6 MeV energy electron beam assisted synthesis of Ag–rGO nanocomposite and its photocatalytic activity

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Abstract
Electron beam assisted method has been employed for the synthesis of silver-reduced graphene oxide (Ag–rGO) nanocomposite in the presence of isopropyl alcohol and polyvinyl pyrrolidine. The decoration of face centered cubic silver nanoparticles (AgNPs) of size 8 nm on reduced graphene oxide has been confirmed by UV–visible spectroscopy, X-ray Diffractogram and Transmission electron microscopy. Raman spectra showed the increase in the disorder parameter \((I_D/I_G)\) of Ag–rGO after electron irradiation due to the formation of large number of small \(sp^2\) domains. Moreover, as an application of the synthesized Ag–rGO sample showed an enhanced photo-catalytic degradation of methylene blue compared to graphene oxide, rGO and AgNPs under sunlight.

1. Introduction
Electron beam irradiation has nowadays become a useful tool for sterilization of medical items, preparation of biomedical materials, insulation jacketing of power cables, membrane technology and for the preparation of nanocomposites [1].

Recently, graphene based nanocomposites can be synthesized by the decoration of nanoparticles on graphene oxide (GO)/rGO which have application in lithium ion batteries [2], surface enhanced raman spectroscopy [3], sensor [4], photo-catalytic activity [5] etc. AgNPs have gained interest due to its usage in optoelectronics, information storage, biomedical imaging, catalysis and antibacterial applications etc. [6]. There are many reports for the synthesis of Ag–rGO by different methods [7–9]. But, as per the reported work so far, no one has studied the synthesis of Ag–rGO nanocomposite by 6 MeV electron beam.

Therefore, in this work 6 MeV electron beam assisted synthesis of Ag–rGO nanocomposite has been synthesized in the presence of isopropyl alcohol (IPA) and polyvinyl pyrrolidine (PVP). The synthesized samples have been characterized by UV–visible spectroscopy, X-ray diffractogram (XRD), Raman spectroscopy and Transmission electron microscopy (TEM). Also, these samples have been checked for the photo-catalytic degradation of methylene blue (MB) after exposing it to sunlight.

2. Experimental details
GO was synthesized by modified Hummers’ method and the preparation procedure is explained elsewhere [10]. This prepared GO was dispersed in IPA (0.25 mg/ml) and sonicated for 1 h. 25 mM of AgNO₃ was dissolved in double distilled water and stirred it for 30 min. 10% PVP was added to this 25 mM of AgNO₃ solution and stirred it again for 30 min. 2 ml of AgNO₃–PVP solution was added to 20 ml of GO dispersed in IPA. 4 ml of this solution was taken in a thin plastic bottle and exposed it to 6 MeV electron beam obtained from Race track Microtron Accelerator having pulse width 2 \(\mu\)s and pulse repetition rate 50 pulse/s. The fluences delivered to the samples were \(1 \times 10^{14}, 5 \times 10^{14}, 1 \times 10^{15}, 1.5 \times 10^{15}, 2 \times 10^{15} \text{ e}^-/\text{cm}^2\). After irradiation, the sample was centrifuged, washed with double distilled water (DDW). UV–visible spectroscopy for all the samples was carried out using JASCO, V–670. XRD was done using a Bruker AXS D8 Advance X-ray diffractometer with CuKα radiation at a wavelength of 1.5406 Å. 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, LaB₆ filament. Raman measurements were carried out using Renishaw Invia laser Raman microscope with laser excitation wavelength of 532 nm. The sun light catalytic activity of Ag–rGO nanocomposite was estimated by degradation of MB dye. 1 mg of MB dye was dissolved in 100 ml of double distilled water. 5 mg of Ag–rGO nanocomposite was added to 20 ml of MB dye solution and firstly stirred in dark for 10 min. After that, the solution was
exposed under sunlight with coordinates 18° 31' 13" N, 73° 51' 24" E and intensity of sunshine was \( \sim 820 \text{ W/m}^2 \). The absorbance spectrum of the solution was measured. Similar type of experiment was repeated for GO, rGO and AgNPs prepared at a fluence of \( 2 \times 10^{15} \text{ e}^-/\text{cm}^2 \).

