An Investigation of Silver Nanoparticles Formation under Presence of Graphene Quantum Dots as Reducing Reagent and Stabilizer

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In this work, we have studied effect of various reaction conditions for silver nanoparticles (AgNPs) production by a green and simple method. In our proposed method, silver nanoparticles have been formed and growth under presence of graphene quantum dots (GQDs) as reducing reagent and stabilizer. First, the small sized graphene quantum dots (GQDs) ($5\text{ nm} \pm 2\text{ nm}$) with abundant oxygen containing functional groups have been synthesis by hydrothermal method, then GQDs have been used to adsorb Ag^+ ions from solution onto GQDs's surface and after that, Ag^+ ions have been reduced into silver nanoparticles (AgNPs) by GQDs without adding any reducing reagents. GQDs were coated on the surfaces of the resultant AgNPs, leading to the formation of AgNPs/GQDs nano-hybrids. The optimized reaction conditions (such as pH, reaction time, temperature. . .) for synthesis of AgNPs using GQDs as a reducing reagent and stabilizer have been investigated. The synthesized AgNPs/GQDs have been characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Ultraviolet–visible spectroscopy (UV-Vis), and Dynamic Light Scattering (DLS). Results indicated that mono-dispersed AgNPs were obtained with particles size around 20 nm–40 nm. [doi:10.2320/matertrans.MD201713]

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1. Introduction

Recently, metallic nanoparticles have been receiving great attention due to their broad range of usage in different fields such as catalysis, photo-catalysis, chemical and bio-sensing, and nanobiotechnology. Among the low-cost noble metallic nanostructures, silver nanoparticles (Ag-NPs) have been much attended due to their unique properties, such as good electrical conductivity, photoelectrochemical activity, antimicrobial activity, and strong reduction power. The application of AgNPs has been extended to water disinfection in addition to water purification,¹⁾ antimicrobial coatings,^{2,3)} wound dressings,^{4,5)} textile industries,⁶⁾ agriculture,⁷⁾ sensor^{8,9)}/biosensor^{10,11)} and catalyst.^{12–14)} In addition, AgNPs hold incredible properties that are identified as localized surface Plasmon resonance (LSPR). Due to the sharp LSPR, Ag-NPs can be applied as colorimetric sensors in chemical sensing.¹⁵⁾

Silver nanoparticles can be synthesized by chemical, green and microbial approaches. Each approach has its own advantages and limitations. In chemical approach, AgNPs are synthesized by various methods, such as ultrasonic radiation, laser ablation, evaporative cooling, chemical vapor deposition, explosion, impregnation, co-precipitation, sol-gel, deposition–precipitation, microwave, and microbes.¹⁶⁾ In recent years, the green method for synthesis of AgNPs has been attended because of the safety and ecofriendly. Synthesis of AgNPs using plant extracts as the reducing agents and stabilizers is one of the most widely used green methods.¹⁷⁾ A variety of plants have been successfully utilized for synthesizing silver metal (Ag^0) nanoparticles from silver ions (Ag^+), such as *Jatropha curcas*,¹⁸⁾ *Capsicum anuum*,¹⁶⁾ *Argemone mexicana*,¹⁹⁾ *Ocimum sanctum*,²⁰⁾ *Ficus benghalensis*,²¹⁾ *Hibiscus rosa sinensis*,²²⁾ etc. Recent reports have also shown the potential use of low-cost agricultural

waste materials. However, the synthesis of AgNPs using using plant extracts as the reducing agents and stabilizers also has some limitations, such as purity of AgNPs product, which limits the application of AgNPs in many industrial fields such as electronics, chemical sensors and biosensors.

