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RESEARCH **Open Access**

Influence of different stabilizers on the morphology of gold nanoparticles

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Abstract

Objectives: The current study revealed that the used stabilizers greatly affect the morphology as well as the aspect ratio of the obtained gold nanoparticles.

Background: Control of the morphology and dimensions of gold nanoparticles during the preparation is an important task for targeting certain applications in demand.

Material and methods: Gold nanoparticles were prepared by the reduction of tetrachloroauric(III) acid in the presence of different stabilizers: polyethyleneimine (PEI), polyvinylpyrrolidone (PVP), and chitosan.

Results: In the case of using polyethyleneimine, the produced nanoparticles showed a homogenous spherical structure. Meanwhile, in the case of using polyvinylpyrrolidone and chitosan, the produced nanoparticles experience non-homogenous morphology with great diversity. Transmission electron microscopy (TEM) and UV-visible spectrophotometry (UV-vis) techniques were employed to study the criteria of the obtained gold nanoparticles.

Conclusions: It was obviously concluded that the type and concentration of the reducing agents that were added during gold preparation and acted as stabilizer templates affect to a great extent the morphology and particle shape. Also, stabilizers affect the homogeneity of the produced gold nanoparticles. In the case of using polyethyleneimine, the produced nanoparticles showed a homogenous spherical structure. Meanwhile, in the case of polyvinylpyrrolidone and chitosan, the produced nanoparticles experience non-homogenous morphology with great diversity.

Keywords: Gold nanoparticles, Stabilizer, Aspect ratio, Transmission electron microscopy

Background

Nanogold is one of the most important noble metal nanoparticles that attracts the attention of scientists around the world. Even though the majority of researches concerned its applications in the medical field, nanogold has a wide variety of applications such as catalysis (Huang et al. 2012; Mallat and Baiker 2004; Obradović and Gojković 2013; Panjan et al. 2012), drug delivery systems (Huang et al. 2006; Norman et al. 2008; Stone et al. 2011), sensors (Pérez et al. 2015; Wu and Tseng 2011), and cancer diagnosis and therapy (Pérez et al. 2015; Arachchige et al. 2015; Suneetha et al. 2014). This wide range of applications of nanogold is devoted to its unique Optical as well as Thermal properties, controllable aspect ratio, and low toxicity (Allen et al. 2017). There are many studied techniques for the preparation of nanogold. These include a green biochemical method (Abdel-Raouf et al. 2017; Chen et al. 2001; Pol et al. 2003; Reed et al. 2003), the seed-mediated mechanism (Brown and Natan 1998; Jana et al. 2001), photochemical reaction (Sau et al. 2001), phase transfer reaction (Esumi et al. 2000; Zhu et al. 2005), and many other techniques. Among these techniques, the stabilized reduction reaction using different types of polymeric materials is considered one of the promising preparation methods (Carotenuto and Nicolais 2004; Corbierre et al. 2001; Esumi et al. 2001a, b; Shimmin et al. 2004; Teranishi et al. 1998). There is a strong relationship between the morphology and dimensions of nanogold particles and

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their potential applications (Allen et al. 2017). For example, rod-like structure attracts scientists working in the field of chemistry and biotechnology as it is widely used in the diagnosis and treatment of cancer (Huang et al. 2012; Allen et al. 2017; Nikoobakht and El-Sayed 2003). In addition, spherical morphology was found to have antibacterial, antiviral, and catalytic activities. Meanwhile, former studies reported the utilization of the triangular and prism-like structures in catalysis and sensing applications (Alabbad et al. 2014; Mena et al. 2005; Zeng et al. 2011; Zheng et al. 2006). Nowadays, controlling the morphology and dimensions of nanogold particles during their preparation is an important goal to be achieved for the sake of their utilization in particular applications. The present work is concerned with studying the effect of different stabilizing polymers in the morphology and aspect ratio of the prepared gold nanoparticles. Gallic acid at room temperature has been used in the presence of polyethyleneimine (PEI), polyvinylpyrrolidone (PVP), and chitosan as organic stabilizers. The criteria of the produced gold nanoparticles were investigated using UV-vis spectrophotometry and transmission electron microscopy.

