One step approach towards the green synthesis of silver decorated graphene nanocomposites for the degradation of organic dyes in water

Gopakumar Karthik¹, A Harith¹, N Nazrin Thazleema¹, Shaji Vishal¹, S Jayan Jitha¹ and Appukuttan Saritha¹

¹Department of Chemistry, Amrita School of Arts and Sciences, Amritapuri, Amrita Vishwa Vidyapeetham, Amrita University, Kollam, Kerala, India

E-mail: sarithatvla@gmail.com

Abstract: Recently the decoration of graphene with metallic nanoparticles by a one pot reduction of graphene oxide (GO) coupled with the synthesis of metallic nanoparticles has gained momentum. Graphene and GO have been proved to exhibit excellent biocompatibility and high antibacterial activity and hence a vast possibility lies in the utilization of GO as an antibacterial reinforcement in biomaterials and exploration of the antiseptic properties as well as the cytotoxicity of GO-containing composites. Moreover GO decorated with metal/ metal oxide paves way towards an inevitable role in water purification. The use of graphene oxide as the nano scale substrates for the development of nanocomposites with metal oxides is a novel idea to obtain a hybrid which would exhibit both the properties of GO as an enthralling paper-shape material and the quality of single nano-sized metal particles. The heavy metal ions and pollutants are considered as a major problem in environmental contamination. Hence detection of trace level pollutant has become a hot topic in the present research scenario. Modified graphene oxide nanocomposites prepared using a green approach has the capacity of absorbing pollutant material ions in high efficiency and selectivity. The green synthesized nanocomposites were characterized using FTIR and UV spectroscopy and the consequence of pH and concentration on the preparation of the nanocomposites was evaluated. The efficiency of these nanocomposites towards degradation of organic dyes like methylene blue has been evaluated.

1. Introduction

Graphene, the monoatomic thin sheet of carbon fashioned in a honeycomb crystalline lattice is an area of promise for the future researches. They are extremely thin and show fascinating properties of adsorption, electronic transportation antibacterial activity and mechanical strength that holds a strong future for the production of various carbon based technical devices and composites. Synthesis of large scale of graphene can be achieved by chemical reduction of another significant derivative of graphene known as Graphene Oxide (GO). [1,2 ]. Since this fascinating material is decorated on its planes as well as edges with phenolic, carboxyl, and epoxide groups, it is easily prone to further chemical modifications [3,4]. GO shows effective dispersion in water as well as in polar organic solvents due to the hydrophilicity activated by the oxygeneated groups [5,6]. Furthermore the extraordinary surface area of the material would prominently expand its capacity for loading as a filler material [7].
Accordingly it is assumed to be a favourable elementary unit possessing multifunctional ability for the preparation of graphene oxide-metal composites (GO-MNPs). Much works are already done on graphene-based nanocomposites due to their implicit optical, electronic and catalytic applications. Xiu-Zhi Tang et al. [8] have reported the synthesis of these types of composites using a reducing agent like glucose. The graphene decorated with silver nanoparticles exhibit distinct SERS effects. Sang-Woo Yun et al. [9] have reported on the preparation of GO silver nanocomposites using silver carbamate. This microwave method is reported to be able to control the particle size of silver nanoparticle arranged on the lattice of graphene. The study on the decoration of various metal ions on the graphene is still at its initial stage. A controlled green synthesis of metal decorated graphene nano composite is a challenging factor. Chemicals such as PVP, Amino methyl piperazine, formaldehyde, etc are used for the reduction of graphene oxide. But most of them being toxic make them hazardous in nature. Usage of green extract that could be used as both the reducing agent and the decorating agent in the decoration of silver nanoparticles can be novel and safe mode of preparation. The preparation of silver nanoparticles using pome peel extract has been reported by several authors. In this work we aim to synthesize nano silver decorated rGO composites using a green synthetic pathway enabling a simultaneous reduction of GO and silver using pome peel extract as the biological medium. The nanocomposites prepared by the above eco-friendly pathway were further utilized for the elimination of heavy metal ions present in water. Lu kui et al. [10] conducted a study on graphene based material synthesis and its application in the treatment of environmental pollutants. Zhang et al. [11] synthesised of ZnO/graphene composites by a chemical deposition method and analysed its control on photocatalytic degradation.

