ENVIRONMENTAL FRIENDLY NEW METHOD FOR THE PRODUCTION OF NEW METAL NANOSTRUCTURES FOR OPTICAL ENHANCEMENT

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The most efficient and cost effective methods for fabrication and characterization of metal nanoparticles involves colloidal chemistry, from which it has been inferred that the shape, size, size distribution, and stability of nanoparticles depends on specific preparation methods, especially on the reducing agents used. Chemical methods use the salt of the metal, a reducing and a protective agent, dissolved in water or any other appropriate solvent. In this context, the use of macromolecules seems to be advantageous, since they offer control over the rate of the oxidation process, and may act both as the reducing and protecting agents [1]. In this communication we use of fulvic acid (FA) in the synthesis of gold nanoparticles, demonstrating unprecedented control of particle size and shape, by varying the experimental conditions. FA is the most water-soluble fraction of humic substances (HS), which are the main components of organic matter of soils and sediments in waters [2, 3]. The formation of colloidal gold particles by HS was observed by Machesky in his studies concerning the mechanisms of interaction of Au with HS in the natural environment [4, 5]. In the present work, gold nanoparticles of different shapes and sizes are produced through the reaction of FA and gold tetrachloric acid. FA-Au films prepared by casting are used as substrates for analytical applications of optical enhancement such as surface-enhanced Raman scattering (SERS)[6].

Gold nanoparticles were produced by mixing 20 mL of 0.01% $HAuCl_4$ (Aldrich) water solution with an equal volume of fulvic acid solution (250 mg L^{-1}) at three different pHs (5, 8 and 11) and concentrations. In order to study the effect of pH and FA concentration on the shape and size of the gold nanoparticles, we employed high-resolution transmission electron microscopy (HRTEM). Figure 1 shows that the size of the colloidal particles increases as the pH decreases. For pH 11 the size of the nanoparticles is in the range from 4 to 10 nm (Figure 2a). The colloids at pH 8 produce a slightly larger size range, from 10 to 15 nm (Figure 2b). At pH 5 the micrographs show two different sizes, hexagonal and triangular particles of ~50 nm and truncated triangles of ~200 nm (Figure 2c-d). In summary, controlling the pH of FA, nanoparticles of distinctly different sizes and different shapes can be produced.

The control of size and shape of gold nanoparticles that can be used embedded in fulvic acid films opens the way for a variety of applications. For example, we have prepared films by casting FA-Au solution on glass slides that can serve as substrates for SERS [6, 7]. Optical microscopy and AFM characterization of the cast films revealed distinct morphologies according to the method of preparation. At pH 5 fulvic films form small aggregates. At pH 8 and 11 (Figure 2a, b) fractal-like morphology is observed. These fractal-like structures, are also observed in the sub-micrometer range for pH 11, as shown in the AFM images. They are probably formed through the ionized acidic groups, which induce organization in a fractal fashion [8].

SERS activity was tested by casting 5 μL of 10^{-3} M ethanolic solution of the organic contaminant 2-naphthalenethiol (2NAT) [9]. SERS spectra were recorded using several laser lines (488, 514, 633 and 785 nm). However, the best SERS results were obtained with the 785 nm laser line. The characteristic SERS spectrum of the 2NAT analyte can be used as a probe to test the optical enhancing properties of the fulvic-gold films. For comparison, and as a reference for SERS, the spectra of 2NT on citrate-gold colloids, and on a gold island film of 9 nm mass thickness are shown in Figure 3c. The optical enhancing properties of Fulvic acid films containing gold nanoparticles prepared from solutions at pH 11 are negligible. However, the enhancement of the Raman scattering increases for Au-FA films obtained from solutions at lower pHs. There is considerable enhancement for the Au-FA films prepared at pH=8, but the best enhancement is attained from Au-fulvic acid film cast from a pH=5 solution. At this pH, the enhancement decreases with the fulvic acid concentration. The differences in the enhancement could be related to the extension of the adsorption of 2NT. The highly charged FA formed at high pH values may hinder the adsorption of 2NT onto the gold nanoparticles. Notably, the SERS spectra show that samples containing a higher number of truncated triangles give a stronger signal. The enhancement factor provided by the Au-FA films fabricated at pH 5 is similar or even better than that obtained by using the most common optical enhancers: metal island films or metal colloids.

