Facile green synthesis of Ag, Au, AuAg@C-reduced graphene oxide nanohybrids and its catalytic studies

P. Kavitha[a,*], C. Shanthi[a], R. Kannan[b]
[a]*Department of Physics, Sona College of Technology (Autonomous), Salem – 636 005, Tamil Nadu, India*
[b]*Department of Chemistry, Sri K.G.S. Arts College, Srivaikuntam – 628 619, Tamil Nadu, India*

Facile green synthesis of gold, silver and silver-gold on graphene oxide nanohybrid using ascorbic acid at room temperature has been studied in this communication. Further the interaction between the metal and graphene oxide was enhanced with the help of the ascorbic acid/dehydroascorbic acid by the calcination process. The ascorbic acid acts as reductant as well as a stabilizer of metal nanoparticles on the support. The micrographs reveal the formation of metal nanoparticles as quantum dots (~ 3-5 nm), results improved catalytic activity towards methylene green degradation in room temperature was studied. The proposed method is facile, fast and eco-friendly for the synthesis of metal nanoparticles over the carbon nanostructures.

1. Introduction

The textile, paper, and leather industries are discharging a large quantity of coloured effluents containing dyes into water bodies. Most of these dyes have toxicological effects on the environment and human health. In addition, there are other highly toxic chemical compounds in the discharges that increase environmental issues [1, 2]. On the other hand, it is known that these dyes in water bodies decreases the passage of sunlight, increases biochemical (BOD) and chemical (COD) oxygen demand, averts the photosynthesis and inhibits plant growth [3,4]. Number of treatments are used for colour removal through chemical, physical, biological or hybrid methods. Among them, chemical oxidation using suitable catalyst finds attentions, due to its fast and easy process, the dyes are degraded [5,6].

Noble metal especially gold (Au), silver (Ag), platinum (Pt) and palladium (Pd) with nanostructures have attracted considerable attention, due to their potential applications in sensors, catalyst, active materials for energy storage and conversion [7-9]. In the recent past, progress has been made in the field of nanoscience and technology and numerous methods are suggested for the tailor made development of metal nanoparticles of particular size and the shape. The activity of these materials triggers with the size and shapes [10, 11]. Besides, these metal nanoparticles (MNPs) have been developed using number of hazardous chemicals [12, 13]. Due to environmental concern, eco-friendly method of synthesis is greatly essential in the present scenario.

Due to the high surface energy and strong interaction/attraction between these metal nanoparticles (MNPs) agglomeration or shape-change occurs during the catalysis reaction [14-24]. This result, the decreased catalytic ability due to the reduction of active catalytic sites. To overcome these difficulties, various methods are suggested and one among them is to place the metal NPs in suitable support. Carbon based supports including carbon nanotubes [14], graphene

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materials [14, 24] etc., have been used as support materials and the resultant C/MNPs composite materials exhibited improved catalytic response with good stability.

MNPs such as Au, Ag and AuAg NPs have been prepared by several reducing agents such as sodium borohydride [19], ascorbic acid (AA) [24], hydroquinone [20,21], glycerol [22], polysaccharides [23] etc. Among these reducing agents, AA acts as excellent reducing agent. Recently number of research group have studied the AA mediated reduction of MNPs [24] However, the complete reduction mechanism of MNPs is still not well studied.

In our recent report, we have reported the synthesis of nanofibrous Au, Ag and AuAg using ascorbic acid by room temperature [24, 25]. Due to the very high surface affinity of MNPs, it will be placed on the suitable support. These supported MNPs offers better catalytic activity compared to unsupported [24]. On other hand the interaction between MNPs and support is highly essential to obtain the good catalytic activity [24]. To keep in mind, we have synthesized Au, Ag, AuAg NPs over the various graphene oxide by simple one-pot approach using eco-friendly reducing agent, to reduce the metal content and improve the catalytic platform for the better interaction between catalyst and pollutants. Herein, we present a novel strategy for in situ growth of Au NPs, Ag NPs and AuAg NPs @C on Graphene oxide, which leads to the formation of 2-8 nm sized Au, Ag, AuAg NPs at room temperature. The excess of reducing agent turned into carbon at high temperature leads to Au@C-GOs. These carbons will help to improve the interaction between MNPs and support. The scheme of synthesis, formation mechanism and the catalytic activity are reported in detail.