Recent time, graphene quantum dots (GQDs) have been known as excellent reducing reagent for synthesis of noble metal nanoparticles. These methods follow green approach but it can improve some disadvantages of using plant extracts, which have been mentioned above. There are several reports on synthesis of GQDs and using its application for synthesis of noble metal nanoparticles such as gold nanoparticles (AuNPs)²³⁾ or silver nanoparticles (AgNPs).^{24–26)} However, the influence of reaction factors on the formation of AgNPs still have not presented yet.^{9,23,25–30)} Therefore, the investigation effect of various factors for synthesis of AgNPs using GQDs as reducing reagent and stabilizer is much needed. In this work, we have synthesized of nitrogen graphene quantum dots (GQDs) and using it as reducing reagent and stabilizers for simple and green synthesis of silver nanoparticles (AgNPs/GQDs) by simple hydrothermal process. Various influent factors for synthesis process such as pH, reaction temperature, reaction time and ratio of reaction reagents have been carefully evaluated in the first time was reported.

2. Experimental Procedure

2.1 Materials

Silver nitrate powder (AgNO_3 , >99 mass%), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$); urea ($(\text{NH}_2)_2\text{CO}$); ammonia (NH_3) solution 28 mass% and acetic acid (CH_3COOH) solution 99 mass% were purchased from Sigma Aldrich.

2.2 Synthesis of graphene quantum dots (GQDs)

3.44 g citric acid and 3.005 g urea were dissolved into 100 ml distilled (D.I) water. The mixture was transferred to

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Fig. 1 (A) (i) UV-vis and (ii) FL spectra of GQDs; (B) TEM of GQDs; (C) Digital photographs of (i) water and (ii) GQDs solution under (a) normal light and (b) UV-light.

an autoclave and heated at 160°C for 8 h. Then, the mixture was centrifuged at 5000 rpm for 20 min to remove the big carbon particles. The supernatant containing graphene quantum dots (GQDs) was collected.

2.3 Synthesis of silver nanoparticles (AgNPs) using GQDs as reducing reagent and stabilizer

100 μ L of GQDs stock solution was added into 3 mL of D.I water, then 0.1 M NaOH and 1 M CH_3COOH solution were used to control pH of GQDs solution from pH = 3 to pH = 11. After that, 20 μ L of 0.1 M AgNO_3 solution was added into the GQDs solution. These mixtures were heated at 26°C to 90°C for 60 minutes to 180 minutes to reduce of Ag^+ ion to silver nanoparticles (AgNPs). AgNPs-GQDs solutions then were cooled to room temperature (RT) and stored at 4°C for further characterization.

2.4 Characterization

Absorbance measurements (UV-Vis) spectra were measured using Agilent 8453 UV-Vis spectrophotometer system with the wavelength in a range of 200–1200 nm. Particles size and shape of GQDs, AgNPs/GQDs nanohybrids were analyzed by Transmission Electron Microscope (TEM, JEOL, Voltage: 100 kV, magnification: $\times 200,000$). X-ray Diffraction (XRD) patterns of AgNPs/GQDs was obtained at room temperature by D8 Advance, Bruker ASX, using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of $2\theta = 10^\circ$ – 60° , and a scanning rate of 0.02 s^{-1} . Particles size distribution was analysed by Dynamic Light Scattering (DLS) on the Nano Partica SZ-100 (HORIBA Scientific, Japan).

3. Results and Discussions

3.1 Characterization of GQDs

The UV-vis absorption spectrum of GQDs (Fig. 1(A), curve (i)) exhibited two distinct absorption peaks at about 220 nm and 345 nm, which were attributed to the π – π^*

transition of $\text{C}=\text{C}$ and the n – π^* transition of $\text{C}=\text{O}$, respectively. The fluorescence emission spectra of the GQDs were recorded and maximum fluorescence emission ($\sim 520 \text{ nm}$) was obtained with an excitation wavelength of 380 nm (Fig. 1(A), curve (ii)). Figure 1(C) presented the color of water (i) and GQDs solution (ii) under normal light (Fig. 1(C).a)) and violet light (Fig. 1(C).b)). It can be seen the emission at blue light of GQDs in solution under excited of the violet light. Moreover, the emission wavelength showed a red shift with increasing excitation wavelength (data not shown). These results are high agreement with previous reports.^{31–33} According to the TEM image (Fig. 1(B)), the synthesized GQDs were of spherical shape and monodisperse nanoparticles with size distribution in the range of $5 \pm 2 \text{ nm}$.

