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Formation of Copper Nanoparticles Supported onto Inclusion Compounds of α -cyclodextrin: A New Route to Obtain Copper Nanoparticles

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This work presents the preparation of copper nanoparticles (CuNPs), using as support, inclusion compounds (ICs) formed by α -cyclodextrin (α -CD) with alkylamines as guests. These ICs provide a suitable environment to anchor and immobilize the nanoparticles, because the functional group of the guest molecule provides outwards from the plane of the IC crystal. The characterization of metal nanoparticles was carried out by transmission electron microscopy (TEM) and UV-visible spectrophotometry.

Keywords Cu nanoparticles; cyclodextrin; inclusion compounds

Introduction

Supramolecular chemistry is a field of science that studies the chemical, physical and biological properties of species called supramolecules. These entities are formed by molecules which are held together by intermolecular interactions rather than covalent bonds.

The inclusion compounds concept, was introduced to define one of these systems consisting of entities having appropriate cavities capable of accommodating within them guest molecules, through selective binding cavity-substrate. These systems exhibit the phenomenon of *molecular recognition*, ie that there is an affinity and specificity between the cavity of the matrix and the guest molecule [1].

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In previous studies, our research group has reported the synthesis of inclusion compounds of α -CD with different host molecules as alkylthiols [2], carboxylic acids [3] and dialkyl- [4], alkyl- [5] and bicyclic-amine [6]. It has also been shown that compounds with these characteristics offer a suitable environment to stabilize nanoparticles, due to the spatial arrangement showing the functional groups of guest molecules included in the matrix [7].

The broad interest in the manufacturing of nanoscale materials is primarily in the wide range of applications that they have due to their interesting properties. Macroscopic properties such as electrical conductivity, color, mechanical strength or melting point, among others, can vary dramatically with respect to the same material in nanometric scale [8].

There are various methods to produce nanoparticles which are divided into two groups, "chemical methods" and "physical methods. Chemical methods are based on growth and nucleation of metal atoms means of the chemical reduction of transition metal salts in the presence of stabilizing agents. Among the "physical methods" is found the technique of deposition by cathodic pulverization in high vacuum called *sputtering*, which has several advantages, they are a simple physical process and a versatility technique with flexibility and customization possibilities [7,9].

This work has as main purpose, to obtain Cu nanoparticles using as support stabilizers and binders of these nanoparticles inclusion compounds with α -cyclodextrin with alkylamines as guest. Since the functional group-NH₂ of the guest molecules are arranged outwards from the plane of the crystal of IC, these are capable of interacting with metal nanoparticles, which are deposited on the preferential face of the crystal (001). The deposit is carried out by sputtering technique, which allows the formation of nanoparticles on the substrate of different diameters depending on the exposure time [10].

Experimental

Preparation of Inclusion Compounds

The IC were synthesized mixing directly 1.5 mmol of each of the alkylamine (octylamine (OA), Decylamine (DA) and Dodecylamine (DDA)) with a saturated solution of 0.5 mmol of α -CD in approximately 10 mL distilled water. The amines were added drop wise with constant stirring, checking the formation of the IC by precipitation of fine white crystals. After about two days the crystalline solids were filtered and washed with distilled water to remove traces of α -CD unreacted. Subsequently the crystals were washed with 15 mL of methanol to remove excess alkylamine. Finally, the compounds were dried under a vacuum for about 4 hours.

Synthesis of Metal Nanoparticles

Fine copper targets cathode was utilized in the sputtering equipment. A glass sample-holder containing a fine powder of the IC, evenly distributed, was introduced into the sputtering camera. Subsequently a vacuum of 0.5 mbar and Ar flux was introduced. A current of 30 mA is used to ionize the Ar. The Cu atoms presents in the plasma were deposited on the IC in apparently in epitaxial form, conducting to the formation of metal nanoparticles [4].

During the process, the IC crystals were removed manually in the equipment to facilitate the deposit of CuNPs onto preferential plane.

