

Short Communication

Synthesis of Gold Nanoparticles in Aqueous Solutions by Electrochemical Reduction Using poly(ethylen glicol) as Stabilizer

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A simple electrochemical method to produce gold nanoparticles (AuNPs) in aqueous media is presented. This method is based on the potentiostatic reduction of auric ions in the bulk of a potassium nitrate solution containing poly(ethylene glycol) (PEG_{20,000}) as a stabilizer. The electroreduction process is obtained when a negative polarization potential is applied to the system. To our knowledge, this is the first time that PEG_{20,000} is used as a stabilizer, and its influence on the synthesis of gold nanoparticles is examined. The analysis and characterization of the synthesized AuNPs by cyclic voltammetry, XRD and TEM is presented.

Keywords: Gold nanoparticles, electrochemical method, poly(ethylene glycol), electroreduction

1. INTRODUCTION

The synthesis of nanoparticles (NPs) has been an interesting research topic for decades. Currently, studies related to a more efficient preparation pathway in relation to size, stability and applications of NPs are still relevant to the scientific community [1-3]. Among the different types of NPs, gold nanoparticles (AuNPs) possess unique properties to be applied to several fields, such as medicine, optic, sensor technology and catalysis, and drug delivery, among others [2].

Several methods, such as chemical, physical, biological and electrochemical methods, are employed to synthesize AuNPs [3]. Chemical methods are most likely the most common preparation routes used and reported [1,3-4]. Conversely, electrochemical methods are less known and applied; even when they have revealed that electrochemical synthesis enhances the quality and control of the NP size distribution, improving its preparation by using cleaner reaction mediums and avoiding subproducts [1,5-9]. Electrochemical methods are commonly used for preparing gold nanoparticle-modified

electrodes [10] and to characterize their application as sensors. However, in those cases, electrochemical methods are not used to synthesize the nanoparticles. They are commercially acquired and then immobilized at the electrodes.

The production of AuNPs by electrochemical methods is based on the electroreduction of auric ions in organic or aqueous solutions, which includes the presence of stabilizers [1,11-13]. The electroreduction can take place in a two- or three-electrode cell. The gold ions can come from either a sacrificial anode or a gold salt, such as HAuCl₄ [5, 8-12]. According to the literature, the main electrochemical production of AuNPs is carried out in organic solvents that include the presence of ligands such as tetraalkylammonium salts, acetonitrile, cefazolin, polypyrrole, poly(N-vinylpyrrolidone), penicillin and cationic surfactants that behave as stabilizers [6, 8, 11-18]. There is scarce information about AuNPs produced by electrochemical methods in aqueous medium [6]; however, Liu et al. recently introduced the preparation of AuNPs in aqueous solutions containing poly(N-vinylpyrrolidone) as a stabilizer. The method proposed by Liu et al. includes a rotating platinum electrode as the cathode and a platinum plate as the anode [5]. The rotating electrode avoids the deposition of gold film in the cathode, which improves the efficiency in the formation of AuNPs in solution. An excellent control in size, shape and morphology has been reported by this method [5-6].

The aim of this work is to synthesize AuNPs by electroreduction of auric ions coming from an HAuCl₄ salt in KNO₃ aqueous solution using poly(ethylene glycol) average molecular weight 20,000 (PEG_{20,000}) as an alternative stabilizer. The electrosynthesis is carried out in a conventional three-electrode cell, avoiding the use of rotating electrodes and simplifying the experimental setup. The application of a negative polarization potential to the electrochemical cell allows the reduction of gold ions in solution to form AuNPs.

The presence of PEG_{20,000} and its influence on the production of AuNPs were explored. The analysis of the synthesized AuNPs was carried out by cyclic voltammetry (CV), TEM and XRD.

The advantages of the method proposed in this work are based on the use of eco-friendly polymers, which efficiently produce AuNPs and simplify the operation and experimental set-up for the electrochemical synthesis of NPs. As a consequence, it is possible to dispense with the use of rotating electrodes, as suggested by other methods. Furthermore, the chemical nature of PEG_{20,000} is compatible with the use and application of the synthesized AuNPs in medical areas, including drug delivery, cancer treatment and others.

2. EXPERIMENTAL

2.1. Solutions

The working solution consisted of 0.1 M KNO₃ as the supporting electrolyte, 5 mM HAuCl₄ as the gold precursor and PEG_{20,000} at 20 g/L as the stabilizer. Potassium nitrate salt, HAuCl₄ (99.999%) and PEG_{20,000} were obtained from Sigma Aldrich.