2. Experimental

2.1. Materials

Natural graphite powder, Ascorbic acid were received from Alfa Aesar chemicals, Republic of Korea and Chloroauric acid, silver nitrate were obtained from Sigma-Aldrich. Potassium permanganate sulfuric acid and nitric acid were received from Samchun pure chemicals, Republic of Korea. Analytical grade chemicals were purchased and used as received without further purification.

2.2. Synthesis of graphene oxide

The graphene oxide was prepared by the modified Hummer's process [26]. In brief, natural graphite powder (4.0 g) was added to concentrated H_2SO_4 (70 mL) under stirring in an ice bath (0-2°C). Then, under vigorous stirring, potassium permanganate (12.0 g) was added slowly to keep the temperature of the suspension lower than 20°C. After 15 min, the reaction system was transferred to a 40° Coil bath and stirred for about 1h. Then, 150 mL water was added, and the solution was stirred for 30 min at 100°C. Additional 500 mL water was added and followed by a slow addition of 30 mL H_2O_2 (30%). The mixture was filtered and washed with1:10 HCl aqueous solution (500 mL) to remove manganese ions. The resulting solid (GO, GS1) was dried in air and diluted to 1000 mL, making a graphene oxide aqueous dispersionusing ultrasonic irradiation.

2.3. Synthesis of AuAg @C–GO

The AuAg@C over the RGO was prepared by same process, about 5 mg of H_4AuCl_6 and 5 mg of $AgNO_3$ and 20 mg of GO were mixed well using a mortar, after which about 20 mg of solid ascorbic acid was added to the mixture and grounded well. After one minute, the part of the solid mixture was turned little sticky and further grinding results, solid product with dark brown in colour. Then the solid was dried in a hot air oven for about 2h at 90°C and calcined at 800°C.

2.4. Characterization

The prepared catalysts were characterized using powder X-ray Diffraction (XRD, Rigaku Instrument diffractometer with Cu K☐ radiation). The surface Plasmon and the catalytic activity were monitored using the double beam UV-Vis spectrophotometer (Wenser double beam spectrum).Further characterization was performed employing Field emission Scanning Electron

Microscopy (FE-SEM) equipped with the Energy Dispersive X-ray Spectrometer (EDS) for the quantitative determination of the elements present in the catalyst on a JEOL, JSM-6200 equipped with an Oxford instruments, at an accelerating voltage of 5-20 kV. The images from High Resolution Electron Microscopy (HRTEM) were recorded with JEOL, JEOL 2100 electron microscope operated at 200 kV.

2.5. Catalytic studies

The catalytic studies were carried out by using de-colorization process of Methylene green (MG) by batch method. In brief, about 100 mL of MG dye solution (Sigma-Aldrich, 0.1 mmol) was taken in a 100 mL conical flask and 10 mg of different catalysts (Au@C-RGO, Ag@CRGO, AuAg@C- RGO) were added with constant stirring. After 2 minutes, 1mL of H_2O_2 was added slowly. The mixture was allowed to react at room temperature. Then, at different time intervals, a part of the solution was collected, centrifuged, diluted and was analyzed using double beam UV-Visible spectrophotometer (Wensar double beam spectrometer). About 100 mL of dye solution and 100 mg of catalyst mixed together and subjected to catalytic reaction to evaluate the total organic carbon analysis.

