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Short Communication

Preparation and Stabilization of Monodisperse Colloidal Gold by Reduction with Monosodium Glutamate and poly (Methyl Methacrylate)

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In this research, gold nanoparticles are prepared via chemical reduction method by varying the concentrations of monosodium glutamate as reducing agent and stabilizer. Characterization studies are carried out using TEM, UV-visible, photoluminescence and FTIR spectroscopy. Image from TEM reveal that spherical shaped and well-dispersed gold nanoparticles were produced successfully. The absorption spectra exhibit a blue-shift with decreasing particle size. The quantum efficiency of gold nanoparticles is found to be higher for high concentrations of monosodium glutamate. However, this is negated by the fact that the particles exhibit the tendency to aggregate with higher concentrations of monosodium glutamate. In this work, PMMA is introduced as a capping agent to improve the stability of gold nanoparticles. The FTIR spectra confirms the influence of PMMA as a capping agent.

Keywords: Nanostructures; metals; chemical synthesis; optical properties

1. INTRODUCTION

Metallic nanoparticles have recently received much attention due to their unique optical, electrical and catalytic properties [1, 2]. The extremely small size, large surface to volume ratio and increased surface activity of the nanoparticles have rendered them applicable to a widespread range of chemical and physical aspects. To utilize and optimize the chemical/physical properties of nanosized metal particles, a large spectrum of research has been devoted to the control of the size and shape of the particles which is crucial in tuning their physical, chemical and optical properties [3-6]. In order to prepare nanoparticles with high monodispersity and controllable size, which in turn, prevent aggregation without disturbing the desired properties, a crucial issue is to achieve protection of the particles [7]. In most cases, the surface passivation reagents, including surfactant molecules and polymers are needed to prevent the nanoparticles from aggregation. The surface modification of these colloidal nanoparticles is very important to facilitate their application to biotechnology, catalysis and nanocomposites.

Among the various metallic nanoparticles, gold had been widely studied due to its chemical inertness and resistance to surface oxidation [8]. With regards to the preparation of gold nanoparticles, many synthetic methods have been developed to form and to stabilize gold nanoparticles, among which reduction in homogeneous solutions remains the simplest and most versatile method [9]. Various approaches differ mainly in the way the electrons needed for the reduction are provided.

Synthesis of gold nanoparticles involves reduction of a gold solution ($AuCl_3$ or $HAuCl_4$) by tri-sodium citrate to form gold crystals [10-11]. The excess citrate ions in the medium are adsorbed onto the nanoparticles until there is sufficient electrostatic repulsion to keep them from agglomerating. Other methods used to obtain gold nanoparticles involve the use of organic solvents [10].

In this work, gold nanoparticles are synthesized using monosodium glutamate as a reducing agent. However, the particles possesses the tendency to aggregate in high molar ratios of gold capped with glutamates, and are therefore, unstable. Consequently, PMMA is introduced as a polymer capping agent tp stabilize the gold nanopartices.

2. EXPERIMENTAL

Gold nanoparticles were prepared using the following method, 100 ml of 5 mM of $AuCl_3$ (Sigma-Aldrich) was heated until the boiling phase. Upon boiling, 3 mL of 100 mM monosodium glutamate was added to the solution. The solution changed in colour from light yellow to a deep red colour, which is typical of gold nanoparticles. At this point, the solution was rapidly quenched to room temperature. The above procedure was repeated for 150, 200, 250 and 300 mM of monosodium glutamate. In order to cap the gold nanoparticles with the organic solvent, 10 mL of PMMA was added into the solution after water quenching. This step was then repeated for 150, 200, 250 and 300 mM of monosodium glutamate.

The absorption spectra of gold nanoparticles suspension were measured by using a UVIKON 923 Double Beam UV-vis spectrophotometer.