2. Experimental

2.1 Preparation of GO

Tour group reported first an upgraded method where graphite was exfoliated to form GO. In this method graphite and KMnO₄ was mixed and a 9:1 concentrated H₂SO₄/H₃PO₄ was added to it. The reactants were heated to 50 °C, allowed to stir for 12 h, and cooled in an ice bath. This was followed by the addition of deionised water and 30% H₂O₂. The mixture was centrifuged and washed with water, 30% HCl and finally with ethanol. Using ether the solid mass was coagulated and dried overnight at room temperature. Aqueous suspension of GO with a concentration of around 0.35 wt% was prepared for the preparation of the nanocomposites.

2.2 Synthesis of Ag-rGO nanocomposite

Ag NPs were synthesized by in situ reduction of AgNO₃ with the use of pome peel extract as reducing and stabilizing agent. The extract was added to the aqueous GO solution and ultrasonicated for 20 minutes followed by the addition of silver nitrate solution and the mixture is again stirred to maintain homogeneity. The formation of the nanocomposite was monitored through periodic analysis of the mixture by taking the UV spectrum. To inspect the effect of pH on the formation of Ag–GO nanocomposites, different amounts of NaOH with 2 M were poured into the above mixed solution of GO, plant extract and AgNO₃.

3. Results and Discussion

Graphene-based photo degradants are considered more advantageous than pure photo degradants. Due to the sp² hybridized carbon atoms. Electron transfers in these composites occur from the conductors in the excited state to the exfoliated graphene sheets. The size of silver nano particles is controllable and the less aggregated form of graphene enhances the photocatalytic efficiency. In addition transparent nature of graphene sheets enhances the light of excitation. The distinctive structure and elegant properties of graphene make it fit for chemical and structural modification and hence forms composites with nanomaterials like
silver. Hence the modified graphene and graphene-silver composites will have elevated light absorption and photocatalytic nature. Vibrations at 3400 cm\(^{-1}\) (O-H stretching vibrations) and at 1720 cm\(^{-1}\) in the FTIR spectrum can be used to identify various oxygen functionalities in graphene oxide[10]. Therefore, it confirms the existences of plenty of hydroxyl groups and oxygenous groups of GO, which makes GO to be suitable for advance modification with plasmonic NPs, like Ag NPs. From the FTIR peak of reduced graphene it can be understand that O-H stretching vibrations at 3400 cm\(^{-1}\) was considerably reduced due to deoxygenation. Even though, stretching vibrations of C=O at 1720 cm\(^{-1}\) were still observed [11] as indicated in figure 1.

![Figure 1: FTIR spectrum of GO and rGO](image)

There is every likelihood that both large and small Ag particles coexist on the rGO sheet. Compared to inside atoms those on the surfaces are less stable. Simultaneous effect of vibration and temperature due to the ultrasonication drives the surface atoms which tend to detach from Ag and diffuses into the solution. As a result, extended ultrasonication interval increases the concentration of free molecules in solution. After the supersaturation of these free molecules, they will condense on the larger particles. As a result, average size will increase due to the smaller particles shrink, and the larger particles grow. So we have chosen minimum time for ultrasonication process. Moreover the amount of silver nitrate added into the extract is less and hence the SPR band is less intense and difficult to detect owing to the very low concentration of silver ions immobilised on the graphene sheets.