3. Results and discussion

Number of research reports reveals the reduction ability of AA towards the MNPs especially noble MNPs. Initially, we are interested to prepare the Au and Ag and AuAg MNPs at room temperature. For that suitable quantity of metal precursors and AA was grounded in mortar for about 5 to 10 min. It results excellent fibrous nanostructures. The detailed report was communicated [25]. To reduce the MNPs and improve its catalytic ability, we made an attempt to develop the Au, Ag, and AgAu on graphene oxide nanosheets by solid state approach. Our earlier report suggested that the excess reductant acts as stabilizer. Hence to utilize the excess reductant as source for carbon, will be developed by in-situ process. This carbon will enhance the interaction between MNPs and graphene oxide sheets (platform). The appropriate quantities of GO, metal precursors and AA, mixture are subjected to mechanochemical process at room temperature. The metal nanoparticles formation was characterized after the initial reaction which means that, after the mechanochemical grinding of precursors, the powdered materials are analyzed. After the process, the mixture was subjected to heat treatment at 800°C at inert atmosphere.
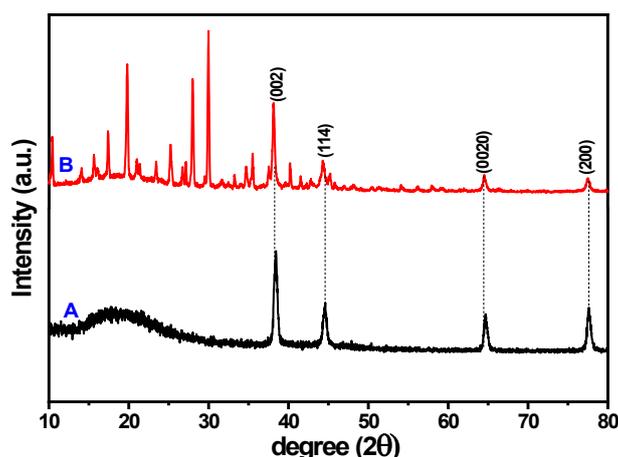
Fig. 1. Powder XRD profiles for (A) graphene oxide, (B) AuAg@C-RGO.

The XRD analysis results the formation of AuAg MNPs over the graphene oxide sheets and the graphene oxide also got reduced into reduced graphene oxide. The presence of diffraction peaks located at 38.39, 44.59, 64.57 and 77.50 corresponds to (002), (114), (0020) and (200) plane

of rGO (JCPDS: 01-074-2330) (Fig. 1a) respectively. The addition peaks are involved at 15.66, 17. 41, 19.76, 21.13, 23.48, 25.23, 27.83, 29.95 and 35.53 corresponds to presence of AuAg in the fabricated AuAg@C-rGO nanomaterial (Fig. 1b). The presence of more intense sharp diffraction peaks located at 19.76, 27.96, 29.95 and 38.26 are clearly indicate the synthesized nanomaterial are highly crystalline nature. The estimated crystalline size of rGO are 21 nm and AuAg@C-rGO nanomaterial are 32 nm. As a result the addition of Au and Ag into rGO the particle size was increased. The Particle size determination using Debye-Scherrer equation.