Experimental

Materials

About 0.3 mM stock solution of tetrachloroauric(III) acid was provided from Sigma-Aldrich (molecular weight = 393.83 g/mole) used throughout the work; the solution 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 g/mole) was prepared by dissolving 0.0213 g of gallic acid in 500 mL deionized water. Polyethyleneimine, Polyvinylpyrrolidone, and Chitosan (Fig. 1) were provided from Acros Organic and usedas polymeric stabilizers.

Characterization

The UV-vis spectroscopy of the prepared samples was studied using UV-vis spectrophotometer (Perkin Elmer model GBC 902). 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 stabilized liquid samples were prepared by sonication for 30 min.

Methods

Gold nanoparticles were synthesized (as reported elsewhere) (Ibrahim et al. 2016). The reaction was carried out in the presence of 1 ml and 1 M solution of PEI, PVP, and chitosan. It was observed that the solutions were changed from pink to wine red color with the addition of the stabilizers. The reactions were kept for 30 min at room temperature.

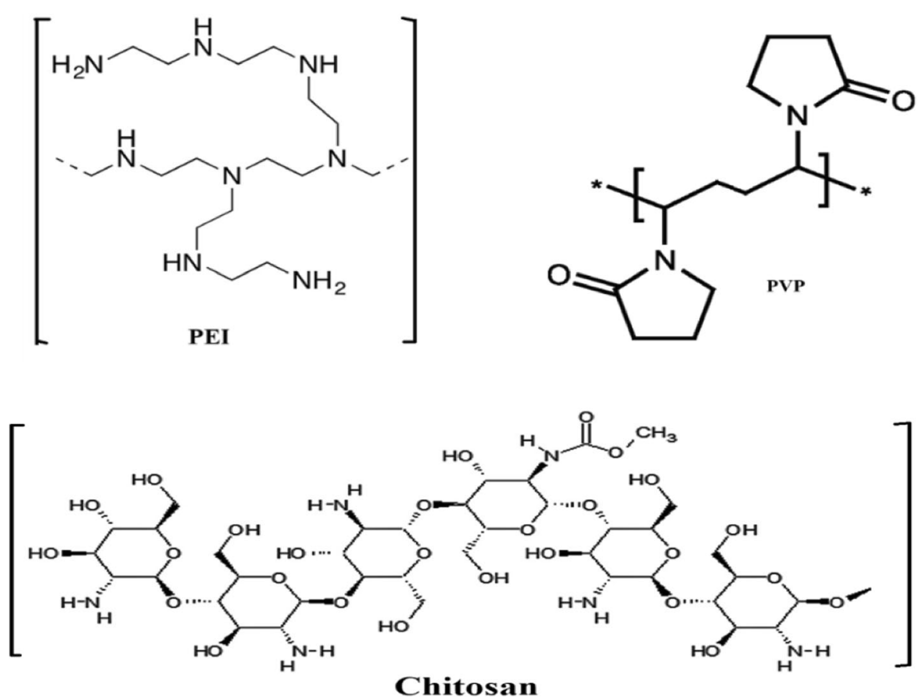

Fig. 1 Chemical structure of polyethyleneimine, polyvinylpyrrolidone, and chitosan

Results

Transmission electron microscopy

Transmission electron microscopy images (Fig. 2) of the obtained gold nanoparticles using PEI, PVP, and chitosan showed that the used stabilizer influenced to a great extent the morphology and also the size of the obtained nanoparticles. Meanwhile, using PEI as stabilizer leads to the production of uniform spherical gold nanoparticles with an average diameter of 7 nm; on the other hand, the use of PVP results in the appearance of different morphologies. Tetrahedral, double tetrahedral pyramid, and truncated tetrahedron morphologies appeared, but among them, the predominant morphology that appeared was the truncated tetrahedron. It was noticed that the particle size increased to 18 nm average size. Chitosan as stabilizers also showed the appearance of the tetrahedral, double tetrahedral pyramid, and truncated tetrahedron with the appearance of the rod-like structure. Also, it was noticed the increase of the particle size to 25 nm average particle size.