Characterization

The UV-Visible absorption spectra were measured at room temperature in a spectrophotometer (Shimadzu UV-2450). The size distribution of nanoparticles was obtained by a transmission electron microscope, TEM, (Zeiss EM 109). TEM images of nanoparticles were obtained preparing a ethanol suspension of substrate onto a carbon-coated copper grid disks and by evaporating the solvent in air. The TEM images of all samples were measured with a maximum acceleration voltage of 50 kV.

Results and Discussions

Figure 1 shows a schematic representation of CuNPs deposition on the (001) crystal plane of the cyclodextrin inclusion compound. The immobilization of CuNPs is due to the formation of an Cu–NH₂ bond with the free-dangling –NH₂ groups of the guest molecule, located at the entrance to the cavity of the α -CD ((001) crystal plane). This leads to the stabilization of the particles on the surface.

The verification of the deposit of Cu nanoparticles on supramolecular substrate is also demonstrated by the absorption of decorated supramolecular specie [10]. Figures 2–4, show the surface plasmon resonance of spherical CuNPs with maximum absorptions at a 258 nm, 273 nm, and 261 nm respectively. No significant differences in the absorption for amines including: octylamine, decilamina, dodecilamina were observed.

The cooper deposits were prepared in a short time (5s). The size of the deposited CuNPs could be estimated from the time of exposure of the substrate. This is indicative that the particles are not formed in the plasma phase before landing, but that they are formed on the IC. The CuNPs are located preferentially on selected faces of the crystal.

Figure 5 shows that an optimal sequence of 5 seconds produced a uniform nanoparticle population.

With longer time, 55 seconds, for example, a decreased absorbance or a shifting toward longer wavelengths of surface plasmon resonance of the NPs is produced. Probably a single exposure to a longer time, larger size nanoparticles are generates.

The CuNPs were characterized by Transmission Electron Microscopy (TEM). Spherical Cu nanoparticles with a low dispersion in size were observed (Figure 6). Figure 7 shows a histogram with a nanoparticle average size of 30 nm.

Preferential deposition on the (001) plane of the α -CD IC crystal occurs because –NH₂ groups from the guest molecules found within the α -CD protrude into this



Figure 1. Representation of the deposit of the CuNPs on the plane (001) crystal of the IC.

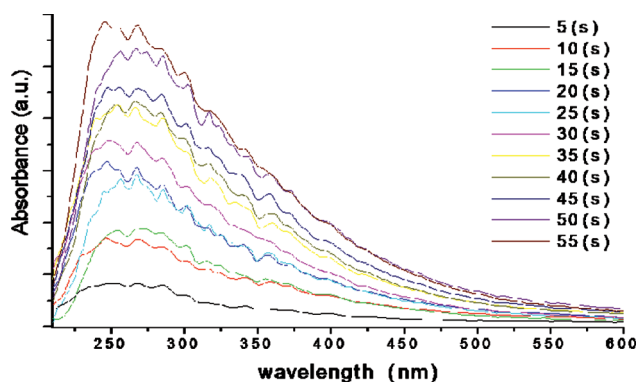


Figure 2. Absorption spectra of α -CD/OA with CuNPs about 55 seconds (5 in 5) of exposure to the sputtering.

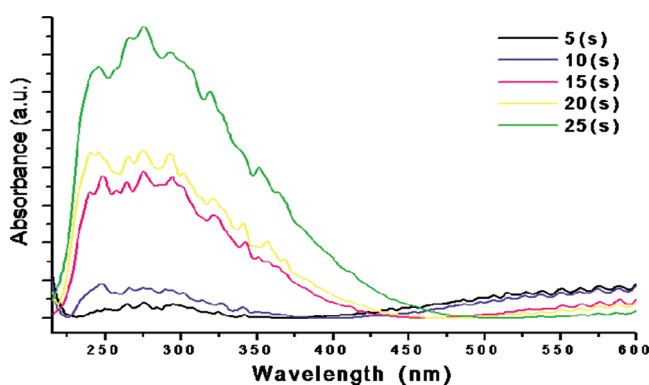


Figure 3. Absorption spectra of CuNPs on α -CD/DA with 25 seconds (5 in 5) of exposure to the sputtering.

