to π→π* transition of aromatic C–C bond and n→π* transition of C≡C bonds [4]. After gamma irradiation for a dose of 29 kGy, the peak at 230 nm was red shifted to 270 nm corresponding to rGO and a new peak appears around 430 nm which is due to surface plasmon resonance of Ag nanoparticles respectively. This result suggests the successful synthesis of Ag nanoparticles on rGO. With increase in gamma dose, the surface plasmon resonance of Ag nanoparticles blue shifted slightly to 420 nm indicating the decrease in the particle size of Ag [16]. The preliminary radicals produced during gamma radiolysis are eaq, •H, •OH. The first two are reducing in nature and later one is oxidizing in nature. For the reduction of metal ions to zero-valent state a total reducing condition in required. The isopropyl alcohol present in the reaction system acts as electron scavenger for •OH. In addition to this, isopropyl radical which is a reaction product of isopropyl alcohol and •OH is also reducing in nature. The interaction mechanism of gamma radiation with silver and rGO is mainly through photoelectric effect, Compton scattering and pair production. Since, the energy of gamma radiations are 1.173 MeV and 1.333 MeV, the cross section for Compton scattering and pair production. Therefore, this gamma radiation transfer energy to loosely bound electrons and obtain energy around 0.5 MeV. This energy of electron is enough to make further disorders or formation of Ag or rGO. Therefore, the mechanism of gamma radiation assisted synthesis of Ag nanoparticles in presence of PVP can be explained as follows.

The following chemical reaction can be initiated in a chemical mixture.

\[
n\text{H}_2\text{O(radiolysis)} \rightarrow e_{aq}^- \text{•H}^+, \text{•OH}^-, \text{H}_2, \text{H}_3\text{O}, \text{H}_2\text{O}_2...... \text{etc}
\]

(1)

\[
\text{AgNO}_3 \rightarrow \text{Ag}^+ + \text{NO}_3^-
\]

(2)

This Ag$^+$ ion may interact with PVP as follows [17,18].

\[
\begin{align}
\text{Ag}^+ + & \text{OH}^- + \text{PVP} \rightarrow \text{Ag} \cdot \text{PVP} \\
\text{Ag} \cdot \text{PVP} + & \text{H}_2\text{O(radiolysis)} \rightarrow e_{aq}^- \text{•H}^+, \text{•OH}^-, \text{H}_2, \text{H}_3\text{O}, \text{H}_2\text{O}_2...... \text{etc}
\end{align}
\]

(3)

\[
\begin{align}
\text{Ag}^+ + & \text{OH}^- + \text{PVP} \rightarrow \text{Ag} \cdot \text{PVP} \\
\text{Ag} \cdot \text{PVP} + & \text{H}_2\text{O(radiolysis)} \rightarrow e_{aq}^- \text{•H}^+, \text{•OH}^-, \text{H}_2, \text{H}_3\text{O}, \text{H}_2\text{O}_2...... \text{etc}
\end{align}
\]

(4)
Thus, PVP molecule acts as protecting molecules for the synthesis of AgNPs by gamma radiolysis because nitrogen atom preferentially, oxygen atoms in the polar groups of the PVP repeated unit may donate electron pair to the $sp^3$ hybridized $Ag^+$ ions forming a linear coordination bond. These Ag nanoparticles will be decorated on rGO. Ding et al. [4], have found that PVP acts as a stabilizer to prevent the large agglomeration of rGO. Therefore, in this work PVP acts a stabilizer for both Ag nanoparticles and rGO from agglomeration.

3.2. XRD result

The XRD of GO and Ag-rGO nanocomposite are shown in Fig. 2. As shown in Fig. 2 (A), GO exhibited a sharp peak at 10.61° and is corresponding to (001) plane [12]. However, after irradiation with a dose of 29 kGy, this peak vanishes and a new broad peak appears around 24.51° as shown in Fig. 2 (B) indicating the reduction of GO. Similar kind of peak was also observed by Wang et al. [12], which is due to the removal of oxygen containing functional groups from GO and a disordered stacking of rGO sheets. In addition to this, one more new peak at 38.03° appears as shown in Fig. 2(C) corresponding to (111) plane of face centered cubic structure of Ag nanoparticle and the corresponding interlayer spacing is found to be 2.36 Å which is also supported by TEM results in the next section. With increase in gamma dose, this peak remains same at the same position. However, the intensity of this peak increases with increase in gamma dose indicating the formation of more (111) planes, in turn represents the more formation of AgNPs, as a result increase in crystallinity of the sample. At higher dose, i.e. 115 kGy, XRD showed some more peaks at 44.22°, 64.27° and 77.29° corresponding to (200), (220) and (311) planes of Ag nanoparticles which is in agreement with JCPDS File No. 04-0783. The non appearance of these peaks at low dose may be due to less content of Ag. Similar kind of observation was also reported by Hsu and Chen [9] for Ag-rGO nanocomposite synthesized by microwave irradiation.

3.3. TEM result

Fig. 3 shows TEM images of GO and Ag-rGO nanocomposite synthesized at a gamma dose of 115 kGy. Fig. 3 (B) showed the...
uniform decoration of Ag nanoparticles on overall rGO sheet. The average particle size of Ag nanoparticles deposited on rGO is found to be around 10 nm. From Fig. 3 (C), it is observed to found that the interlayer spacing is 2.39 Å which corresponds to the (111) plane of face centered cubic of Ag nanoparticles. This result is also supported by the XRD results.