A 0.5 M H₂SO₄ solution, prepared from sulfuric acid (99.999%) from Sigma Aldrich, was used as a method to probe the synthesis of AuNPs.

All solutions were prepared with bidistilled water. All experiments were carried out at 25°C.

2.2. Electrochemical Synthesis of gold nanoparticles

The synthesis of AuNPs was carried out in a conventional three-electrode cell. The working electrode was a glassy carbon electrode (0.07 cm^2). A platinum wire and a mercury sulfate electrode (SSE) were used as counter and reference electrodes, respectively. Hereafter, all the potentials given in this work are referred to as the SSE electrode. The three electrodes were immersed in 10 mL of the working solution.

The auric ions in the working solution were electroreduced by a potentiostatic experiment using an AUTOLAB PGSTAT 128N potentiostat. The electroreduction was performed by applying -0.9 V for one hour. To enhance the mass transfer and improve the production of AuNPs, a magnetic stirrer was used during all experiments. Once AuNPs were synthesized, they were maintained in solution inside a dark box and stored at room temperature.

2.3. Characterization of AuNPs

The AuNPs were analyzed by Cyclic Voltammetry (CV), TEM and XRD.

For CV, the solution obtained from the electroreduction was centrifuged and rinsed to obtain a powder with AuNPs. This powder was analyzed using CV. A three-electrode cell was used with the same counter and reference electrode previously described, but a modified glassy carbon electrode was used as the working electrode. A clean glassy carbon electrode was coated with a mixture of powder of AuNPs and a drop of Nafion 117 solution obtained from Sigma Aldrich. The electrode was allowed to dry, and then it was ready to use. The cyclic voltammetry response was obtained in 0.5 M H₂SO₄ solution in a potential range from -0.75 to 1.3 V measured at a rate of 100 mV s⁻¹.

For TEM analysis, 1 mL of the electrolyzed solution was diluted in 4 mL of bidistilled water and sonicated for 15 minutes. Then, a drop of this suspension was placed onto a TEM carbon-copper grid. After water evaporation, TEM images were obtained. All measurements were carried out in a JEOL transmission electron microscope (JEM-1010) operating at 100 kV.

For XRD, the electroreduced solution was centrifuged and rinsed several times to obtain a precipitate that was dried, pulverized and analyzed. The XRD patterns were obtained with an Empyrean X-ray diffractometer using a Cu-K α radiation ($\lambda = 0.15418\text{ nm}$) at room temperature in the 2θ range 10 to 90° at 45 kV and 40 mA.

3. RESULTS AND DISCUSSION

When a negative potential is applied to the electrochemical cell, the production of AuNPs occurs through the electrochemical reduction of the auric ions via the transference of three electrons. However,

according to the literature, this process can produce metal nanoparticles suspended in the working solution and gold deposition on the working electrode [6,8-12].

To avoid this last phenomenon, the use of a stabilizer is highly favorable. To our knowledge, this is the first time that PEG_{20,000} is used as a stabilizer in the production of AuNPs by electrochemical methods. According to the results presented in this section, PEG_{20,000} not only enhances the production of nanoparticles and avoids its agglomeration but also averts the massive gold deposition on the glassy carbon electrode. This is visually confirmed at the end of the electroreduction process, when the color of the working solution changes from its original yellow to a weak purple, which is the characteristic color of gold nanoparticles [19,20]. As has been extensively probed, the weak purple color is associated to the plasmon band observed for colloidal gold at 520 nm in an UV-vis spectrum [20, 21]. Moreover, after electroreduction, the working solution exhibits the Tyndall effect, which proves the colloidal nature of the solution due to the presence of gold particles dispersed in it [17]. An incipient and thin gold film is deposited on the working electrode. This is probably due to the well-known adsorption and partial oxidation of PEG_{20,000} on the electrode [22-23], which modifies the kinetics of the metallic deposition. The presence of PEG_{20,000} not only stabilizes but also enhances the efficiency in AuNP production. All of the above assertions were experimentally proven by CV, TEM and XRD.

