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Research Article
Effect of Polyethyleneimine Stabilizer on Size and Morphology of Gold Nanoparticles

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Abstract

Background: Gold nanoparticles have attracted much more attention in many applications and the kind of these applications depends on the size and morphology of gold nanoparticles. Many polymers were used to control the size and shape of gold nanoparticles. **Methodology:** Herein, gold nanoparticles were prepared at room temperature by reducing tetrachloroauric (III) acid using gallic acid as a reducing agent in the presence of polyethyleneimine as a stabilizer. The role and the effect of the amount added from polyethyleneimine (PEI) on the size and morphology of the prepared gold nanoparticles were studied. The colloidal gold nanoparticles solutions were characterized using UV-vis spectrophotometer, transmission electron microscopy and fourier transform infra-red spectroscopy. **Results:** The prepared gold nanoparticles were found to be uniform circular particles with size range 5-12 nm. The UV-vis spectrophotometer revealed that in the absence of polyethyleneimine no gold nanoparticles were developed, this clarifies that polyethyleneimine is not only acted as a stabilizer but also as a reducing agent. **Conclusion:** The particle size of the prepared gold nanoparticles was found to be decreased as the amount of polyethyleneimine increase.

Key words: Gold nanoparticles, polyethyleneimine, UV-vis spectrophotometer, transmission electron microscopy, fourier transform infra-red spectroscopy

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In recent years, the synthesis and applications of gold nanoparticles have attracted the interest of many researchers, due to their attractive and unique properties. Available literature provides information about potential applications of gold nanoparticles in sensing[1], drug delivery[2], catalysis[3,4], cancer diagnosis and therapy and many other domains in medicine and technology[5-7]. Many chemical and physical methods have been used to prepare a variety of gold nanoparticles; these methods include seed-mediated growth[8,9], use of reverse micelles[10], phase transfer reactions[11,12], thermolysis[13], radiolysis[14,15], photochemistry[16], sonochemistry and green biosynthesis[17-20]. Among these, chemical methods are still the preferred method for the preparation of gold nanoparticles. Gold nanoparticles, in general are prepared by chemical reduction of chloride precursor under aqueous conditions by a well-known Turkevich method[21], which involves the reduction of tetrachloroauric acid ($HAuCl_4$) by sodium citrate in water. Several other groups have reported the synthesis of Au-NPs either by $NaBH_4$ or citrate reduction of $HAuCl_4$ in the presence of a stabilizer (e.g., small organic molecules, polymers and biomacromolecules) containing at least one NH_2, COOH or SH group in a non-polar medium[22-29]. It is well known that nano-sized metal clusters were stabilized during synthesis by the existence of polymeric stabilizers. The addition of hydrophilic long chain polymer during such synthesis not only provide stabilization due to the intensive short-range steric repulsions that polymers are able to produce but also act as a ligand for functionalization of gold nanoparticles[30]. High molecular weight polymers[31-35], thiol derivatives[36-40] and other ligands[41-43] used as capping reagents are often used to control the particle size and shape, prevent aggregation and improve the function of the particle surface for application in bio-analytical methods.

In this study, a one-step method for the synthesis of biocompatible gold nanoparticles using gallic acid as the reducing agent in the presence of polyethyleneimine as a polymeric stabilizer at room temperature is reported. The effect of the amount of PEI on the size and shape of gold nanoparticles were investigated. The UV-vis spectrophotometry, transmission electron microscopy and fourier transform infra-red spectroscopy were employed in the characterization of the prepared gold nanoparticles.

MATERIALS AND METHODS

Chemicals: About 0.3 mM stock solution of tetrachloroauric (III) acid (Molecular weight = 393.83) used throughout the work was prepared by dissolving 0.1181 g $HAuCl_4.3H_2O$ in 1 L deionized water. This stock solution of gold (III) ions can be prepared in advance if stored in a brown bottle. The 0.25 mM stock solution of gallic acid (Molecular weight = 170.12) was prepared by dissolving 0.0213 g of gallic acid in 500 mL deionized water. Polyethyleneimine molecular weight 60000 as a polymeric stabilizer was used as a 1 M solution.