3.4. Raman spectroscopic result

Raman spectroscopy of GO and Ag-rGO nanocomposites are shown in Fig. 4. As shown in Fig. 4, on excitation at 532 nm, the GO exhibited two peaks at 1345 cm$^{-1}$ and 1592 cm$^{-1}$, respectively corresponding to the D and G band representing amount of disorder and relative degree of graphitization [19]. The intensity of both D and G bands increases with increase in gamma dose for Ag-rGO nanocomposite. However, for the sample irradiated at 115 kGy dose, the D peak of the Raman spectra showed very marginal shift towards lower wave number due to reduction of graphene oxide [20]. The ratio of D to G band intensity (I_D/I_G) which is measure of degree of disorder and average size of sp$^2$ domain [19] increased after irradiation to 1.04 (for Ag-rGO prepared at 115 kGy) from 0.81 (for GO) which is attributed to the smaller size of the in-plane sp$^2$ domains in rGO sheets [12].

3.5. Photo-catalytic degradation of Methylene blue

The photocatalytic degradation of MB by Ag-rGO nanocomposite prepared by a gamma dose of 115 kGy was studied by exposing it to a 250 W mercury lamp with UV filter and it is compared with bare GO and Ag nanoparticles (prepared by a gamma irradiation at a dose of 115 kGy). The absorbance spectrum of degradation of MB by Ag-rGO is shown in Fig. 5 (A). UV–Visible absorption peak of MB showed two peaks, one around 610 nm corresponds to $\pi-\pi^*$ transition (of benzene ring) and another around 667 nm corresponds to $n-\pi^*$ transition ($n$ is the free doublet on the nitrogen atom of C=\text{N} bond and free doublet of S atom on S=C bond in MB). The peak around 610 nm is not a band but a shoulder and it corresponds to a vibronic transition 0–1 (level 0 of ground state to level 1 of the excited state). Therefore, the peak around 667 nm is considered here which is the characteristic peak of MB. After exposing it to UV light, the absorbance of this peak decreased indicating the degradation of MB. The mechanism of photocatalytic degradation of MB by Ag-rGO nanocomposite is as shown in Fig. 6. When Ag-rGO nanocomposite is exposed to visible

![Fig. 4. Raman spectrum of GO and Ag-rGO nanocomposites.](image)

![Fig. 5. (A) UV–Visible absorption of spectrum of degradation of MB recorded over time for Ag-rGO nanocomposite prepared at a gamma dose of 115 kGy; (B) Variation of concentration of MB versus time for GO, Ag and Ag-rGO nanocomposite. C$_0$ is initial concentration of MB solution and C is concentration of Ag-rGO nanocomposite at time t.](image)

![Fig. 6. Schematic representation of photocatalytic degradation of MB over Ag-rGO nanocomposite under visible light irradiation.](image)
light, the electron–hole pairs will be produced in AgNPs due to its surface plasmon resonance [9]. Then the electrons will transfer into rGO sheet by the interface between AgNPs and rGO. The two dimensional planar conjugation structure of rGO facilitate charge transfer along the rGO sheets to electron acceptors like oxygen molecules, and thus an effective charge separation is achieved. O2− radicals will be produced by the reduction of oxygen molecules adsorbed on the rGO surface by the photo generated electrons which are very powerful oxidizing agents and can degrade MB dye effectively under visible-light irradiation [10]. Thus the enhanced photocatalytic degradation of Ag-rGO is achieved compared to Ag nanoparticles and GO as shown in Fig. 5B. The photocatalytic degradation for the Ag-rGO nanocomposite prepared at other gamma doses (29, 58, 86 kGy) was also carried out at similar conditions and is shown in Fig. S3 (ESI).

To study the cycle performance of Ag-rGO (prepared at a dose of 115 kGy) catalyst, cyclic stability test was carried out. After the complete degradation of MB dye, the Ag-rGO catalyst was recovered using centrifugation with subsequent wash by water several times and dried at 60 °C. Ag-rGO sample was confirmed by XRD analysis. Then, it was mixed with fresh MB dye and degradation experiment was carried out at identical condition. For the first cycle, Ag-rGO showed 99.71% degradation of MB dye. Even after 8th cycle, Ag-rGO showed 92.88% degradation of MB dye, indicating the good cyclic performance of Ag-rGO sample towards MB degradation. The dye removal (%) versus cycle number is shown in Fig. S4 (ESI). XRD of Ag-rGO sample after 7th cycle is shown in Fig. S5 (ESI).

4. Conclusions

The graphene oxide was reduced and simultaneously Ag nanoparticles were synthesized by gamma radiation assisted method. The Ag nanoparticles of size 10 nm were decorated on reduced graphene oxide sheet which is confirmed from TEM, UV–Visible spectroscopy and XRD results. Raman spectroscopic results showed slight increase in disorder parameter due to formation of sp2 domains in rGO sheets. The photocatalytic degradation of MB by Ag-rGO showed enhanced photocatalytic degradation activity compared to Ag nanoparticle and GO.

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Appendix. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.vacuum.2015.11.011.

References