The photoluminescence (PL) spectra were measured using a Perkin Elmer LS55 fluorescence spectrophotometer with an excitation source from Xe lamp within the wavelength range of 450 - 750 nm. Quartz cuvettes were utilized in both absorbance and emission measurements. Transmission electron microscopy (TEM) samples were prepared by placing a drop of dilute methanol suspension of gold nanoparticles onto the surface of a 300-mesh copper grid which was then dried for five days. TEM images were acquired using LEO LIBRA operating at 120 kV. To identify and characterize the organic species on the surface, Fourier transform infrared spectroscopy (FTIR) spectra were obtained using NICOLET IS 10 spectrophotometer, within the wavenumber region between 4000 and 400 cm^{-1}.

3. RESULTS AND DISCUSSIONS

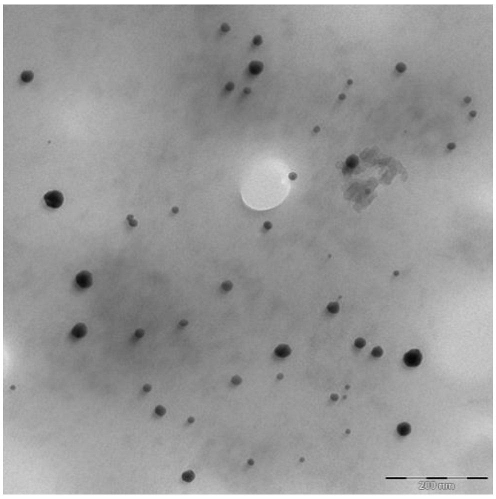

Figure 1. TEM image of gold particles reduced with 100 mM of monosodium glutamate.

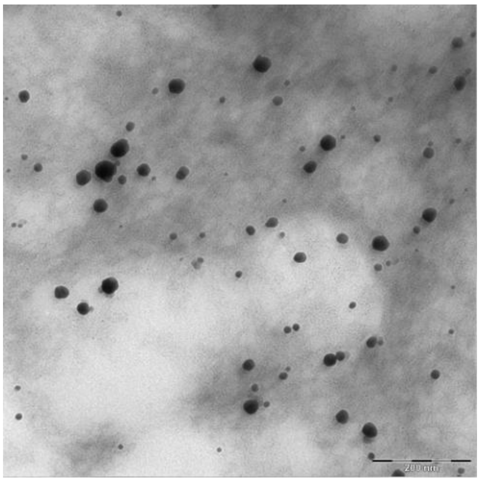

Figure 2. TEM image of gold particles reduced with 200 mM of monosodium glutamate.

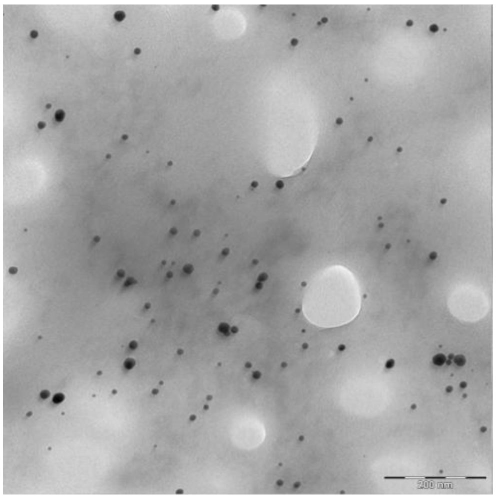

Figure 3. TEM image of gold particles reduced with 300 mM of monosodium glutamate.

Figs. 1 – 3 show TEM images for gold particles prepared with different concentrations of monosodium glutamate. The surface morphology of the particles is nearly spherical and the samples display high dispersion. The average size of the particles for 100, 200 and 300 mM monosodium glutamate is 18, 15 and 9 nm, respectively. It is clearly shown that high molar ratios of monosodium glutamate produce smaller particle size.

Fig. 4 shows TEM image of gold nanoparticles with PMMA as capping agent. It can be clearly seen that the samples display high dispersion and homogeneity when prepared via this method. It can be concluded that PMMA is a favourable stabilizer for gold particles to prevent further growth and precipitation of the nanoparticles' core.