$$D = K\lambda / \beta\cos\theta$$

where,

D = is crystalline size, K = is constant (0.9)
λ = is the wavelength of x-ray source (0.15406 nm)
β = is the full width half maximum of sharp diffraction peaks
θ = is the Brag angle
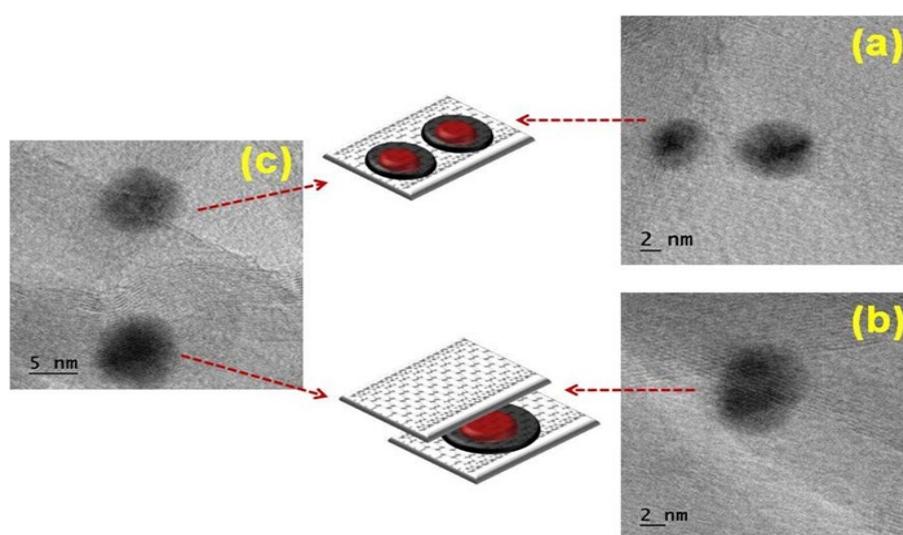
Fig. 2. TEM micrograph for the AuAg@C-RGO hybrid catalyst and their schematicrepresentation.

The structural characteristics were analyzed by HRTEM, the micrographs indicate the metal nanoparticles formed as tiny particles with the size ranging from 28 nm. Additionally the metal nanoparticles formed over the edges of the graphene oxide nanosheets and in between the graphene oxide nanosheets were presented with schematic representation in figure 2. (Fig. 3) shows the TEM image of AuAg@C-RGO nanoparticles. The image clearly depict the spherical shaped AuAg nanoparticles are successfully embedded surface of the rGO nanosheet. The synthesized AuAg@C-RGO nanoparticles exhibits the particle size are 28 nm the particles size determination using histogram diagram.
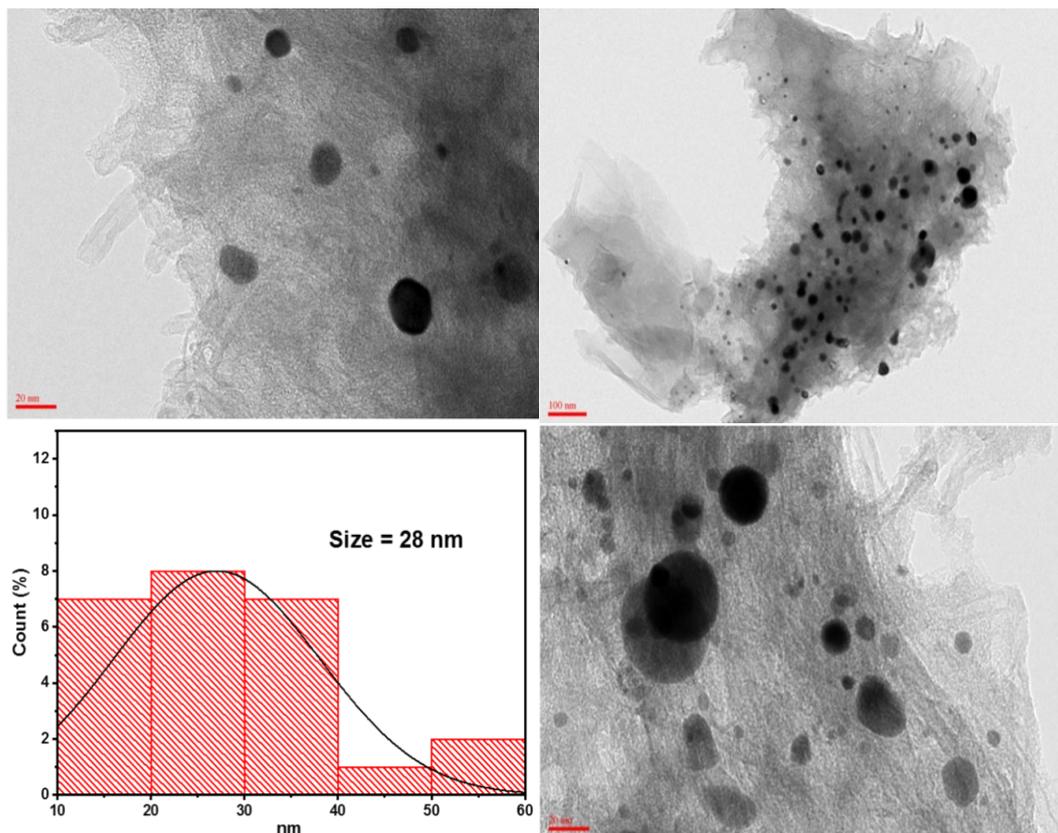
Fig. 3. TEM micrographs of AuAg@C-RGO nanoparticles.

