Selective Adhesion of Gold Nanoparticles onto Microcrystal Faces of Cyclodextrin/Octanethiol Inclusion Compound Produced by Magnetron Sputtering

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ABSTRACT

This paper described the stable gold nanoparticles (AuNPs) onto microcrystal faces of αcyclodextrin /octanethiol (αCD/OT) inclusion compound (IC) by means of magnetron sputtering technique was obtained. Comparison of the ^{13}C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C CP-MAS NMR) spectra for pure IC with those for IC interacting with AuNPs evidenced different orientation of the guest into the channels of the matrix of αCD. Diffuse Reflections Spectroscopy for the sputtered gold nanospheres on the surface of αCD/OT showed the characteristic surface plasmon resonance. Transmission Electronic Microscopy (TEM) demonstrates that this technique produces AuNPs in a size range about 2-6 nm. Scanning electron microscopy (SEM) show the selective adhesion of AuNPs onto IC.

Keywords: Gold nanoparticles, sputter deposition, cyclodextrin inclusion compound.

1 INTRODUCTION

In recent years, gold nanoparticles are of great research interest due to their unique quantum size effect [1], optical [2], electronic [3], magnetic [4] and supramolecular [5,6] properties. In particular, structural order has been one of the major concerns in most applications of self-assembled thin films, in one- or two-dimensional arrays. AuNPs generally were deposited on different kind surfaces, such as: inorganic substrates, polymer surfaces and single atomic monolayer, as example [7]. Only recently, Fujiki and co-workers reported organic single crystal of L-cystine coated with AuNPs onto specific crystal face [8]. The authors claimed that the surface of organic single crystals could be more varied than those of inorganic single crystals, giving the opportunity to explore a wide variety of composite materials with anisotropic properties.

There are two different classes of techniques for making gold nanoparticles: chemical and physical. Chemical methods typically involve the decomposition or precipitation of gold from a gold precursor like $HAuCl_4$. These are the most widely used techniques because of the availability of reactants and the low costs on the laboratory scale. These chemical methods are described in several papers and reviews [7,9]. Physical methods typically involve the production of gas phase gold atoms or clusters [10]. Other preparation method can briefly be described as the sputtering of a high-purity gold target with argon ions, followed by the subsequent deposition of the sputtered gold atoms on the surface of a powder support material to create a uniform dispersion of nanoparticles. [11] This technique has several advantages over existing preparation methods. For example, there is no contamination from solvent or precursor molecules on the surface. The process is economical and environmentally friendly, since the excess gold is recoverable from the chamber and there is no liquid waste.

In the nanoscience field, the Cyclodextrins (CDs) has been used to preparate of AuNPs capped with thiolated α- and β-CDs [3], preparate of AuNPs by femtosecond laser ablation [4] and by chemical reduction in the presence of unmodified CDs [5]. The CD-IC, particularly the ones leading to supramolecular self-assemblies continue to be a fascinating topic in modern organic chemistry as they serve as models for understanding molecular recognition [12, 13] and as precursors for designing novel nanomaterials[6]. In cyclodextrin inclusion compounds the matrix channel is formed by the cones unities which interact through Van der Waals forces and are ordered to encounter the similar end of neighbouring units (larger opening-larger opening, smaller opening-smaller opening) [13]. In solid αCDs-alkylthiol inclusion compounds, for example, the –SH group of the guest could be located at the extreme boundary of a CD unit, in the rich electron space density with the alkyl chain located in the apolar and poor electron density zone of the CD cavities [14,15]. These -SH group, located in the opening of the CD ({001} crystal plane), are available to interact with the particles being able to stabilize it (Figure 1).

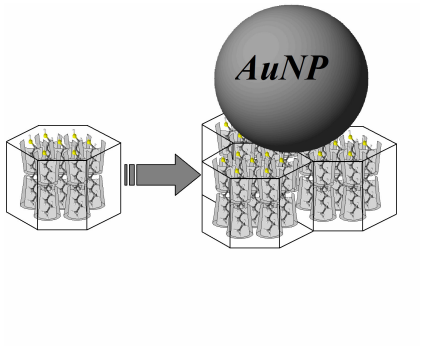

Figure 1. Schematic representation of AuNPs onto crystal plane (001) of αCD-IC.