Methods of preparation: Gold nanoparticles were synthesized by dropping $HAuCl_4$ (0.3 mM and 80 mL) on gallic acid (0.25 mM and 20 mL) solutions. The reactions were kept under stirring (rpm = 1500) for 30 min after complete addition of gold solution. It was observed that the solution was colorless. This precursors solution was divided equally into four parts then PEI 1 M solution (0, 0.125, 0.5 and 1 mL) was added, respectively. It was observed that the solutions were changed into wine red color with the addition of PEI. The reactions were kept for 30 min at room temperature.

Characterization techniques: The UV-vis spectroscopy of the prepared samples was studied using UV-vis spectrophotometer (Perkin Elmer model GBC 902). The FTIR analysis was performed using fourier transform infra-red spectrophotometer FTIR-8400 S Shimadzu-Japan. The morphology of the prepared samples was studied by Jeol JEM transmission electron microscope (TEM) with Max. Mag. 600 kX and resolution 0.2 nm. For TEM measurements, the samples were prepared by sonication for 30 min.

RESULTS AND DISCUSSION

In this study, PEI plays a role in the preparation of gold nanoparticles by enhancement of the formation of Au^0 through coupling of Au^+ with the lone pair of electrons of the nitrogen atom of the amino group. As it is observed the condition applied without using seed solution of gold nanoparticles gallic acid is not strong enough to achieve complete reduction of Au^{3+} to Au^0 and the mechanism approach may be explained by two-step reduction process. 1st step assumed to be the reduction of Au^{3+} species to Au^{1+} species forming a linear $AuCl_2^-$ complex which does not absorb in UV-vis region[44] as Eq. 1:

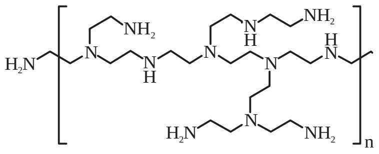


Fig. 1: Polyethyleneimine structure

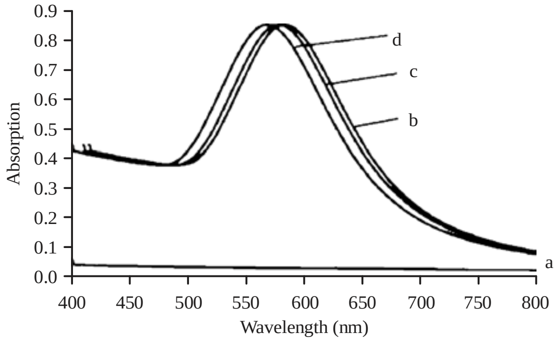
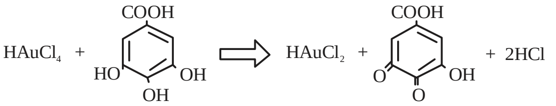


Fig. 2: UV-vis spectra of colloid solutions of gold nanoparticles stabilized by different concentrations of 1 M PEI, a: 0, b: 0.125, c: 0.5, d: 1 mL



(1)

This step is followed by the reduction of Au^+ to Au^0 with the addition of PEI (Eq. 2) through electron transfer from nitrogen atom in an amino group (Fig. 1):

$$AuCl_2^- + e^- \Longrightarrow A^0 + 2Cl^- \tag{2}$$

Ultra violet-visible spectroscopy: The UV-vis absorption spectroscopy is one of the most important methods used for characterizing the optical properties and electronic structure of nanoparticles as the absorption band are correlated to the diameter and the aspects ratio of the nanoparticles[45]. The colloidal solution of gold nanoparticles have wine red color due to tiny dimensions. Surface Plasmon Resonance (SPR) is a phenomenon arises from the fact that the electron cloud in case of nanoparticles oscillate on the particles surface and absorb electromagnetic radiation. In the present study (Fig. 2a) shows the UV-vis spectra of the colloidal precursor solutions prepared without PEI, the Fig. 2 has no absorption band indicating that gold nanoparticles are not formed as it was explained elsewhere. Meanwhile, Fig. 2b-d show the colloidal nano-gold prepared in the presence of 1 M solution of PEI with different concentrations 0.125, 0.5 and 1 mL, respectively. The spectra revealed that as the concentration of PEI increase the absorbance exhibit blue shift from 548-538 nm. This behavior could be devoted to the decrease of the particles size in agreement with TEM images.