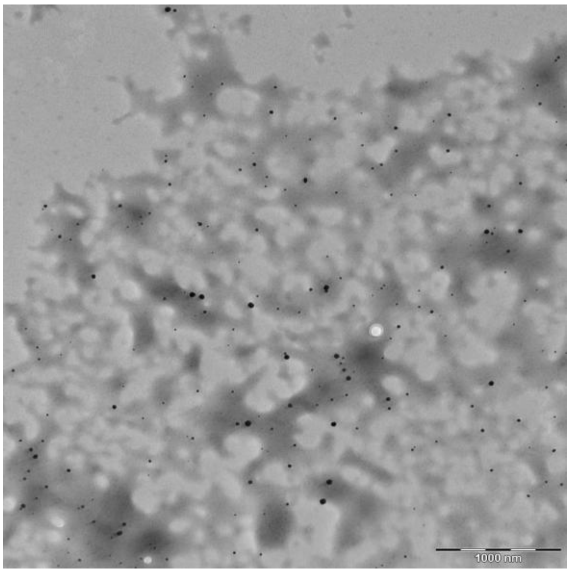

Figure 4. TEM image of gold particles stabilized with PMMA.

Table 1. Surface plasmon resonance (SPR) and full width at half maximum (FWHM) for gold particles at different concentrations of monosodium glutamate and stabilized with PMMA.

Concentration of glutamate (mM)	SPR peak (nm)	FWHM (nm)
100	528	44
150	525	32
200	524	28
250	517	22
300	512	24

Fig. 5 shows the absorption spectra obtained for gold particles with different molar ratios of monosodium glutamate. The results are summarized in Table 1. With an increase in glutamate concentration, the synthesis of gold nanoparticles shows different SPR peaks and FWHM, as shown in Table 1. This result indicates that the gold particles produced possess different size and blue-shift in SPR peaks and FWHM varies with decreasing gold diameter. It has been well established that the maximum wavelength of nanoparticles strongly depends on size, shape and the dielectric environment, so this directly corresponds to a shift of the absorption peak, whereby small gold particle sizes will cause an absorption peak shift to smaller wavelengths, higher frequency and energies [12]. The nanoparticles are stabilized by physical adsorption of excess anions (glutamate ions) in the solution medium. Consequently, such colloidal suspensions are very sensitive to change in the concentration of ions in the solution. As the concentration of glutamate is increased, the absorption spectra show blue-shift in SPR peak. The adsorbed glutamate ion onto the gold nanoparticles is increased higher concentrations of glutamate. This introduces the negative charge onto the particle surface and thus repels the particles away from each other, preventing them from aggregation.