The SEM images (Fig. 4a) show the uniform distribution of AgAu over the graphene oxide nanosheets and EDX profile confirms the presence of Ag and Au (Fig. 4b). High angle annular dark field imaging (HAADF) is STEM technique to analyze the distribution of Au and Ag on the graphene oxide nanosheets. Fig. 5 shows the HAADF image and AgAu@C-RGO, reveals the Ag and Au distributed over the graphene oxide nanosheets and Ag cover up over Au nanostructures was formed on the graphene oxide. It has also supported by EDX profile. Hence we presumed that, these results indicate the presence of Ag on the top of the surface over the Au like sandwich structures.
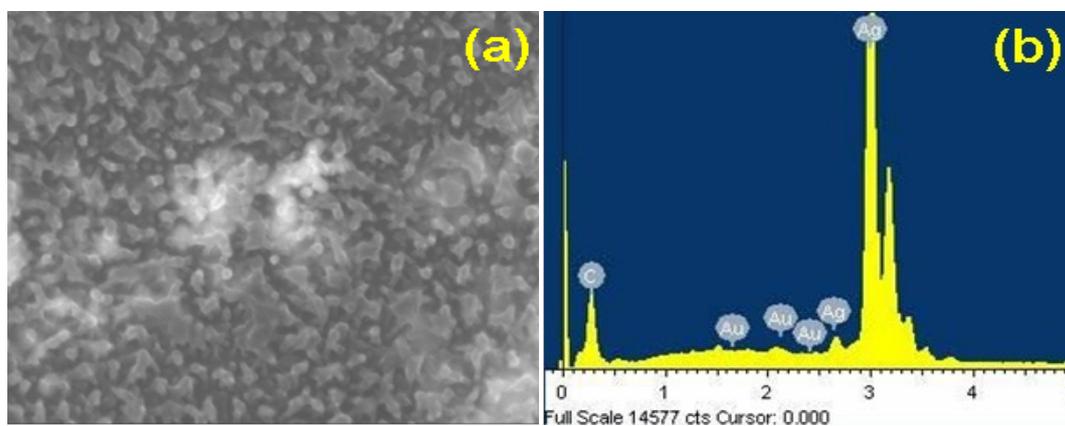
Fig. 4. SEM image of and EDX micrograph of AuAg@C-RGO hybrid catalyst
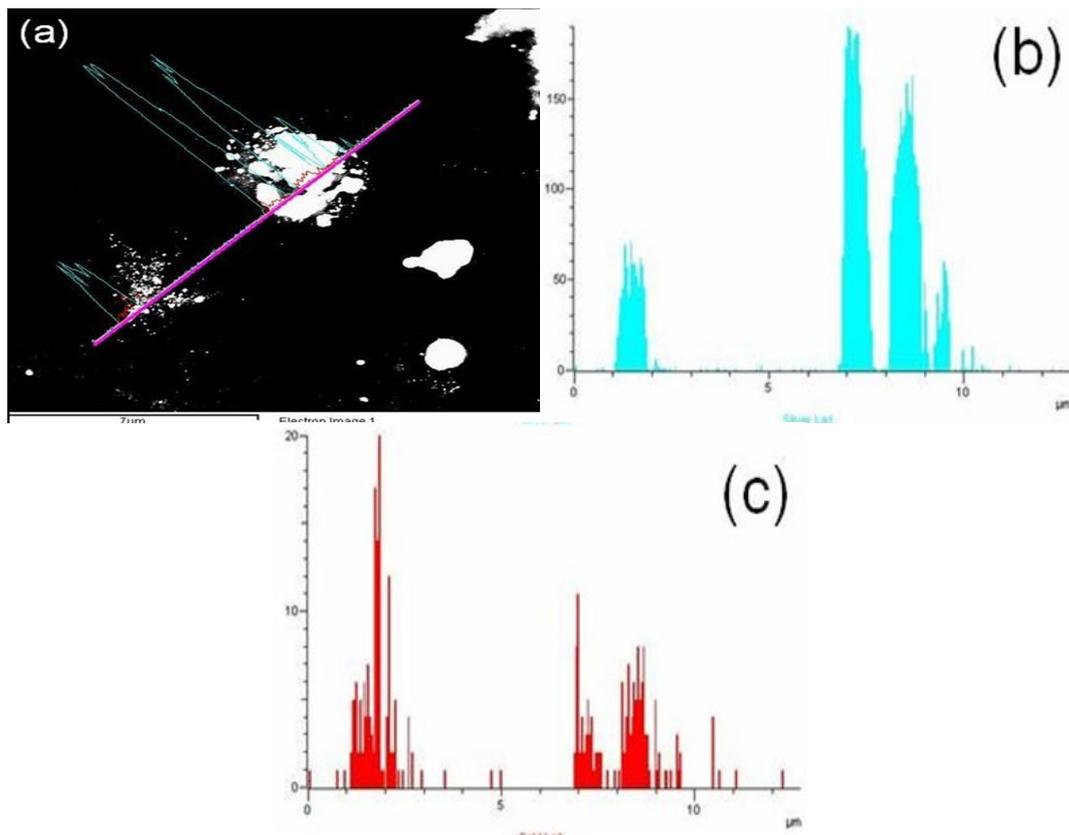
Fig. 5. A HAADF STEM image of RGO with embedded Au-Ag@C nanoparticles.