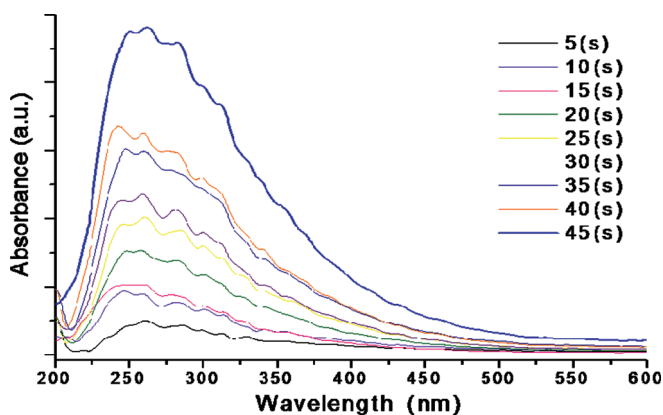


Figure 4. Absorption spectra of CuNPs on α -CD/DDA with 45 seconds (5 in 5) of exposure to the sputtering.

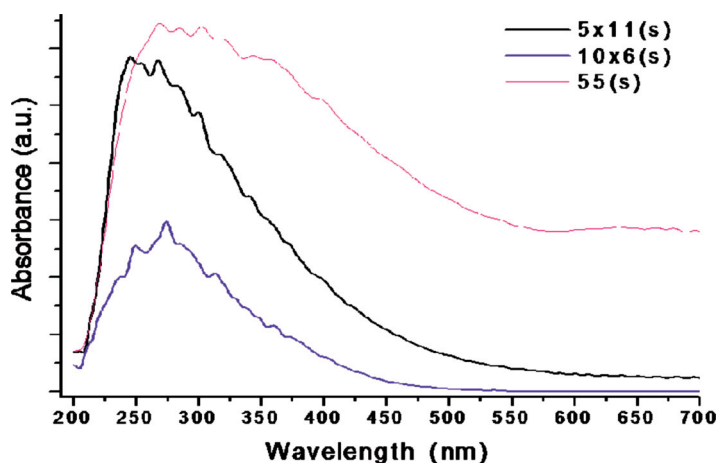


Figure 5. Comparison of the absorption spectrum of CuNPs on α -CD/OA of 5 in 5, of 10 in 10 or once the 55 seconds of exposure to sputtering.

plane. These $-\text{NH}_2$ groups form a two-dimensional hexagonal lattice that interacts with metal nanoparticles, stabilizing and arranging them in an ordered way. The magnetron sputtering technique used to prepare ordered CuNPs has several advantages, such as the scalability, that make it attractive for industrial applications.

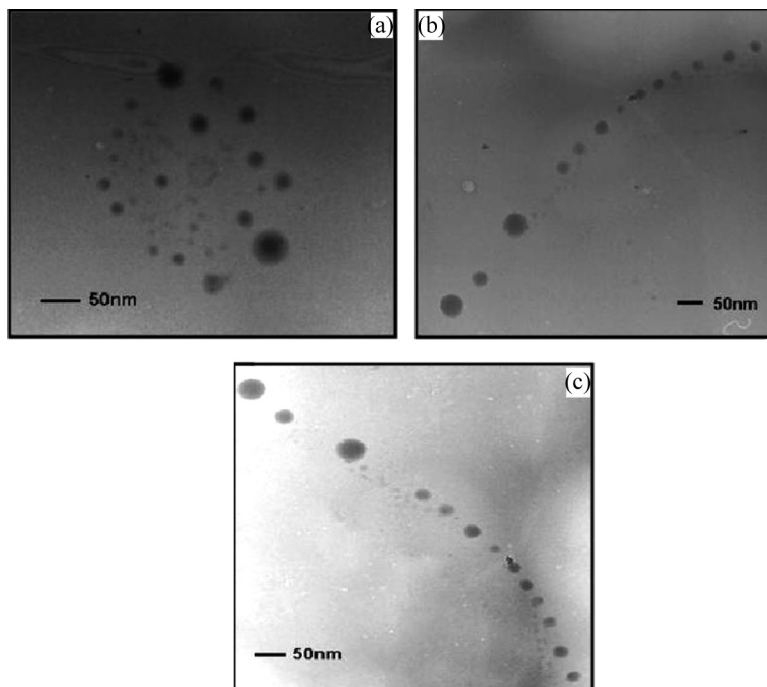


Figure 6. CuNPs micrographs supported on IC of (a) α -CD/OA, (b) α -CD/DA, and (c) α -CD/DDA.