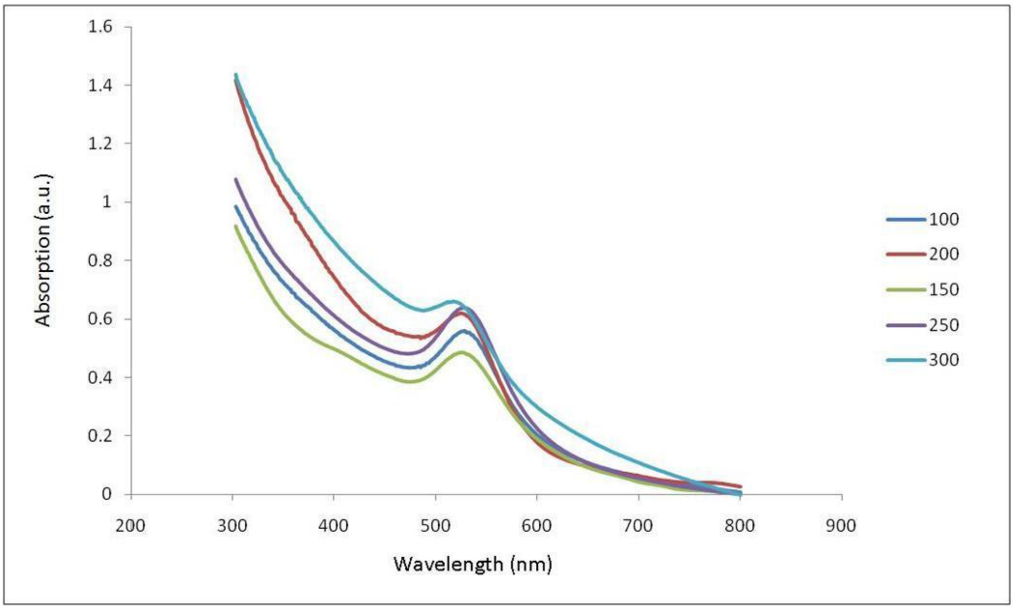

Figure 5. UV – vis absorption spectra of gold particles with different molar ratios of monosodium glutamate stabilized with PMMA.

Fig. 6 shows the PL spectra of gold particles with different concentrations of monosodium glutamate at 533 nm when subjected to excitation of 265 nm. It can be clearly seen that the PL peak is independent of the particle size whereas the intensity increases with decreasing particle size [13]. The increase in PL intensity is presented in terms of the increase of the PL quantum efficiency [14]. Based on these results, it can be concluded that the PL quantum efficiency increases if the glutamate concentration increases. This result is attributed to increased emission from the surface states. The number of atoms and ions on the surface is specifically larger than that in the bulk material, and therefore the surface structure and particle states affect the characteristics of the particles significantly. If the presence of surface traps is significant, the quantum efficiency of the sample is reduced, which in turn, gives the lower PL intensity.

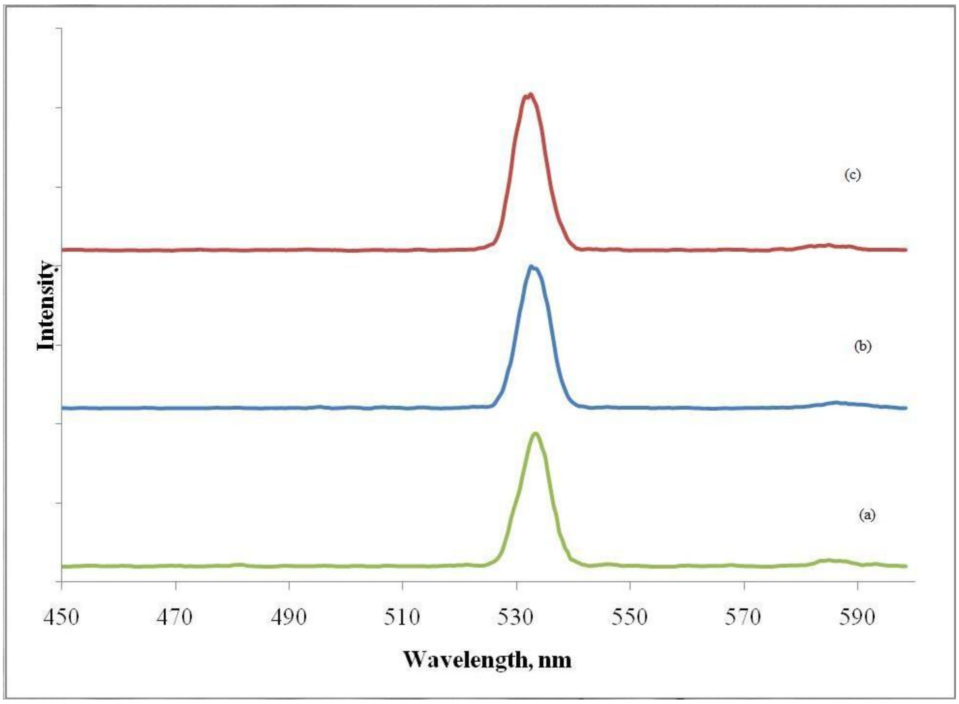

Figure 6. PL spectra of gold particles stabilized with PMMA with different molar ratios of monosodium glutamate (a) 100 mM (b) 200 mM (c) 300 mM.