Ultraviolet-visible spectroscopy

The fact that the electron cloud in case of nanoparticles oscillates around the surface of the nanoparticle creates a phenomenon due to the absorbance of electromagnetic radiation—Surface Plasmon Resonance a phenomenen arised from the absorbance of electromagnetic radiation by the electron cloud oscillates around the surface of the nanoparticle. Figure 3 shows the UV-vis results of the obtained gold nanoparticles with PEI, PVP, and chitosan stabilizers; it was obviously in agreement with TEM results.

Discussion

The effect of PEI, PVP, and chitosan on the particle size and morphology of the produced gold nanoparticles

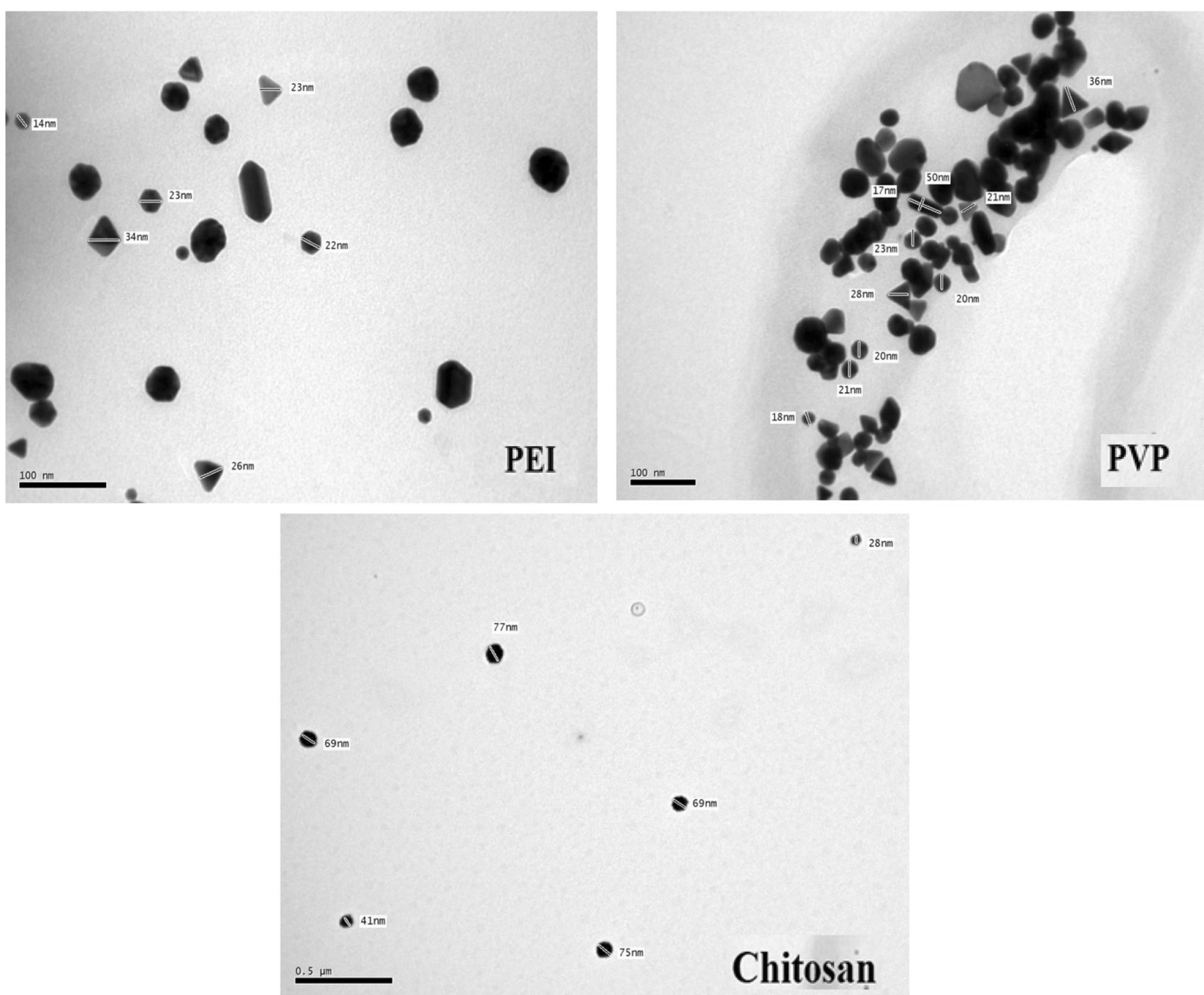

Fig. 2 TEM images of gold nanoparticles using PEI, PVP, and chitosan stabilizers

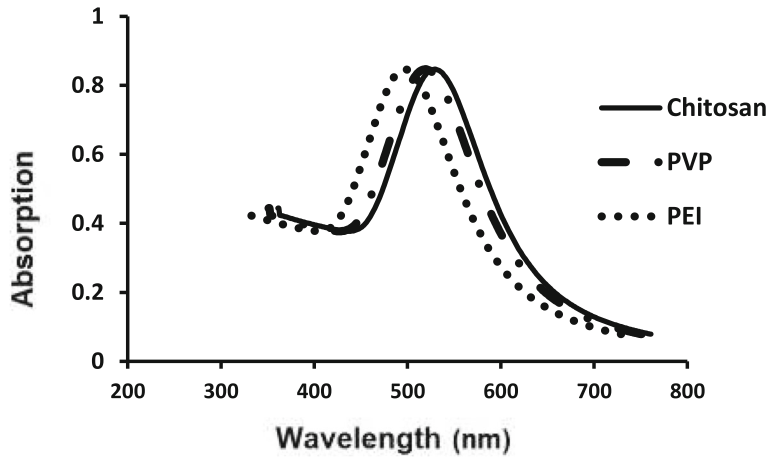

Fig. 3 UV-vis spectra of colloid solutions of gold nanoparticles stabilized by PEI, PVP, and chitosan

could be explained in terms of their chemical structure. The linearity of the chemical structure of PEI, without possessed ring moieties, enhances the uniformity of the produced gold nanoparticles and narrows the particle size range. Meanwhile, the presence of five-membered ring moiety and long chain structure in the case of PVP probably generates various lattice planes for gold nanoparticles to grow through, leading to the various morphologies that appeared, and the majority of the morphologies were closer to a spherical shape (Teranishi et al. 2000). In the case of chitosan stabilizer, it was noticed that the rode-like structure started to appear with a noticeable extent. The appearance of rode-like morphology