Transmission electron microscopy: Figure 3 shows the TEM images of gold nanoparticles investigating the effect of PEI as a stabilizer. The TEM images revealed that the particle size decrease dramatically with using PEI in Fig. 3a represent the images of colloidal precursors solution in the absence of PEI, the image shows mass particles in the range 80-150 nm which are believed not to be gold nanoparticles and it may be polymer particles. Figure 3b-d show the images of PEI stabilized nanogold clusters with 1 mM PEI 0.125, 0.5 and 1 mL, respectively, the particle size of these samples were found to be in the range 6-12, 6-9 and 5-7 nm, respectively. These images show that the size of the gold nanoparticles decreases with increase PEI amount added, also, it is obvious that the existence of PEI enhances the uniformity of the produced particles. Figure 4 shows TEM image of a spherical single particle of the prepared nanogold, the image showing the uniformity of the atoms distribution with interplanar space 0.12 nm.

Fourier transform infra-red spectroscopy: Figure 5 shows the FTIR spectrum for PEI, gallic acid and colloidal nano-gold solutions with different PEI concentrations. The IR spectroscopy explains the interaction between the metal and polymer. Figure 5a shows the IR spectrum of pure PEI, the peak at 3000-3422 cm^{-1} could be devoted to the stretching vibration of NH_2 group of the primary amine branch in PEI. Meanwhile, the peaks at 1539 and 1632 cm^{-1} could be assigned to be due to pending vibration of N-H bonds. The multiple peaks in the region 1000-1300 cm^{-1} could be assigned to be corresponding to N-C bond vibrations.

Figure 5b shows the IR spectrum of gallic acid in which the strong band in the range 3000-3700 cm^{-1} could be assigned to be the stretching vibration of OH group of the carboxylic group in gallic acid. The strong narrow peak at 1702 cm^{-1} could be assigned to be the stretching vibration of the carbonyl group. Multiple peaks appeared in the region 1400-1650 cm^{-1} are corresponding to the stretching vibration of C=C bonds in the aromatic ring. There are various peaks at the region 1000-1300 cm^{-1} that could be assigned to be the stretching vibration of C-O bond and bending vibration of O-H bond. Figure 5c-f show the IR spectrum of the colloidal gold nanoparticles stabilized by 1 M solution of PEI (0-1 mL), respectively, the samples show broad band at

