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Microwave Assisted Green Synthesis Of Luminescent Graphene Quantum Dot-Gold(GQD-AU)Hybrid Nanomaterials for Environmental Applications

Sijo Francis[*], **Akshaya Sasikumar**, **Manasy KS**
St. Joseph's College Moolamattom,
[*] Email: srsijofrancis@gmail.com

Abstract: Luminescent carbon quantum dots (CQDs) epitomize a new form of nanocarbon materials which have gained widespread attention in recent years. Carbon dots (C-dots) are a new class of carbon nanomaterials having size of less than 10 nm and possess excellent optical and electrical properties. Application of microwave power of 800 W for a period of 3 minutes to aqueous glucose solution, extraction of resulting solution with stabilizing agents, addition of aqueous $HAuCl_4 \cdot 3H_2O$ solution are done. Extraction of GQD using stabilizing agents leads to particle size reduction of Au and stability of the colloidal solution. This method provided an ultra-fast, more effective, economical, and easier synthesis. The formed carbon quantum dots were characterized by using UV–vis and optical techniques. The synthesized GQDs has excellent spectral, optical, and catalytic properties.

Keywords: Graphene quantum dots, microwave, hybrid nano materials

INTRODUCTION

Green is a strong color, the color of chlorophyll in plants. Protecting our environment cum planet is our responsibility. Green innovation currently receives international attention as the dreadful conditions of natural resources and environmental pollution. It encourages environment friendly techniques with minimum or zero waste. The major concepts are cleaner production, green innovation, social sustainability etc. Green technologies utilize less energy than conventional technologies. It is a clean technology and based on principles of environmental science, green chemistry, and modern technologies. It considers impact of the technology on the environment. Efficiency of the technology, recycling provisions, and health effects are the major concerns of the technology. Green technology has a significant impact on environmental, economic, and social status of society.

Green technology routes are holistic approach. Environmentally safe routes for the synthesis of materials, green methodology, less costly and less hazardous pathways are the needs of modern world. Biomass sources are economically important for the manufacture of technologically relevant molecules. Many polymer precursor moieties like acrylic acid, adipic acid and ε-caprolactam etc. derived from bio renewables and their bio-based preparation pathways are sustainable alternatives. Studies showed that green technology routes alone are insufficient in efficiencies, prices, and processing costs. They supplement their petrochemical equivalents in a greater manner. Renewable technologies facilitate the large-scale production of materials, novel innovation methods, prevention of pollution, and energy in a low-costly manner.

Numerous top-down and bottoms-up approaches utilized for the synthesis of GQDs include laser ablation, exfoliation, hydrothermal, catalyzed cage-opening, *etc.*

Microwave heating or microwave assisted hydrothermal method offers numerous advantages over other synthesis techniques such as formation of uniform particle size, facile and rapid synthesis, minimal use of chemicals, easy scalability, no requirement of additional surface passivating agents, etc. Facile methodology maybe employed for the reduction of other metal ions from their stable salts to metal atoms (such as Ag, Ni), thereby resulting in the synthesis of GQD-metal hybrid nanomaterials.

Here we followed Microwave-assisted hydrothermal synthesis of GQD. Optimization of important parameters that affect microwave assisted synthesis like power of microwave, reaction time, and role and mechanism of Stabilizing agents were conducted. Synthesis and Characterization of GQDs and GQD-Au hybrid particles using UV-Vis, TEM, XRD etc were also conducted. Applications of GQD-Au hybrid particles in catalysis were performed.

Materials and Methods

D-glucose (Fischer Scientific), Trisodium citrate dihydrate (Fischer Scientific) , Gold (III) chloride trihydrate (Merck) are used. GQDs and GQD-Au hybrid nanoparticles that are characterized using High Resolution Transmission Electron Microscopy (HR-TEM), UV–Visible (UV–Vis) spectroscopy, X-ray diffraction (XRD)

(a) Microwave-assisted hydrothermal synthesis of GQD

The synthesis of GQD involves pyrolysis of glucose facilitated by microwave assisted hydrothermal method. Measure 5 mL of D-glucose solution in a 50 mL of Erlenmeyer flask and place it in a domestic microwave. Irradiate the sample at 800 W microwave power for 3 min. The resulting viscous paste is extracted using 5 mL of tri-sodium citrate solution. A pale-yellow coloured solution conforms the synthesis of GQDs. Synthesized citrate stabilized GQDs are stable up to 3 weeks when stored at temperature < 4°C.

(b) Synthesis of GQD-Au hybrid particles

GQD-Au hybrid particles were formed by addition of aqueous $HAuCl_4.3H_2O$ solution to the pre-formed GQD solution at room temperature. The final GQD-Au solution was stored at temperature < 4°C. 5 mL of GQD-Au hybrid nanoparticles that are characterized using, UV-Visible (UV-Vis) spectroscopy, The synthesized citrate stabilized GQD-Au hybrid nanoparticles are stable upto 3 weeks when stored at temperature < 4°C.