3. Results and discussion

Fig. 1 (A) shows the UV–visible spectrum of GO and Ag–rGO sample synthesized by EB irradiation. GO exhibited two peaks around 230 nm and 296 nm respectively corresponding to \( \pi-\pi^* \) transition of aromatic C–C bond and \( n-\pi^* \) transition of C¼C bond [10]. After EB irradiation at fluence of \( 1 \times 10^{14} \text{ e}^-/\text{cm}^2 \), these peaks disappear and a shoulder peak appears around 267 nm and a broad peak around 430 nm respectively corresponding to rGO [10] and surface plasmon resonance of AgNPs [11]. With further increase in EB fluence, the absorbance of rGO and AgNPs increases indicating the more formation of rGO and AgNPs. In addition to this, the AgNPs peak decreased to 405 nm (i.e. blueshift) for the fluence \( 2 \times 10^{15} \text{ e}^-/\text{cm}^2 \). The formation and stabilization of AgNPs during irradiation is well explained by Wang et al. [12] in the presence of PVP. Ding et al. [10] have explained that PVP acts as stabilizer to prevent the large agglomeration of rGO. Therefore, in this work PVP acts as a stabilizer for both AgNPs and rGO.

XRD of GO and Ag–rGO are shown in Fig. 1 (B). GO showed a sharp peak around 10.63° corresponding to [001] plane [13]. After EB irradiation, this peak disappeared and a broad peak around 24.5° appeared indicating the reduction of GO [13]. In addition to this, EB irradiated samples also showed peaks at 38.02°, 44.22° and 65.61° corresponding to (111) (200) and (220) planes of Ag which is in agreement with JCPDS (File no. 04-0783). Also, with increase in the EB fluence, the intensity of all the peaks increased indicating the more formation of AgNPs.

Raman spectroscopy of GO and Ag–rGO is shown in Fig. 1 (C). GO showed its characteristics peaks around 1351 cm\(^{-1}\) (D band) and 1595 cm\(^{-1}\) (G band) corresponding to amount of disorder and relative degree of graphitization respectively. After EB irradiation, the intensity of both the bands increased with the fluence. The increase in intensity of G band is due to enhanced isolated double bonds and the D band is due to the enhanced disorder. At fluence \( 2 \times 10^{15} \text{ e}^-/\text{cm}^2 \), the G band (1602 cm\(^{-1}\)) is up shifted by 7 cm\(^{-1}\) with respect to GO (1595 cm\(^{-1}\)) due to electron–phonon coupling [14]. In addition to this, the ratio of D to G band intensity (\( I_D/I_G \)) is increased with increase in fluence which is attributed to the formation of large number of small sp\(^2\) domains [14]. Also, a peak around 2900 cm\(^{-1}\) appears after irradiation corresponding to 2D graphene indicating reduction of GO [14].

Fig. 2 shows TEM images of (A) GO and (B) Ag–rGO synthesized by EB irradiation at a fluence of \( 2 \times 10^{15} \text{ e}^-/\text{cm}^2 \). The uniform decoration of AgNPs of average particle size \( \sim 8 \text{ nm} \) on overall rGO.
The interlayer spacing is 2.35 Å which corresponds to the (111) plane of face centered cubic of AgNPs corroborating the XRD results.

The photocatalytic activity of GO, AgNPs, rGO and Ag–rGO prepared at EB fluence of $2 \times 10^{15}$ e$^-$/cm$^2$ was checked for degradation of MB dye under sun light and is shown in Fig. 3(A–D). The characteristic peak of MB is found to be around 667 nm. After exposing it to sun light, the absorbance of this peak decreased completely in case of Ag–rGO sample indicating the degradation of MB. When the solution (Ag–rGO + MB) is exposed to sun light, the AgNPs from Ag–rGO nanocomposite generates electron–hole pairs due to its surface plasmon resonance [9]. These electrons transfer quickly to rGO sheet by the interface between AgNPs and rGO. The two dimensional planar conjugation structure of rGO which has excellent electron-mobility facilitate charge transfer along the rGO sheet to electron acceptors like oxygen molecule, and thus an effective charge separation is achieved. $O_2^-$ 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 sun light [9]. Thus, the enhanced photocatalytic degradation of MB by Ag–rGO is achieved compared to GO, rGO and AgNPs as shown in Fig. 3(E) and the schematic mechanism is shown in Fig. 3(F).

4. Conclusions

UV–visible spectroscopic results showed the formation of rGO and AgNPs which is also corroborated by XRD results. TEM results revealed the decoration of AgNPs of size 8 nm on rGO. The increase in $I_D/I_G$ ratio after irradiation in Raman spectroscopy is due to the formation of large number of small sp$^2$ domains. The enhanced photocatalytic activity of the Ag–rGO nanocomposite may be due to the synergic effect of the effective separation of the photo generated carriers. Electron beam assisted method may emerge as a promising method for the synthesis of Ag–rGO nanocomposite which is a good photo-catalyst for the environmental issues.

Fig. 2. TEM images of (A) GO (B), (C) Ag–rGO sample (D) particle size histogram.
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