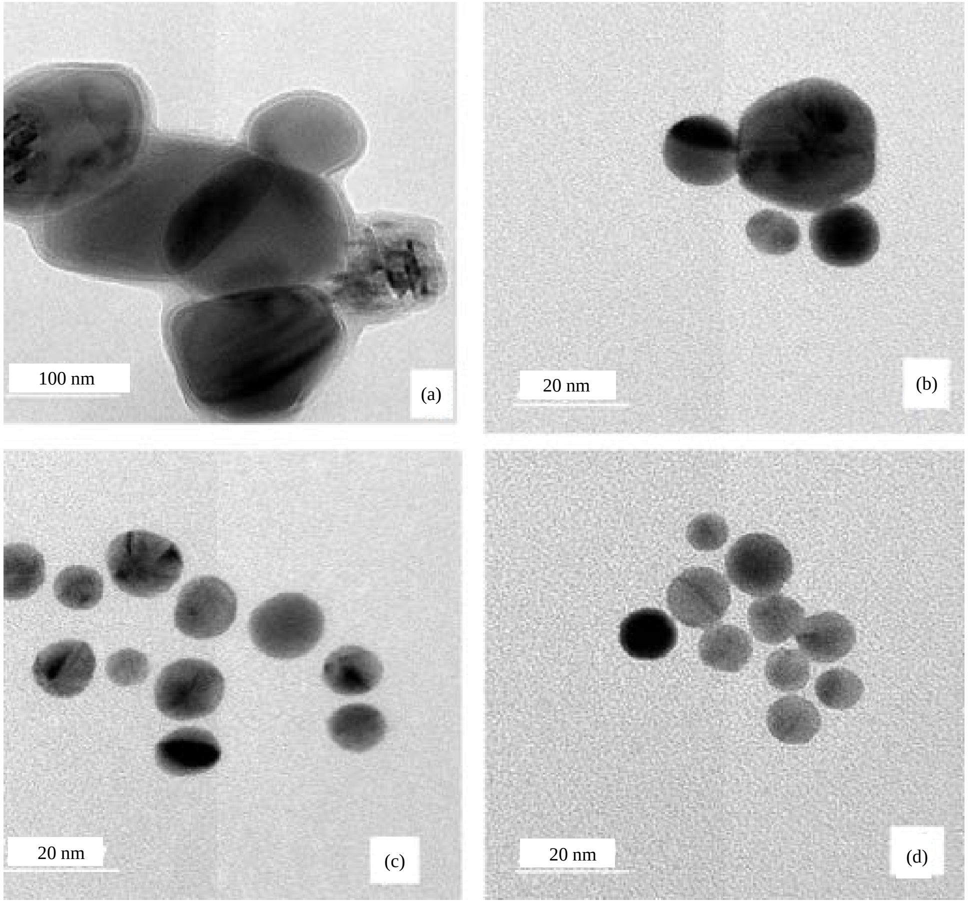


Fig. 3(a-d): TEM images of colloid solutions of gold nanoparticles stabilized by different concentrations of 1 M PEI, a: 0, b: 0.125, c: 0.5, d: 1 mL

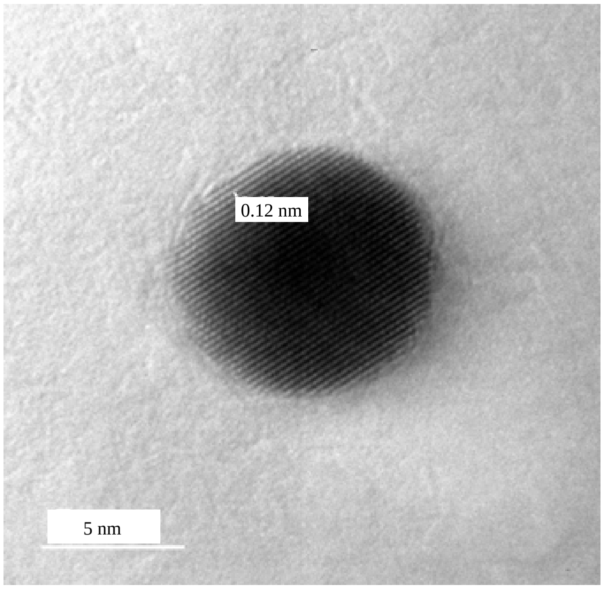


Fig. 4: Atomic-resolution image of a 9 nm gold nanoparticle with 0.12 nm inter-planer distance