RESULTS AND DISCUSSIONS

(*a*) Microwave-assisted hydrothermal synthesis of GQD

Glucose solutions (5 mL of 11% aqueous Glucose solution) were irradiated at different microwave power in the 800 W resulted in self-passivated GQDs with two characteristic absorption peaks in the UV-Vis absorption spectra. The effect of MW power in the range of 100-800 and the effect of MW irradiation time was studied.

(i)Effect of microwave power

Glucose solutions (5 mL of 11% aqueous Glucose solution) were irradiated at different microwave power in the range 100 W –800 W resulted in self-passivated GQDs with two characteristic absorption peaks in the UV–vis absorption spectra. The two characteristic peaks at 225 and 286 nm indicated the synthesis of GQD (Figure 1). The increase in microwave power results in increase in absorption peak intensity accompanied by redshift of absorbance band edge, whereas no change in the peak positions was observed.

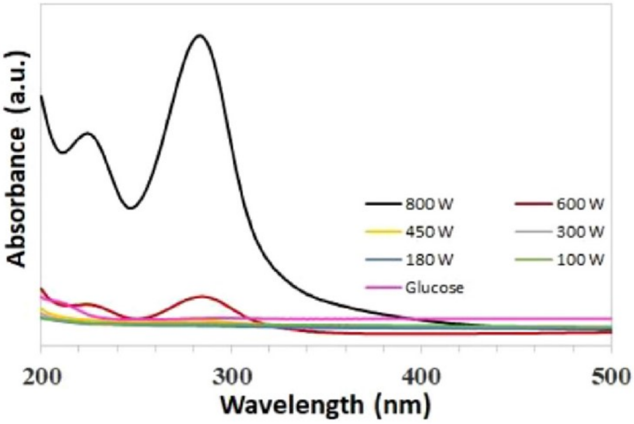

Figure1-Effect of microwave power (100 W –800 W) on the synthesis of GQD.

(ii) ***Effect of microwave time***

At an optimum microwave power of 800 W, glucose solution was heated in microwave with heating time ranging from 1 to 12 min. With increase in reaction time, the colour of GQDs obtained varied from pale yellow to dark brown. Deep UV absorption intensity was found to increase with increase in heating time.

Transmission electron microscopy (TEM) was used to investigate the morphology of GQDs. The TEM image indicates that the GQDs are obtained with the uniform particle size less than 5 nm. The XRD patterns of GQDs shows a broad peak at around 24 Å corresponding to the (002) peak which is matched with JCPDS Card No, 75-0444, suggesting that glucose produced graphene structures through the hydrothermal reaction. The X-ray diffraction (XRD) of the GQDs-Au nanohybrid confirms their crystalline nature and the five diffraction peaks were observed at Au (111), (200), (220), (311) and (222) for nanogold as well as one for graphene in the 2Θ range of 10–80^{O} for (002) plane were observed and are matched with the JCPDS card no. 75-0444 and 04-0784.

(b) **Synthesis of GQD-Au hybrid particles**

The GQD-Au hybrid particles absorb at 282 nm and 536 nm while GQDs show absorption peak at 286 nm (Figure 1). The use of stabilizing agents leads to smaller particle size of Au nanoparticles over GQD surface, as evident from cherry red colour of the solution, and enhanced the stability of the colloidal solution containing GQD-Au hybrid particles upto 7 days at temperature < 4 °C. A broad absorption peak at 536 nm is attributed to Au nanoparticles.

Optical Properties

The obtained GQDs were well dispersed in water with a pale -yellow color in sunlight, whereas the color would change to green under a 365 nm ultraviolet lamp (Figure 2). This is owing to the characteristic unsaturated carbon–carbon double bond in GQDs. Cherry red colour confirms formation of GQDS-Au Hybrid.

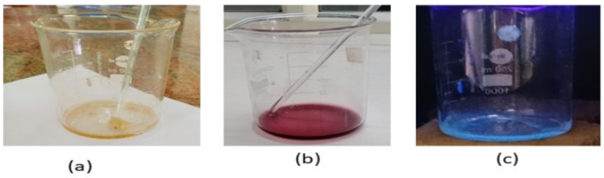

Figure2-Optical images of (a) GQDs, (b) cherry red colour of GQDS-Au nanohybrid Luminescent property of GQDs under UV-light

Optical properties of GQDs are important for their future applications in bioimaging and biosensors. The synthesized GQDs are dispersed well in water with an appearance of transparent, uniform and pale-yellow solution at day light, while exhibits the PL blue emission under UV light irradiation. The exact PL mechanism of GQDs is not clear yet, it may happen because of doping, electron-hole recombination, quantum effect, free zig-zag sites with a carbene-like triplet ground state, edge structure, and surface defects in the functional groups of the GQDs.