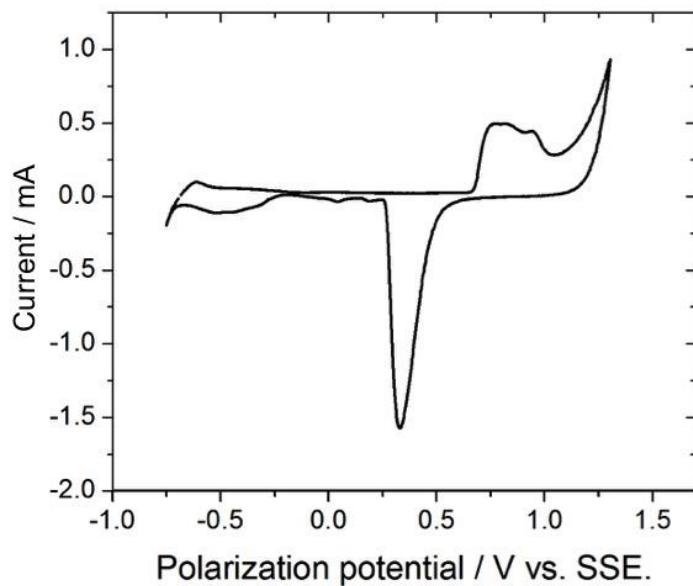


Figure 1. Cyclic voltammogram in 0.5 M H₂SO₄ solution of a glassy carbon electrode modified by the gold particles electrochemically produced.

Figure 1 shows the cyclic voltammogram in sulfuric acid solution of a glassy carbon electrode modified by the gold particles electrochemically produced by the methodology given in section 2.2. After its production, the particles were fixed onto the electrode surface. As observed in Figure 1, the behavior of current vs. polarization potential depicts two peaks: a broad anodic peak at approximately 0.6 and 0.9 V and a well-defined cathodic peak at 0.3 V. According to the literature [24], these peaks correspond to the typical oxidation and reduction of a polycrystalline gold surface, which ensure that the

powder fixed at the working electrode consists of gold particles. Similar results are observed in other papers where the CV response of AuNPs modified electrode is characterized [12, 25].

The production of gold particles via an electrochemical process is well evidenced by CV, as in previous references [10]. However, even when this analysis proves the synthesis, no information about the morphology and size of the particles is acquired by this technique.

The TEM image, shown in Figure 2a, shows that the electroreduction of the working solution by the electrochemical method produces well-defined spherical gold particles with a nanometric size ranging from 1 to 20 nm with a narrow dispersion and an average value of 5 nm, as shown in Figure 2b. Furthermore, the diffraction peaks observed in the XRD pattern, shown in Figure 3, emphasize the metallic nature of these nanoparticles.

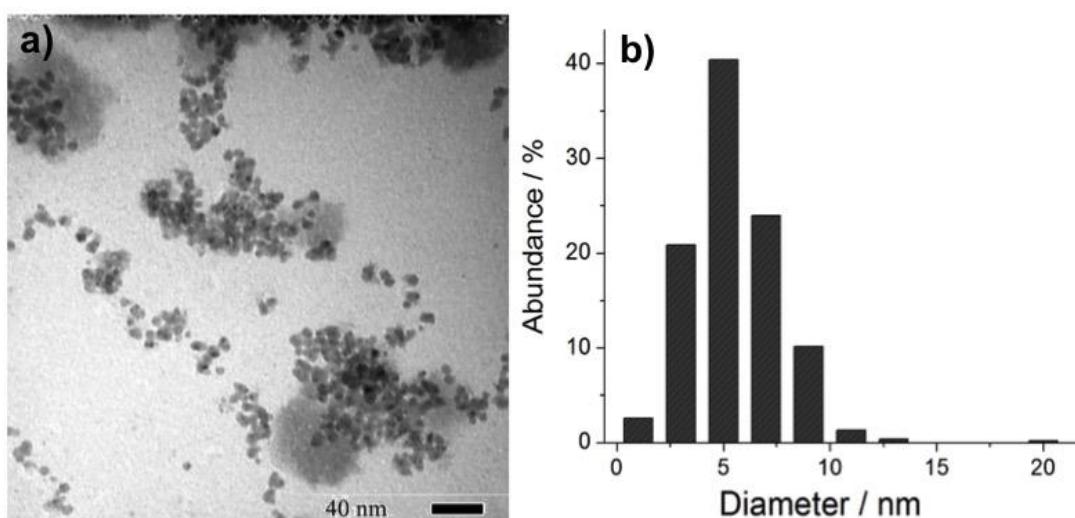


Figure 2. a) TEM image and b) particle size distribution of gold particles electrochemically produced.