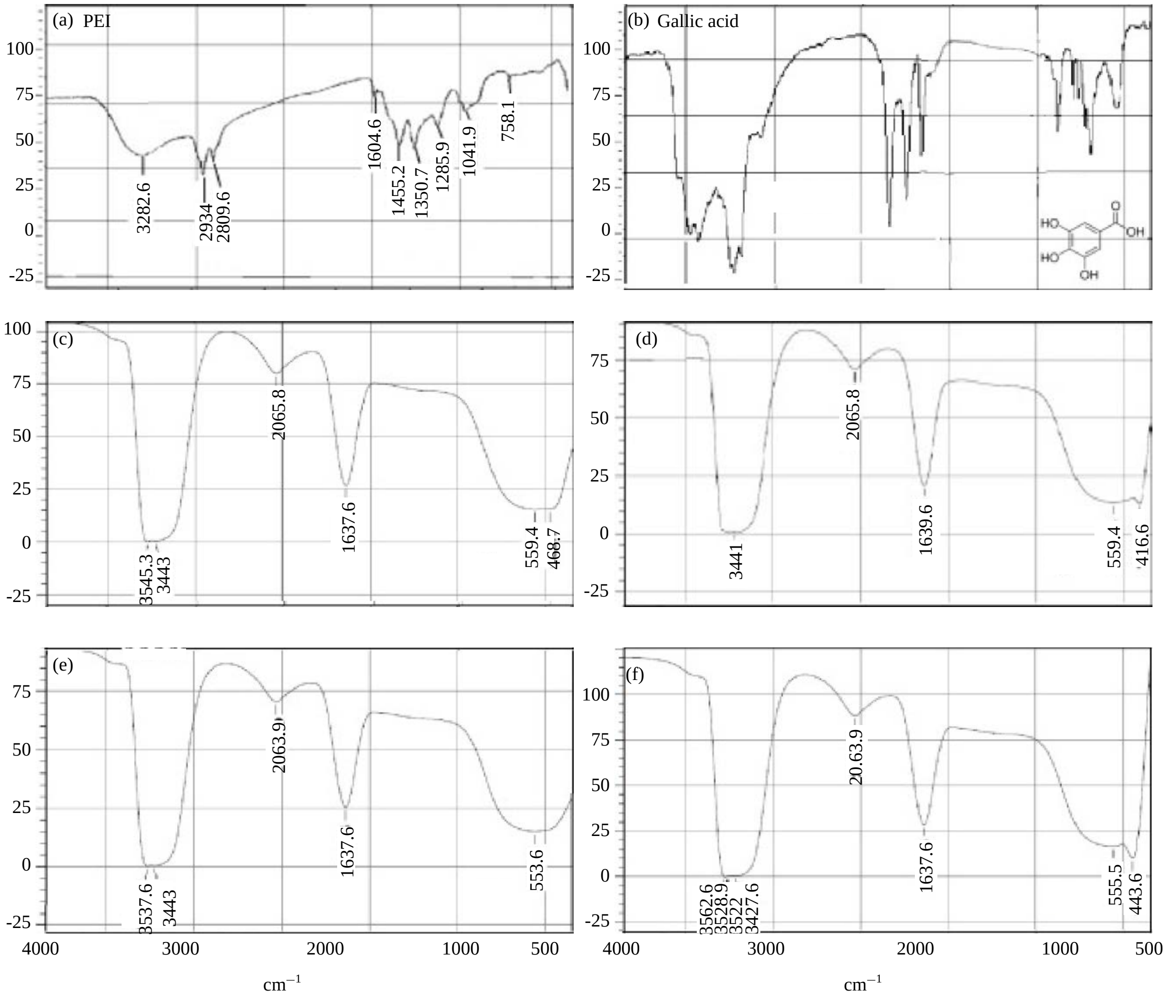


Fig. 5(a-f): FTIR spectra of colloid solutions of gold nanoparticles stabilized by different concentrations of 1 M PEI, a: 0, b: 0.125, c: 0.5, d: 1 mL

3000-3500 cm^{-1} could be assigned to be the stretching vibration of OH group of gallic acid. It is noticed that the stretching vibration of the carbonyl group was shifted from that in gallic acid due to the formation of the quinoid compound. The disappearance of the PEI pattern is due to the overlapping of its peaks with peaks of gallic acid in the same region[46].

CONCLUSION

As it was stated in previous study the morphology of gold nanoparticles affect the type of application that GNPs could be used in it. The new challenge for the researcher is to control the morphology, minimize particle size range and the homogeneity of the produced GNPS. In this study, completely homogenous spherical GNPs were achieved via the reduction process of $HAuCl_4$ using gallic acid in the presence of PEI at room temperature. It was found that in the absence of polyethyleneimine in the applied conditions no GNPs were developed, this indicates that PEI is not only acting as a stabilizer for the produced gold nanoparticles but also enhance the formation gold nanoparticles by contributing in the reduction process through its nitrogen lone pair of electrons. The formation of gold nanoparticles was confirmed by UV-vis spectrometry and the produced colloidal solutions were characterized using TEM and FTIR spectroscopy. Also, it was found that as the amount of PEI increase the particle size of the produced GNPs decreased. Also, the GNPs have uniform spherical shape with a size range from 5-12 nm.

SIGNIFICANT STATEMENTS

Gold nanoparticles have attracted much more attention in past few decades in many applications. The application in which GNPs were used depends on the morphology and size of the prepared GNPs, polymers are commonly used as stabilizers for GNPs and also affect the size as well as the morphology of prepared GNPs. This study discusses the effect of polyethyleneimine as a stabilizer and also as a reducing agent in GNPs preparation.

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