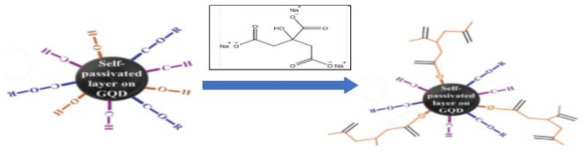

Figure 3-A schematic representation of surface stabilization of GQDs.
GQDs are also successful reductants for the reduction of gold (III) salts. The Au3+ ions were probably bonded and reduced by the –COOH and –OH groups of the GQDs, and further, the as-obtained AuNPs

(ii)Effect of stabilizing agent on the synthesis of hybrid nanoparticles

It is anticipated that the surface stabilization of GQDs affects the reducing power of GQDs due to the formation of an ester bond between the functional groups present on GQDs and that on stabilizing agents (citrate in this case). Tri-sodium citrate, being a bulkier molecule, also provides steric effects, further reducing the chemical reactivity of GQDs. Consequently, surface passivation results in slow and more controlled reduction of $HAuCl_4.3H_2O$ leading to the formation of smaller Au particles and stable colloidal solutions (Figure 3). were stabilized by these –COOH and –OH groups to GQD-Au hybrid nanoparticles show a surface plasmon band (SPR) at approximately 536 nm, the characteristic peak of gold nanoparticles, in the observed UV-vis spectra.

Catalytic activities of in the 4-nitrophenol reduction by $NaBH_4$

4-Nitrophenol is the accessory substance of the procedures used for manufacturing pigments, pesticides, and pharmaceuticals industry and hence regarded as one of the most highly poisonous and hazardous pollutants. The reduction of 4-nitrophenol to 4-aminophenol is extensively catalysed by GQDs-Au nanohybrid material, and this reduction is well-known to be very sensitive to the nature of the hybrid surface. Scheme of reduction reaction is given in Figure 4.

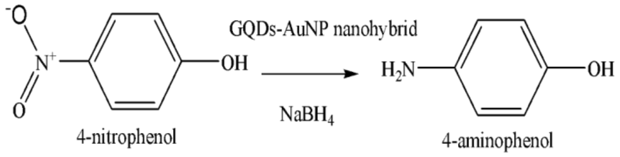

Figure 4-Scheme for the catalytic reduction of 4-nitrophenol

It is very convenient to monitor the progress of the reduction of 4-nitrophenol to 4-aminophenol by UV-vis spectroscopic analysis due to their typical absorption peaks at 400 nm (4-nitrophenol) and 300 nm (4-aminophenol). The degradation of 4-nitrophenol has been carried out in the presence of 5.0 mol% AuNPs with 100 equivalents of sodium borohydride in water at room temperature, and this large excess of sodium borohydride (Figure 5). However, the reduction reaction is not feasible by $NaBH_4$ alone. Moreover, the GQDs alone do not catalyze the degradation of 4-nitrophenol under these conditions (Figure 6).

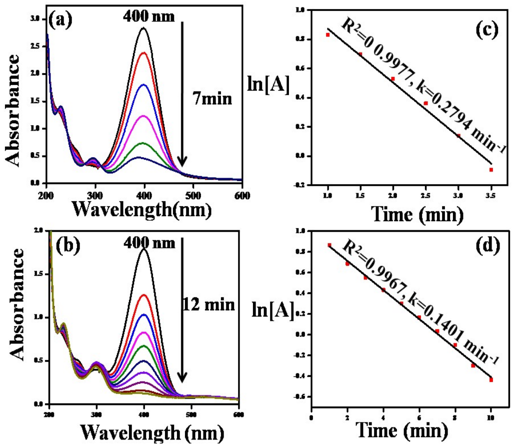

Figure 5-UV-vis. spectra for the reduction of 4-nitrophenol by $NaBH_4$ catalyzed using GQDs-AuNP nanohybrid

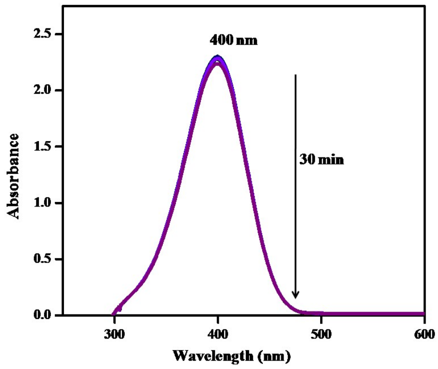

Figure 6-UV-vis. spectra showing the unfeasible reduction of 4-nitrophenol by $NaBH_4$ alone at 25° C

CONCLUSIONS

The GQDs were obtained by microwave assisted hydrothermal treatment of aqueous glucose solution for 3 min at 800 W. The resultant sticky yellow paste of GQDs obtained was extracted with 5 mL 0.01 M stabilizing agent solution prior to addition of aqueous $HAuCl_4 \cdot 3H_2O$ solution. GQD-Au hybrid particles were formed by addition of aqueous $HAuCl_4 \cdot 3H_2O$ solution to the pre-formed GQD solution Fat room temperature. Extraction of GQD using stabilizing agents leads to particle size reduction of Au and stability of the colloidal solution. The synthesized GQDs has excellent spectral and optical properties.

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