3.1 Effect of concentration on the formation of Ag-rGO nanocomposite

To elucidate the effect of increase in concentration of silver ions in the formation of these nanocomposites we increased the concentration of silver ions and monitored the UV spectrum to examine the changes. (Figure 2)
3.2 Effect of pH on the formation of Ag–rGO nanocomposite

Initially Ag–GO composites were characterized by the techniques of UV–vis absorption spectra. The spectra of the composites were taken after sequential addition of AgNO₃ stock solution. It was noticed that upon increasing the concentration of silver nitrate solution, the intensity of the surface plasmon peak exhibited by the composites increases. This confirms the fact that the amount of silver deposited on rGO surfaces increases as the concentration of silver nitrate increases.
To study the impact of pH in the preparation of the Ag–GO hybrids, different amounts of NaOH were added into the GO solutions. Fig. 3 exhibits the UV–vis absorption spectra of the final products when the pH changes from 10 to 13. It can be understood, there is a considerable enhancement in the intensity of the absorption band, as well as the narrowing of the size distribution with the rise in pH. This trend clearly indicates that the presence of NaOH stimulates the deposition of silver nanoparticles on the surface of GO. The maximum intensity of the SPR band of Ag NPs is found at a pH of 11.0 (as shown in Fig. 3 pH 12). On the other hand, the position of absorption band seems to be red shifted. Thus further increase in the pH of the composites causes a reduction in the intensity of the band (as shown in Fig. 3 pH 13). This could be due to the fact that the creation of silver is at such a condition that there is less silver source consumption during the growth process. Also, the synthesis of the nanocomposites from different pH values was evidently perceived from a distinct colour change from light brown to deep black.

At pH 12 the analysis of the black nanocomposites sample showed a red shift in the SPR peak which shows that there in coalescence and instantaneous formation of silver rGO composites. Due to quadrupole resonance, as well as the primary dipole resonance for particles having greater size a secondary peak observed at lower wavelength region becomes perceptible, which in fact specifies that the particle size of silver deposited on the surface rGO increases with increasing pH. Besides, there is a clear broad absorption peak for RGO - Ag that is centred at 600 nm, which can be explained on the grounds of the surface plasmon resonance provide by Ag NPs, indicating the successful construction of Ag NPs. It is evident that the ideal pH for precipitation of nanocomposites is 12. Above 12 there is instantaneous precipitation of the black nanocomposite.
After centrifugation of the mixture, the black composites sample on analysis shows a spectrum as depicted by figure 5. It is evident that the silver has been immobilized on the surface of rGO as the SPR peak of silver has vanished. Moreover the presence of a small peak between 550 and 600 nm shows that the size of silver particles on the surface of rGO is bigger.

### 3.3 Removal of methylene blue using Ag-rGO nanocomposites

To study the effect of nanocomposites on the degradation of dyes, the methylene blue solution is kept in contact with the rGO-Ag nanocomposites and the degradation kinetics was monitored using UV spectroscopy. Usually silver in the nano form promotes degradation of the methylene blue dye. This is usually explained on the basis of electron shutter mechanism. While in the case of nanosilver immobilised rGO nanocomposites instead of degradation, removal of the dye occurs and hence the centrifugate does not show any traces of degradation of the dye. Whereas the residue which contains the rGO silver composite sample adsorbs the dye and shows the removal of dye sequentially with time. Figure 6 shows the UV spectrum of the effect of the nanocomposites on the degradation of the organic dye.

On enhancement or decline of the pH, the dye might be converted to its leuco form. Otherwise it could be adsorbed on the surface of AgNPs due to its high surface area leading to the removal of a large quantity of dye. When the auxochromic groups in the dye are removed, the colour of the dye solution becomes less intense and this accounts for the shift in wavelength observed in the SPR band.
Figure 6: Effect of Ag-rGO nanocomposites on the degradation of methylene blue

The evaluation of kinetic data obtained for methylene blue degradation was fitted into the first order and second order rate equations and it was noticed that the degradation follows first order kinetics as seen in figure 7.
4. Conclusion

A green synthetic pathway was successfully formulated for the simultaneous reduction of GO and silver nitrate which eventually led to the deposition of nanosilver on the surface of reduced GO. The deposition of nano silver was confirmed by the observance of plasmon band. The formation of rGO was confirmed from UV and FTIR. The process of formation of the nanocomposite was influenced by the pH as well as concentration of the solution. The composites exhibited greater absorption capabilities when kept in contact with methylene blue dye and the degradation mechanism was found to follow a first order kinetics.

5. Reference

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