References:

[1] N. Toshima, T. Yonezawa, New Journal of Chemistry 22 (1998) 1179.
[2] R. A. Alvarez-Puebla, C. Valenzuela-Calahorro, J. J. Garrido, Langmuir 20 (2004) 3657.
[3] R. A. Alvarez-Puebla, J. J. Garrido, Chemosphere 59 (2005) 659.
[4] W. O. Andrade, M. L. Machesky, A. W. Rose, Journal of Geochemical Exploration 40 (1991) 95.
[5] M. L. Machesky, W. O. Andrade, A. W. Rose, Chemical Geology 102 (1992) 53.
[6] R. K. Chang, T. E. Furtak, Surface Enhanced Raman Scattering, Plenum Press, New York, 1982.
[7] R. F. Aroca, P. J. G. Goulet, D. S. dos Santos Jr., R. A. Alvarez-Puebla, O. N. Oliveira Jr., Analytical Chemistry 77 (2005) 378.
[8] R. A. Alvarez-Puebla, J. J. Garrido, R. F. Aroca, Analytical Chemistry 76 (2004) 7118.
[9] R. A. Alvarez-Puebla, D. S. dos Santos Jr, R. F. Aroca, The Analyst 129 (2004) 1251.

Figures:

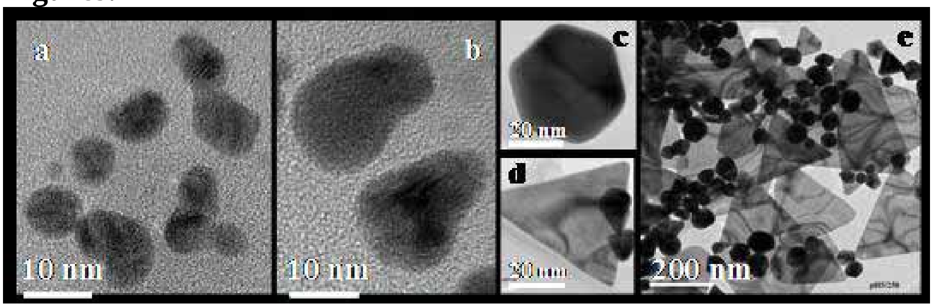

Fig 1. HRTEM images of Au nanoparticles produced at pH (a) 11, (b) 8 and (c-d) 5.

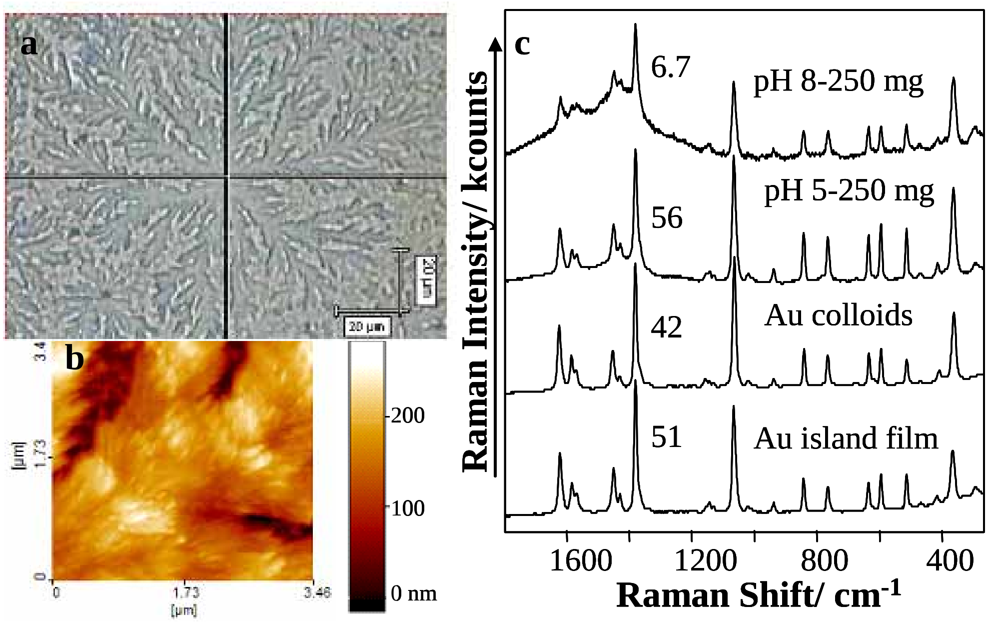

Fig 2. Images (a) optical and (b) AFM of FA-Au film at pH 11. SERS spectra of 2NAT on films produced at different pH, gold colloids and gold island films.