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SÍNTESIS Y CARACTERIZACIÓN DE NANOPARTÍCULAS DE ORO
SYNTHESIS AND CHARACTERIZATION OF GOLD NANOPARTICLES

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Resumen

Las nanopartículas de oro tienen múltiples aplicaciones en electrónica, catálisis, óptica y biomedicina. Este trabajo informa acerca de un protocolo robusto, rápido y fácil para síntesis de AuNPs. El protocolo de síntesis es una variante del método de Turkevich para la obtención de AuNPs. También se informa acerca de la caracterización del producto de síntesis mediante espectroscopia UV-Vis y microscopía electrónica de transmisión. Las AuNPs obtenidas presentaron propiedades de nanoescala, alta pureza y tienen usos potenciales en el tratamiento de cánceres, como agentes antivirales, antibacteriales y biosensores, entre otros.

Palabras clave: nanotecnología, nanopartículas, oro, Turkevich, nanomateriales.

Abstract

Gold nanoparticles (AuNPs) find a number of applications in many fields of electronics, catalysis, optics and biomedicine. This work reports a robust, fast and easy synthesis protocol, based on the Turkevich method to obtain AuNPs. Simple characterization techniques based on UV-Vis spectroscopy and transmission electronic microscopy are also reported. The resulting AuNPs presents properties at a nanometric scale, high purity and they may find potential uses in the treatment of cancer, antiviral and antibacterial agents and biosensors among others.

Keywords: nanotechnology, nanoparticles, gold, Turkevich, nanomaterials.

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1. Introduction

Gold nanoparticles (AuNPs) are of great scientific interest by their ease of synthesis, chemical stability and unique electronic, optical, magnetic, thermal and catalytic properties (Dykman, Staroverov, Bogatyrev, & Shchyogolev, 2010; Verma, Singh, & Chavan, 2014; Zhao, Li, & Astruc, 2013). The understanding of their behavior and properties makes them attractive for a wide variety of technological applications in fields of Physics, Chemistry, Biomedicine, electrochemical sensors and material sciences (Corma & Garcia, 2008; Hainfeld, Slatkin, Focella, & Smilowitz, 2006; Han, Ghosh, & Rotello, 2007; X. Huang & El-Sayed, 2011; Jena & Raj, 2006; Lopes, Alves, Pereira, Granjeiro, & Leite, 2019; Oyelere, 2008; S. Zeng et al., 2011).

AuNps have interesting optical, physical and chemical properties, excellent biological compatibility and great ability to immobilize biomolecules. At the same time, AuNps present biocatalytic activity over several biomolecules commonly used in the fabrication of different kinds of biosensors (Du, Luo, Xu, & Chen, 2007; Magnusson, Deppert, Malm, Bovin, & Samuelson, 1999; Yang, Luo, Tian, Qian, & Duan, 2020).

The use of AuNps have been reported to enhance the electrocatalytic function of glucose oxidase (GOx) in glucose blood and sweat sensors (Magnusson et al., 1999). For instance, Zulkifli et al.,(2017) used AuNPs with sizes between 20 and 60 nm to build sensors with high catalytic activity of the immobilized GOx (Liu et al., 2018). Similarly, Chang et al., (2014), synthesized AuNPs between 26 and 40 nm and confirmed that AuNPs work as excellent electrode materials for glucose sensing. Luo, Xu, Du, & Chen, (2004), also evaluated AuNPs on immobilized enzymes. Electrochemical sensors with AuNPs were reported with higher stability than those without AuNPs. Moreover, AuNPs are also used in virus detection (Draz & Shafiee, 2018; Kumar, Boruah, & Liang, 2011). Currently, AuNPs are used for coronavirus diagnosis. In general, the technique involves colorimetric bioassays to detect virus RNA material (Medhi, Srinoi, Ngo, Tran, & Lee, 2020). Moitra et al., (2020), synthesized AuNps that could be used for diagnosing positive COVID-19 cases from isolated RNA samples. The key factor is the ability of aggregation of AuNPs induced by viral N-gene (nucleocapsid phosphoprotein) of SARS-CoV-2. C. Huang, Wen, Shi, Zeng, & Jiao, (2020), obtained AuNps with size ≈ 30 nm. The excellent stability of AuNPs combined with specific binding forces between the antigen and the antibody were used to develop a method for rapid and on-site detection of SARS-CoV-2.

In 1857, Faraday obtained AuNPs by reducing auric acid with phosphorus [12]. From this early beginning, several chemical methods for obtaining AuNPs have been developed. The Turkevich, the Brust-Schiffrin and the Reez methods are the most used methods for the synthesis of AuNPs (Herizchi, Abbasi, Milani, & Akbarzadeh, 2014). All these methods basically consist of two parts, the reduction of a gold percussive solution of chloroauric acid ($HAuCl_4$) by means of hydrazine, borohydrides, aminoboranes, acetylene, polyols, citrus or oxalic acid, among other reducing agents and the chemical stabilization of the obtained colloidal solution with trisodium citrate dihydrate agents or sulfur or phosphorus ligands (Alex & Tiwari, 2015; Faraday, 1857).

The Turkevich method is the simplest and most widely used technique for the synthesis of AuNPs. The method was developed by Turkevich in 1951 and modified by Frens in 1973. It indicates the preparation of an aqueous solution of $HAuCl_4$ at boiling temperature. Then, trisodium citrate dihydrate is added under vigorous agitation. After a few minutes, the color of the solution changes from light yellow to wine red. The product of this reaction is AuNPs of about 20 nm in diameter (Frens, 1973; Turkevich, 1985).