The catalytic activity of prepared AuAg@C-RGO is tested for the catalytic oxidative degradation of Methylene green dye in the presence of sodium borohydride (NaBH4 0.5x10-5 M) and experimental results show excellent catalytic activity. The degradation was very effective and the catalytic degradation starts within 2 min and the initial degradation of 40 % was observed. Further the maximum degradation of 98% was achieved at 23 min. Fig. 6, shows the absorbance spectrum of MB (0.001 mM) and Fig (b-d) shows the catalytic oxidative degradation of Methylene green dye at different catalysts and [fig.7 (b) Au@C-RGO, (c) Ag@C-RGO, and (d) AuAg@C-RGO, respectively in the presence of H2O2] Graphene oxide shows only the adsorption of dye over the catalyst was observed (figure not shown). We have compared Au, Ag and AuAg with and without graphene oxide. It indicates that all the six catalysts show almost similar catalyst response.
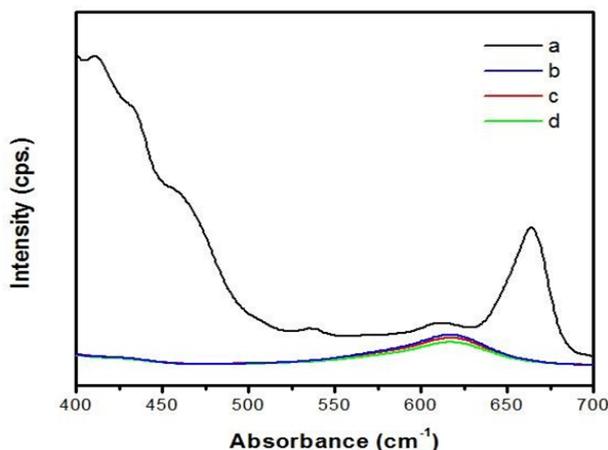
Fig. 6. UV-Visible spectrum of (a) MG, MG degradation using (b)Au@C-RGO, (c)Ag@C-RGO, and (d)AuAg@C-RGO with H_2O_2.
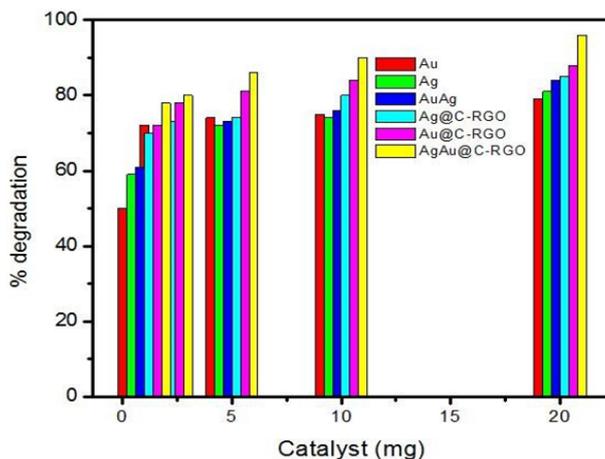
Fig. 7. Catalytic response for the degradation of MG dye with various catalysts