In this work converges two actually very interesting chemistry areas, the molecular recognition phenomenon applied to the CD inclusion compounds and technique for the preparation of gold nanoparticles development. Here we demonstrate the selective adhesion of gold nanoparticles onto microcrystal faces of αcyclodextrin/octanethiol inclusion compound produced by magnetron sputtering technique.

2 EXPERIMENTAL

Commercially available Aldrich reagents were used as received. The inclusion compounds were obtained from thiols and saturated solutions of cyclodextrins in water at room temperature with 2αCD/OT stoichiometrie [14].
The microcrystals of the inclusion compounds were interspersed on the surface of a glass to form a homogeneous layer previously to being exposed to the sputtering. Gold was deposited onto the substrate in inert atmosphere at room temperature (Pelco SC-6 Sputter Coater). Working conditions: Direct current (dc) mode with a discharge of 220 V, argon pressure of 10^{-2} mbar. The gold target was sputtered at an applied power of 5.5 W. The gold deposits prepared by short- time (5 - 10 s). The size of the deposited gold nanoparticles can be estimated with the time of exposition of the substrate.

Powder X-ray diffractograms were recorded in the range $2^{o} < 2\theta < 80^{o}$ on a Siemens D-5000 diffractometer using Cu-K_{α} radiation (40 KV, 30 mA) and a graphite monochromator (λ = 1.540598 Å). The diffractograms of the sample 2αCD/OT indicated absence of any other crystalline phases than those of the reported inclusion compounds. All peaks in the diffractogram, can be indexed on the basis of a hexagonal lattice with parameter values close to a = b ≈ 27 Å, c ≈16 Å, $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$ for α-cyclodextrin [14]. The diffractogram of the 2αCD/OT/AuNPs sample reveal that in addition to the peaks corresponding to the host structure some peaks corresponding to gold nanoparticles may be identified.

UV-Vis Reflectance Diffuse Spectroscopy were measured in the range 800 to 350 nm on a Shimadzu UV-2450 with ISR-2200 Integrating Sphere Attachment, this instrument is controlled by the software UVProve Version 1.10.

The TEM image was recorded in a 200keV JEOL2000FX and the AuNPs were characterized by using a Leo 1420VP scanning electron microscopy.

3 RESULTS AND DISCUSSION

SEM images proved the homogeneity of the sample as well as the expected spherical shape of the AuNPs. A representative SEM image of the selective adhesion of AuNPs onto microcrystal face IC is shown in figure 2.

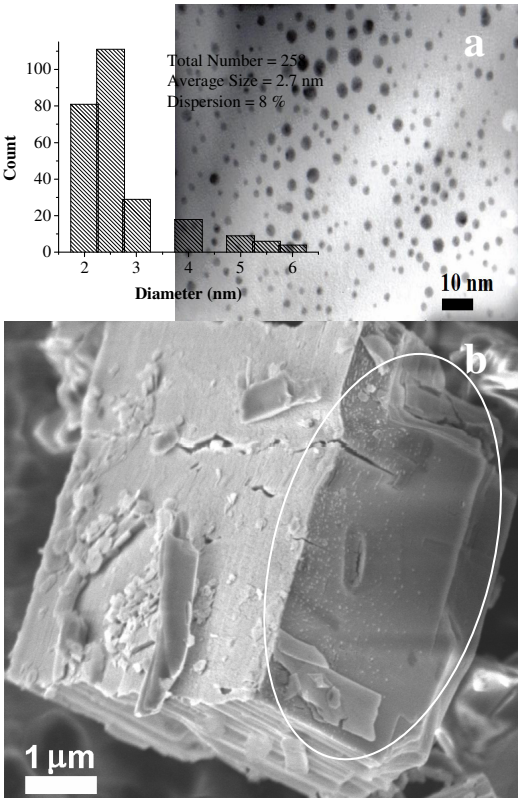

Figure 2. TEM image and histogram of AuNPs onto 2αCD/OT (a). SEM image reveal the preferential deposition of AuNPs onto microcrystal IC (b).

By means of TEM we determined that the optimal time of exhibition to sputtering is of 10 seconds. For this time a so large average of particles of 2.7 nm is observed. With smaller times particles are not observed and with greater times, for example, 40 s the size of particles is of 47 nm. This is demonstrated in diffractograms. For deposited particles of 2.5 nm is observed a wide picks around 40° corresponding to (111) plane. For particles of 40 nm are observed defined picks corresponding to the planes (111), (200),(220) and (311) [16]. A diffractogram for the 2αCD/ OT interact with particles different size is shown in figure 3.