3.2 Synthesis of AgNPs using GQDs as reducing reagent and stabilizer

3.2.1 Effect of pH

Compared with UV-vis spectra of QGDs (Fig. 2(A), curve (a)), it can be seen that the new absorption peak around $\sim 420 \text{ nm}$ to 441 nm has appeared with mixture of GQDs + AgNO_3 solution after reducing process (Fig. 2(A), curve (b) to curve (f)). These specific peaks can be attributed to AgNPs, which have been formed in presence of GQDs as reducing reagent. However, at low pH, i.e., pH = 5 (Fig. 2(A), curve (f)) and pH = 3 (Fig. 2(A), curve (g)), the absorption peak of AgNPs was red-shifted due to increasing of AgNPs's size. Effects of pH on the position of AgNPs's plasmon peak (the absorption maximum, λ_{max}) and peaks's intensity of AgNPs (optical densities at the absorption maximum, OD) were summarized in Fig. 2(B). It is clearly shown that at pH = 9 (pH9) the position of plasmon peak of AgNPs were lowest wavelength which indicated that the smallest size of AgNPs (Fig. 2(B)) have been formed in solution when the reaction was carried out at this pH. Moreover, plasmon peak intensity of AgNPs at pH9 was also highest, which can be attributed to highest concentration of

Fig. 2 (A) UV-vis spectra of (a) GQDs solution; curve (b) to (e) AgNPs/GQDs solutions after reduction at different pH; (B) Effect of pH on position of AgNPs's plasmon peak (the absorption maximum, $\lambda_{\max}$) and peak's intensity (optical density-OD) (insert: digital photographs of the corresponding samples from (A)).

formed AgNPs in solution. These results suggested that pH9 is suitable medium for the reaction.

3.2.2 Effect of reaction temperature

Following Arrhenius equation (eq. (1)), at higher reaction temperature the reducing reaction will be faster:

$$k = k_0 \cdot e^{-\frac{E_a}{RT}} \quad (1)$$

Where: k is the rate coefficient; k_0 is a constant, E_a is the activation energy ($\text{J} \cdot \text{mol}^{-1}$), R is the universal gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T is the temperature (in kelvin, K). In the nanomaterials synthesis reaction, high reaction rate may be led faster particle growth rate and giving bigger particle size. However, in this case, GQDs play the role as reducing reagent as well as protectors therefore they inhibited the growth of AgNPs. It can be observed in Fig. 3(A), at low temperature (26°C and 40°C), the optical density of AgNPs was very low indicating that low concentration of formed AgNPs. Figure 3(B) shown that at 90°C AgNPs/GQDs sample has lowest absorption peak wavelength ($\lambda_{\max} \sim 408 \text{ nm}$) of AgNPs. Moreover, this sample also has highest peak intensity, with the optical density $\text{OD}_{408 \text{ nm}} \sim 1.6$. These results indicated smallest particles size of formed AgNPs in solution. DLS spectra of AgNPs/GQDs solution (Fig. 3(C)) shown two zones of particle size distributions when reaction temperature were 26°C, 40°C, 60°C and 80°C. At 90°C there is only one zone of particles size distribution, which indicated at this temperature, the particles size of AgNPs/GQDs was

Fig. 3 (A) UV-vis spectra of AgNPs/GQDs solutions were synthesized at different temperature: (a) 26°C; (b) 40°C; (c) 60°C; (d) 80°C and (e) 90°C, respectively; (B) Effect of reaction temperature on position of AgNPs's plasmon peak ($\lambda_{\max}$) and peak's intensity (OD) (insert: digital photographs of the corresponding samples from (A)); (C) Particles size distribution of AgNPs/GQDs by DLS method of the corresponding samples from (A).

more homogeneous. Therefore, the temperature of 90°C has been used for further experiments.