However, the AuAg@C-RGO shows higher degradation efficacy over other mono-metals. In addition to that, when compared to Graphene oxide, supported metals (Au@C, Ag@C, AuAg@C) shows lower reusability, it may be due to the adsorption of the dye and their degraded products adsorbed over the catalyst. However, in graphene oxide supported systems are restricted or minimized by the graphene oxide platform. Hence the metal nanoparticles are free and will active towards the catalysis. The reuse of the catalyst shows good catalytic activity and from one to ten runs, the catalytic activity reduces by 7-8% and the stability holds well (Fig. 8). A detailed catalytic activity towards other pollutants such as organic dyes and pharmaceutical compounds are in progress.
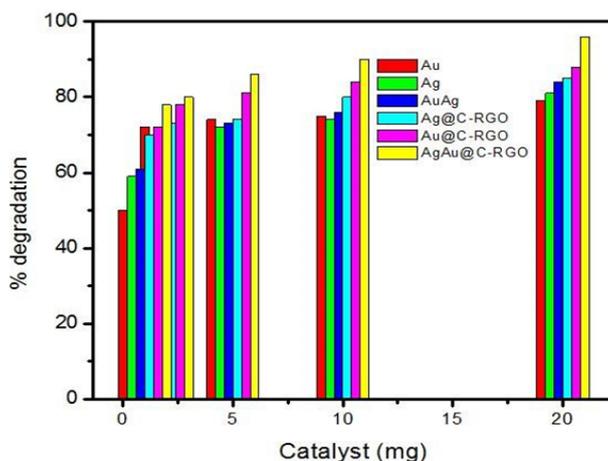
Fig. 8. Catalytic response towards number of reuse for the degradation of MG dye withAuAg@C-RGO hybrid catalysts.

4. Conclusion

The present communication focuses on the synthesis of one-pot green synthesis of the AuAg@CRGO using ascorbic acid through solid state synthesis followed by thermal annealing process. The solid-state reduction process yields complete reduction of metal nanoparticles over the RGO. Furthermore, on heating, a layered type of AuAg-Graphene oxide nanostructures are obtained. The AA plays bifunctional role, as reductant and surface protecting agent. In addition, the prepared catalyst exhibits excellent catalytic activity towards the degradation of Methylene

green dye. The proposed technique is a facile, fast, and eco-friendly method for the synthesis of the AuAg@C- RGO and also for environmental applications.

Acknowledgements

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