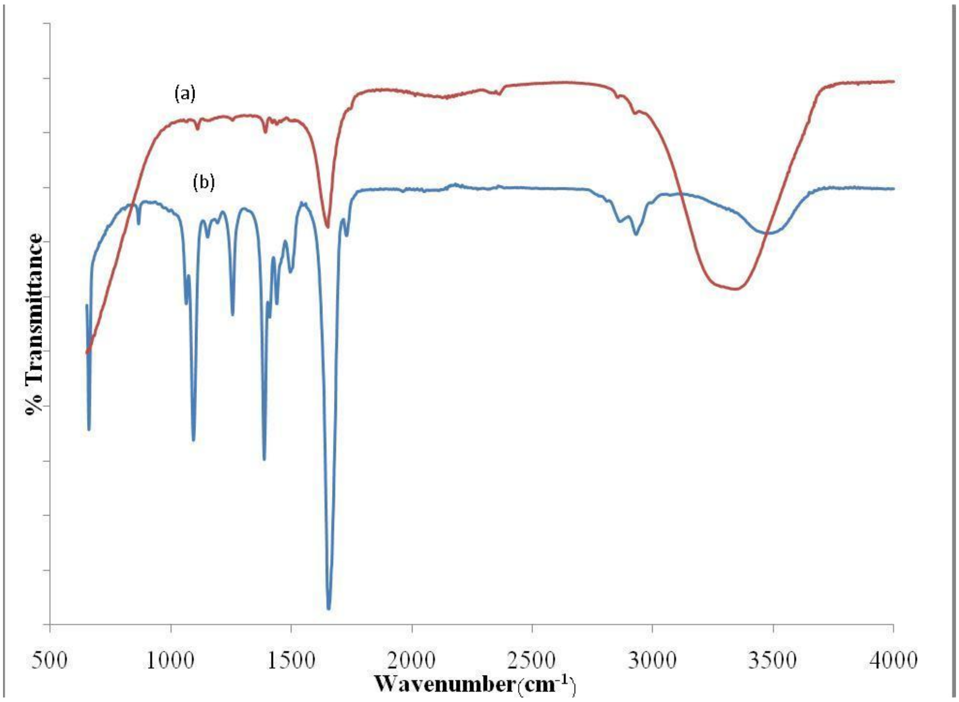

Figure 7. FTIR spectra of (a) PMMA in DMF solution (b) gold particles stabilized with PMMA.

Fig. 7 shows the FTIR transmittance spectra of gold particles and PMMA in DMF solution. For gold particles capped with PMMA, the spectra exhibit reduction in peak intensities in the wave number region of 1000 - 3000 cm^{-1} due to the dilution effect of water during the preparation stage. A new peak appears at a wave number of 3300 cm^{-1}, which represents the O-H bond. A peak which corresponds to the C-O bond appears at 1100 cm^{-1}. The peak at ~1255 cm^{-1} shows the C-N bond representing the amine functional group. C-H scissoring and bending behaviour is shown by a peak between ~1390 - 1500 cm^{-1}. However, the presence of IR peaks at 1650 - 1750 cm^{-1} and 2850 – 2950cm^{-1} indicates the C=O and C-H bond, respectively. On the basis of the FTIR data, the surface of the gold particles is mainly capped with PMMA. Flexible organic molecules provides repulsive interactions between gold particles thus preventing aggregation.

4. CONCLUSIONS

High-quality gold particles with spherical shapes and narrow size distribution have been successfully synthesized, as confirmed by the TEM images. The UV-vis absorption spectra exhibit blue-shift characteristic with decreasing particle size due to increasing glutamate concentration. The quantum efficiency of gold particles was improves with increase in glutamate concentration. The FTIR spectra confirm the presence of PMMA as a capping agent of gold particles. By alteringthe glutamate concentration, the size of gold particles is tunable.

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