3.2.3 Effect of reaction time

In Fig. 4(A) shown UV-Vis spectra of AgNO_3 /GQDs solution after reducing at 90°C for different times. It can be seen AgNPs's plasmon peak ($\lambda_{\max}$) and peak's intensity ($\text{OD}_{\lambda_{\max}}$) of AgNPs were similar for all samples. However, DLS results (Fig. 4(B)) demonstrated that mean particle sizes were shifted to smaller when reaction time increasing. The

Fig. 4 (A) UV-vis spectra of AgNPs/GQDs solutions were synthesized at 90°C for different reaction time: (a) 60 min; (b) 80 min; (c) 100 min; (d) 120 min and (e) 180 min, respectively; (B) DLS analysis of the corresponding samples from (A); (C) Effect of reaction time on mean particles size of AgNPs/GQDs (insert: digital photographs of the corresponding samples from (A)).

relative of reaction time and mean size of AgNPs/GQDs vs. reaction time were summarized in Fig. 4(C). These results suggested that this reaction needs 2 hours to complete.

3.2.4 Effect of Ag^+ /GQDs ratio

In these reactions, AgNO_3 (as Ag^+ ion) plays the role as oxidation reagent and GQDs plays the role as reducing reagent. Therefore, the good product will be obtained if these two reagents are equivalent. However, it is very difficult to estimate the concentration of GQDs in solution as well as estimate the number of reaction centers on one GQD particles. Therefore, the ratio 0.1 M AgNO_3 solution volume

Fig. 5 (A) UV-vis spectra of AgNPs/GQDs solutions were synthesized at 90°C for 120 min with different ratio of AgNO_3 /GQDs solutions. Reaction conditions were described in the text. (B) Effect of volume ratios of AgNO_3 and GQDs solutions on position of AgNPs's plasmon peak (λ_{max}) and peak's intensity (OD) (insert: digital photographs of corresponding samples from (A)); (C) DLS analysis of the corresponding samples from (A), respectively.

and GQDs solution volume were used to find out the optimized point of AgNO_3 /GQDs ratio. It can be seen in the UV-Vis spectra (Fig. 5(A)), samples (a) to sample (e), the absorption peaks were around 418 nm to 425 nm, however, with sample (f) and sample (g) the plasmon peak of AgNPs were shifted to red zone (~ 700 nm to ~ 800 nm). These shifts can be attributed to the agglomeration of AgNPs and/or the change of AgNPs's shape. Figure 5(B) shown the relative of Ag^+ /GQDs ratio on the plasmon peak position of AgNPs (λ_{max}) and optical densities at the absorption maximum

Fig. 6 (A) DLS of AgNPs/GQDs sample was synthesized at optimized conditions (insert: digital photographs of (i) AgNO₃/GQDs solution before and (ii) after reduction); (B) XRD of AgNPs/GQDs product; (C, D) TEM of AgNPs/GQDs was synthesized at pH 9 and (E, F) at pH 7 with low magnification (C, E) and high magnification (D, F), respectively.

(OD_{lmax}). It can be seen that the condition from sample (e) (with $\lambda_{\text{max}} = 417 \text{ nm}$ and OD_{417nm} was 1.185) can be used as the optimized condition for this reaction. Size distributions indicated that condition of samples (a), (b), (c) and (d) have given big AgNPs/GQDs's size however size distributions were very narrow (Fig. 5(C)). Condition of sample (g) and sample (f) have very large size distribution (from 10 nm to 1000 nm). Condition of sample (e) has also large size distribution however its mean size around 20 nm. Therefore condition sample (e) was used as optimized Ag⁺/QGDs ratio for synthesis of AgNPs/GQDs.