Figure 3a shows the pattern of the analyzed AuNPs. The peaks appearing at 38.5° , 44.6° , 64.7° , 77.7° and 81.5° are related to the (111), (200), (220), (311) and (222) indices for face-centered cubic gold unique cell structure, respectively. This pattern is in good agreement with [19, 25].

From this analysis, it is possible to conclude that AuNPs produced are polycrystalline, as evidenced by CV in Figure 1.

In Figure 3b, the XRD pattern for a PEG_{20,000} powder is presented. According to Figure 3b, it is possible to note that the peaks at approximately 10° to 30° observed in Figure 3a are related to the presence of residuary PEG_{20,000} in the sample analyzed.

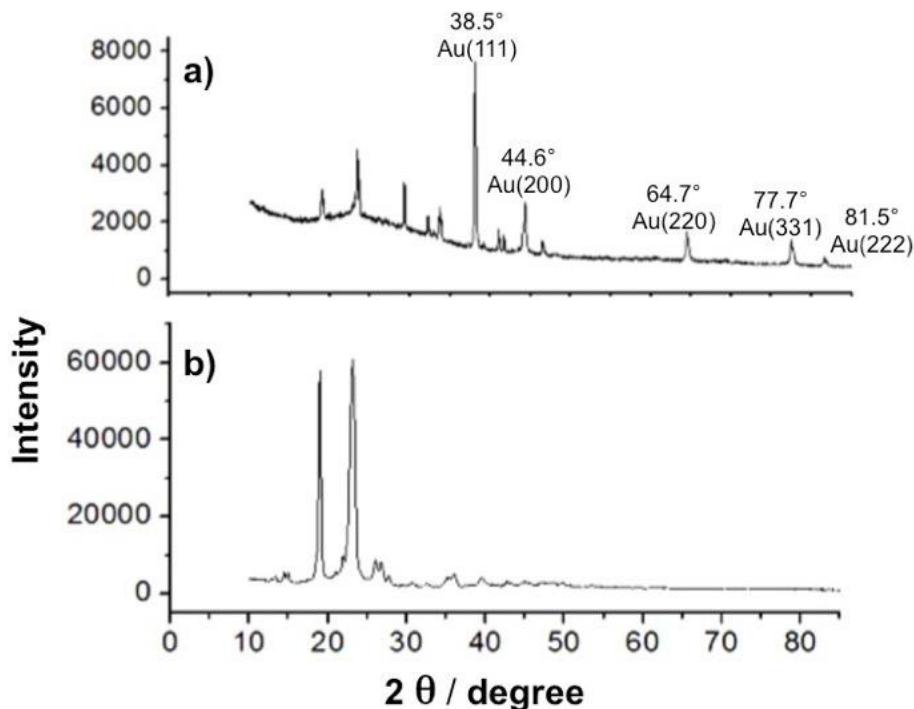


Figure 3. XRD pattern for a) gold nanoparticles electrochemically produced and b) PEG_{20,000}

Thus, CV, TEM and XRD analysis highlighted that AuNPs are successfully produced by the electroreduction of auric ions in an aqueous medium. Additionally, the results show that PEG_{20,000} behaves as an adequate stabilizer of the gold clusters in solution, which in turn allows obtaining well-defined nanoparticles. This is similar to the AuNPs prepared using radiation technologies and a seed-mediated method, which correspond to 5 nm to 25 nm [26].

Furthermore, the presence of PEG_{20,000} diminishes the massive reduction of the gold clusters and its deposition in the cathode. This fact increases the efficiency of AuNP formation.

The obtained result demonstrates the electrochemical method and the use of PEG_{20,000} as an adequate pathway to synthesize AuNPs. Based on the shape and size of the prepared AuNPs under the experimental conditions presented in this work, the nanoparticles can be applied in photodynamic therapy or can be used in biomedical, chemical and electronic purposes [26,27].

The effect of PEG_{20,000} concentration and polarization potential applied to the electroreduction process is actually evaluated by additional experiments.

4. CONCLUSIONS

A simple electrochemical method to produce AuNPs in aqueous medium containing PEG_{20,000} as a novel stabilizer was presented. The use of PEG_{20,000} not only favors the formation of well-defined and non-aggregated gold nanoparticles but also minimizes the massive gold deposition at the fixed working electrode. In this way, the methodology proposed allows the synthesis of well-defined spherical gold nanoparticles with a narrow size distribution, from 1 to 20 nm.

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