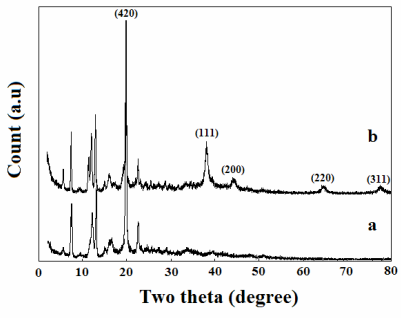

Figure 3. Powder X-ray diffractogram for the 2αCD/OT inclusion compound interacting with different size AuNPs a) 10 s; b) 45 s (time sputtering).

Diffuse Reflections Spectroscopy for the sputtered AuNPs on the surface of αCD-IC showed the characteristic surface plasmon resonance with a maximum absorption around 526 nm (figure 4).

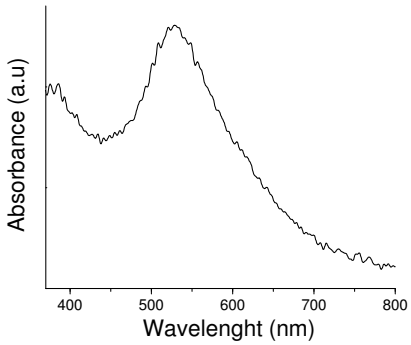

Figure 4. Optical spectra of AuNPs of a microcrystal of IC (recorded in diffuse reflectance).

^{13}C CP MAS NMR spectra of the 2αCD/OT and αCD/OT/AuNPs are as shows in figure 5 along with the assignment of the resonances. The ^{13}C resonances of alkyl chain of the guest appearing from 10 to 40 ppm. In the IC the spectra show an only wide signal of ^{13}C for the atoms C2, C3 and C5. The resonance of carbons 2, 3 and 5 of the CDs is resolute in the spectra of the αCD/OT/AuNPs which is indicative of a greater homogeneity in the distribution of the guest alkylthiol within the channels of matrix αCD. The C1 atom of the CD in the IC shows two resonances which is indicative of two possible preferential directions of the guests within the channels of the structure. Differently the C1 from the CD of the αCD/OT/AuNPs show an only resonance which suggests a single direction within the cavity.

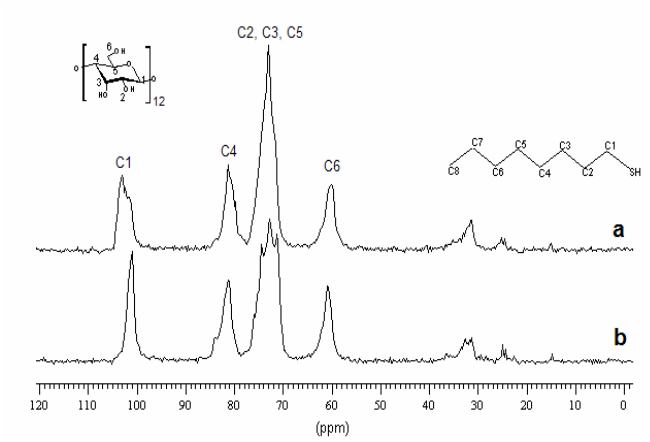

Figure 5. Comparison of ^{13}C CP MAS NMR spectra 2αCD/OT Inclusion Compound (a) with 2αCD/OT/AuNPs (b).

3.1 Conclusion

In conclusion here we demonstrate the selective adhesion of gold nanoparticles onto microcrystal faces of αcyclodextrin/octanethiol inclusion compound produced by magnetron sputtering technique.

The technique used to prepare the NPs has several advantages that make it attractive for industrial applications, Such as no waste stream, cheap reagent, and scalability. In addition, this preparation method can be applied to almost any substrate, and can use almost any metal particles.

From the results discussed above, it can be concluded that (AuNPs) can be formed means sputter deposition technique on the 2αCD/OT inclusion compound, forming solid hetero structure where AuNPs is probably stabilized *via* the alkythiol guest interaction.

It constitutes in addition a new method to preparation of nanoparticles. At the moment we are preparing nanoparticles with other metals using like molecules guests a specific surfactant for the deposited metal.

3.2 Acknowledgements

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