may be explained by the fact that there is an electrostatic attraction force between the amino group in the structure of chitosan and the metal ion; this could enhance the crystal growth in the rod shape. In UV-visible study, the maximum absorbance of the sample using PEI is at 505 nm. Meanwhile, with using PVP and chitosan, there is a red shift for the maximum absorbance to 510 nm and 537 nm, respectively. This red shift is owing to the increase in the particle size and also the different aspect ratio (Philip 2008).

Conclusions

Gold nanoparticles were prepared from the reduction of tetrachloroauric(III) acid with gallic acid at room temperature in the presence of PEI, PVP, and chitosan as polymeric stabilizers. The used polymer affects extensively the shape and size of the produced gold nanoparticles. In the case of using PEI, the obtained gold nanoparticles showed almost complete homogeneity with a narrow particle size range. Meanwhile, in the case of PVP and chitosan, the produced gold nanoparticles experience great diversity of morphologies. Regarding chitosan, the rod-like shape of gold nanoparticles appeared which may be explained by the assumption that the primary amino group in chitosan made a hydrogen bond with a hydroxyl group in the same moiety or in another moiety of chitosan. This behavior enhances the crystal growth of gold nanoparticles in an elongated structure. It is clear that with manipulation of the kind and concentration of the stabilizer used in gold nanoparticle, preparation could control the morphology and aspect ratio of the produced nanoparticles.

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