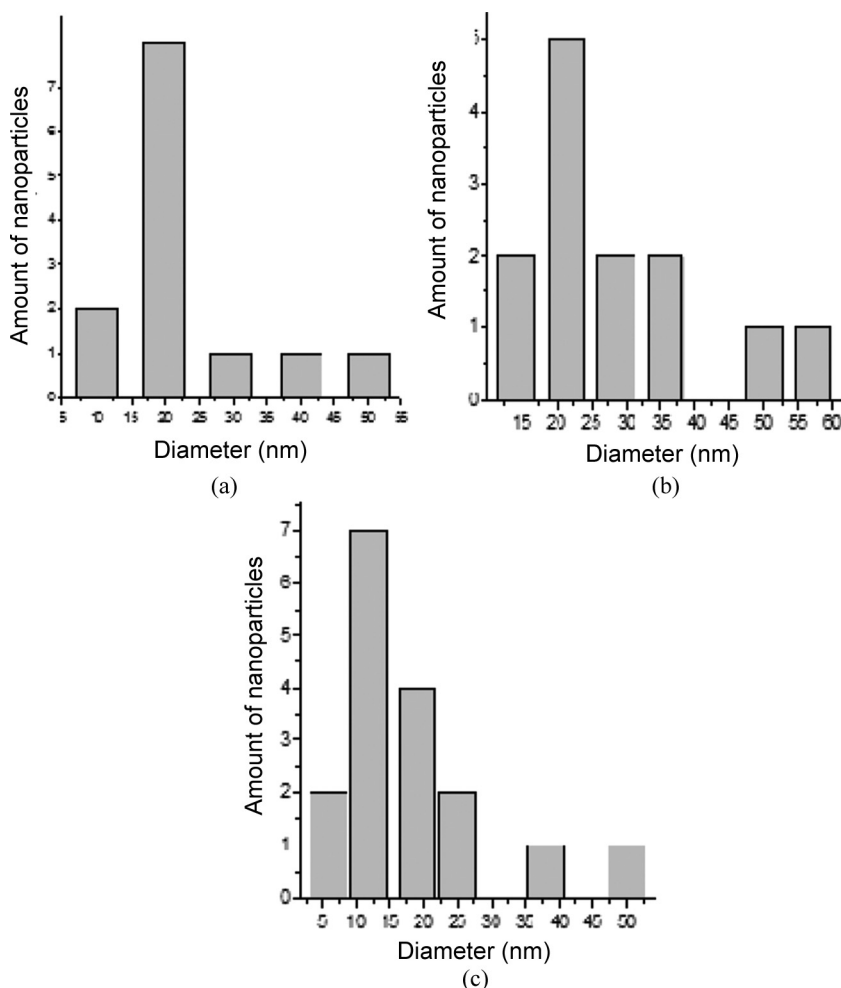


Figure 7. Size distributions of CuNPs supported on IC of (a) α -CD/OA and (b) α -CD/DA, and (c) α -CD/DDA.

Conclusions

The use of cyclodextrin IC substrates with a surface modified for the deposition of nanoparticles is an efficient method for obtaining CuNPs with a low dispersion in size due, probably, to the high affinity between the functional group of the surfactant guest with the metal.

Optical studies determined the optimal time of exposure to sputtering according to the included guest, being 55, 25, and 45 seconds for IC α -CD/OA, DA, and DDA, respectively. Increased efficiency is obtained in sequentially exposition of 5 seconds due to the statistical presentation of the crystals faces.

Acknowledgments

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