3.3 Characterization of AgNPs

Based on the optimized conditions were obtained above, we have synthesized AgNPs/QGDs for further characterizations. Figure 6(A) shown DLS of AgNPs/GQDs

solution with mean particle size of AgNPs/GQDs around 40 nm was obtained. It can be observed AgNPs/GQDs particles have one distribution zone from 10 nm to 150 nm. Figure 6(A) (insert) shown AgNO₃/GQDs solution before as colorless (solution (i)) and after reaction at optimized conditions (solution (ii)) the AgNPs/QGDs was formed as orange color, a specific color of AgNPs colloid. A diffractogram of AgNPs/GQDs is shown on Fig. 6(B), which evidences the typical diffraction planes (111), (200), (220) of the *fcc* lattice of AgNPs. Line broadening in the pattern can be quantitatively evaluated using Debye–Scherrer equation (eq. (2)), which gives a relationship between peak broadening in XRD and particle size:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)$$

Where, D is the thickness of the crystal, k is the Debye–Scherrer constant (0.9), λ is the X-ray wavelength (0.15406 nm) and β is the line broadening in radian obtained from the full width at half maximum, θ is the Bragg angle. According to Debye–Scherrer equation, particle sizes of AgNPs/GQDs are estimated to be 30 ± 5 nm. These results are consistent with those obtained by TEM technique (see below). In addition, it can be seen in Fig. 1(C) that no specific XRD peak of GQDs can be seen, possibly this peak is too weak and overlapped by the background signal. The results confirmed the successful preparation of the AgNPs using graphene quantum dots (GQDs) as reducing reagent and stabilizer.

TEM micrographs of AgNPs/GQDs were shown in Fig. 6(C) to Fig. 6(F). At pH 9 (Fig. 6(C) and Fig. 6(D)), it show that the AgNPs have a spherical shape, a smooth surface morphology and particle sizes from 5 nm to 40 nm. Moreover, it can be observed that almost particles have small size around 10 nm and a part of particles have size around 20–40 nm, which has high agreement with DLS data above. Figure 6(E) and Fig. 5(F) presented TEM images of AgNPs/GQDs were synthesized at pH7. In Fig. 6(E) (low magnification), it can be observed the homogeneous of AgNPs/QGDs in particles size (around 20–60 nm). However, at high magnification (Fig. 6(F)) we can observe that there are many very small particles of AgNPs/QGDs in the sample. This sample is typical for two distribution zones in DLS results (data not shown). Overall, TEM results indicated the very low aggregation of AgNPs was evidenced, which demonstrates the stabilizing role of GQDs. GQDs plays the role of protectors for AgNPs surface by binding between covalent electron pairs of $-\text{COO}^-$ and $-\text{NH}_2$ group of GQDs with d orbitals of Ag^0 atoms and/or Ag^+ ions on AgNPs's surface and therefore it can prevented the aggregation of AgNPs, so that AgNPs/GQDs can be stored for a long period and be stable in aqueous solutions.^{9,23,26,27,30)}

4. Conclusions

As summarized, this work has focused on studying the effect of various reaction conditions on the forming of silver nanoparticles (AgNPs) using graphene quantum dots (GQDs) as reducing reagent and stabilizer. The small sized graphene quantum dots (GQDs) with abundant oxygen containing functional groups have been synthesis by hydrothermal method, then GQDs adsorbed Ag^+ ions and reduced them into silver nanoparticles (AgNPs) without adding any reducing reagents. We have optimized reaction conditions for synthesis of AgNPs using GQDs (such as pH 9, reaction temperature 90°C for 2 hours). The AgNPs/GQDs products with mono-dispersed AgNPs were obtained with particles size around 20 nm–40 nm, which has been observed and characterized by TEM, XRD, UV-Vis and DLS analyst.

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