Literature also reports the Brust-Schiffrin method. This method is used to obtain thermally stable, size-controlled and low-dispersion AuNPs. The synthesis is carried out in organic liquids such as toluene. The method indicates the preparation of a $HAuCl_4$ aqueous solution and subsequent transfer of the $HAuCl_4$ to the toluene phase using tetraoctylammonium bromide (TOAB) as a phase transfer agent. Finally, the $HAuCl_4$ is reduced by sodium borohydride ($NaBH_4$) in the presence of dodecanethiol. The addition of the reducing agent causes a color change of the organic phase from orange to deep brown. This clearly indicates the formation of AuNPs (Brust, Walker, Bethell, Schiffrin, & Whyman, 2000; Faraday, 1857). The Reez method uses tetra alkyl ammonium salts as stabilizers of metal conglomerates in non-aqueous media allowing fast and low cost synthesis of AuNPs from 5 to 40 nm in diameter (Agunloye, Panariello, Gavriilidis, & Mazzei, 2018; Faraday, 1857).

The goal of this work is to report an improved variation of the Turkevich method and the characterization of its resulting AuNPs.

2. Experimental part

Materials

HAuCl4 (CAS 16961, Sigma Aldrich, USA), trisodium citrate dihydrate (CAS 68-04-2, Sigma Aldrich, USA) and deionized water type miliQ with a resistivity of 18.2 MΩ and density δw = 0.99704 g/cm2 have been used as precursor, reducing agent and solvent, respectively.

3. Synthesis and characterization

Equation 1 shows the chemical reaction for the synthesis of AuNPS according to Turkevich method (Kimling et al., 2006; Turkevich, Stevenson, & Hillier, 1951).

Eq. 1

$$6\,AuCl_4^{-1} + C_6H_8O_7 + 5H_2O \rightarrow 6\,CO_2 + 24Cl^{-1} + 6Au^{o} + 18\,H^{+1}$$

Firstly, a solution of 1 millimolar of HAuCl4 and 38.8 millimolar of trisodium citrate dehydrate was prepared. Secondly, the solution was conditioned at 100 °C during fifteen minutes under vigorous stirring. The components of the solution started to react according to equation 1. The progress of the reaction was evidenced by a color switch from yellow to red. Thirdly, the reaction conditions were keeping another fifteen minutes to ensure total consumption of reactants. Fourthly, the synthesis product was cooled down to room temperature, filtered through a 0.22 μm membrane and stored in a glass bottle until use.

The synthesis product was characterized by UV-Vis spectroscopy (PERKIN Elmer Lambda 1050 UV/VIS/NIR). This technique allows to confirm the formation of AuNPs through its plasmon resonance property. The morphology and particle size of the AuNPs were measured by transmission electron microscopy (JEOL 2100F) operating at 200 kV and magnification of 120000.0 x.

4. Results and discussion

Figure 1 shows the optical property of AuNPs determined by UV-Vis spectroscopy. The absorption band develops a peak around 525 nm. This pattern of absorption is characteristic of AuNPs (X. Huang, Jain, El-Sayed, & El-Sayed, 2007; X. Zeng, Zhang, Du, Li, & Tang, 2018). Figure 2 shows a TEM image. Nearly round AuNPs with some degree of aggregation is clearly visible. The average particle size of AuNPs resulted 12.6 nm.

Figure 1.
UV-Vis absorption spectrum of AuNPs.

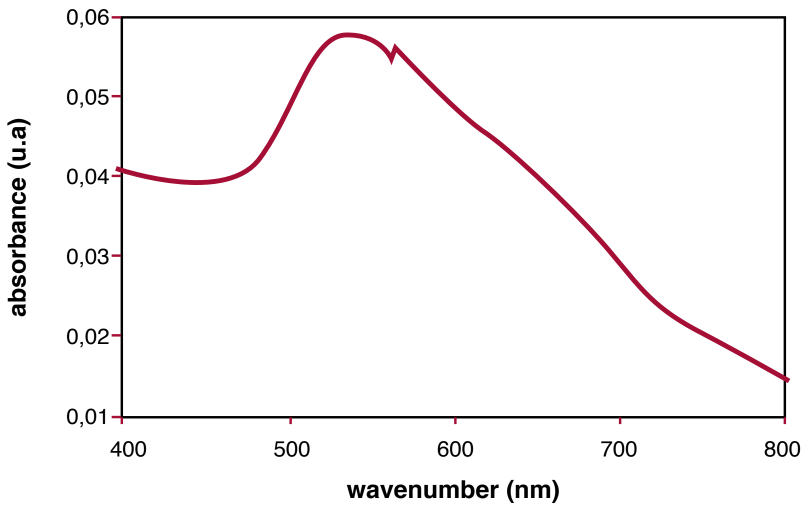
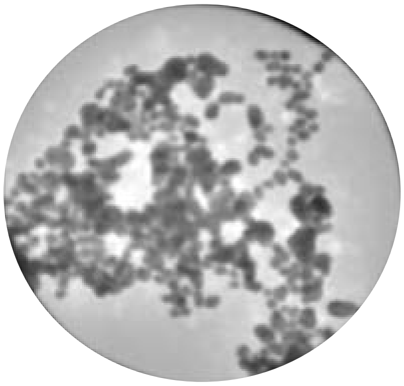


Figure 2.

TEM image of AuNPs obtained by Turkevich method.



200 nm

5. Conclusion

The Turkevich method is a robust, fast and simple method to obtain AuNPs. The characterization protocol of the product of synthesis must include UV-Vis to verify the formation of AuNPs and TEM to measure particle size, morphology and aggregation degree. It is very important to prepare the initial aqueous solution with exact 1:38 molar ratio between $HAuCl_4$ and trisodium citrate dehydrate. The obtained AuNPs resulted within the range of properties suitable for viral detection kits and biosensor catalysts.

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