

Adhesion of gold and silver nanoparticles onto urea–alkylamine inclusion compounds

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Abstract We report the synthesis and characterization of a new series of urea inclusion compounds containing primary alkylamine (octyl, decyl and dodecyl) as guests, as well as the deposition of gold and silver nanoparticles onto the crystalline surface of these complexes. X-ray diffraction confirms the inclusion process of the amine in the urea cavities. The structures determined for the three complexes correspond to a hexagonal channel structure with space group $P6_122$. Alkylamine–urea stoichiometric ratios in all cases satisfy the relationship $1:3n$ ($n = 2$ for octylamine and 3 for decylamine and dodecylamine), determined by elemental analysis. The deposition of gold and silver nanoparticles by the magnetron sputtering technique onto microcrystals of the complexes was analyzed by Diffuse Reflectance Spectroscopy, showing characteristic surface plasmon resonance for metal nanoparticles. Transmission electron microscopy demonstrates the presence of metal nanoparticles (MNPs) in a size range between 5 and 60 nm for gold and between 5 and 20 nm for silver, and

furthermore, in some cases it shows vestiges of a hexagonal arrangement of the MNPs. X-ray diffraction and IR measurements demonstrate that the basic structure of the matrix remains unchanged after the MNPs adhesion. IR also shows increased broadening and intensity of the characteristic NH_2 bending frequencies ($1,597\text{ cm}^{-1}$) when the MNPs interact with the inclusion compounds. We conclude that the interactions between the inclusion compounds and metal nanoparticles occurs mainly through the amino groups of the guest molecules that can emerge from the entrance of the inclusion compound cavities attracted by the metallic nanoparticles, in opposition to the restoring van der Waals interactions present inside channels, which increase with increasing chain length of the guest molecules.

Keywords Urea inclusion compounds · Amine guests · Gold nanoparticles · Silver nanoparticle

Introduction

The coexistence and interaction of two fascinating areas of science, supramolecular chemistry and nanoscience, is currently of great interest. Inclusion compounds (ICs) actually represent suitable supramolecular systems for investigating the nature of molecular host–guest interactions. They have also received increasing attention as materials for applications in electronics and optoelectronics [1–4]. Host materials such as urea, thiourea, cyclodextrins, calixarenes, zeolites, and perhydrotriphenylene permit specific host–guest architectures, where guests molecules are incorporated along channels, within layers, or in isolated cages [5–7]. Among these, urea and thiourea ICs in particular have been investigated, X-ray diffraction studies

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showing that both form characteristic binary compounds. The small typical hexagonal channels of urea ICs (effective tunnel diameter ranging between 5.5 and 5.8 Å) are appropriate for storing non-branched hydrocarbon chains, while thiourea channels are appropriate for storing branched hydrocarbon chains [8, 9]. The formation of molecular adducts, between urea and *n*-paraffins has been known for long time, Schlenk has given a detailed account of their preparation [10]. Urea forms ICs not only with hydrocarbons and their halogenated derivatives, which in general are rather inert substances, but also with other chemical species with carboxylic acid, alcohol, ester [11–14], cyano [15] and amine [16] functional groups which are potentially more active in the formation of hydrogen bonds with urea. In most cases the included species appear to be loosely located in interstitial spaces and no specific host–guest interactions are detected. Guest species containing azacyclo functional groups are also included in urea and thiourea hosts 1,2-diazabicyclo[2.2.2]octane, or hexamethylenetetramine as guest and thiourea as host [17–23] have shown that it is possible to obtain binary layered ICs. The synthesis of new ternary compounds has offered the possibility of obtaining derivatives of urea and thiourea matrices containing channels of sufficient size to accommodate bulky molecules, and it was also interesting to study the conductivity properties of cationic guests included in anionic urea and thiourea matrices [24–28].

Urea ICs, particularly those leading to supramolecular self assemblies, continue to be a fascinating topic in modern organic chemistry as they serve as models for understanding molecular recognition and as precursors for designing novel materials and for biological applications. Studies have revealed that urea inclusion may be a promising alternative for the formulation of poorly soluble potent drugs in immediate release products [29, 30].

On the other hand, gold nanoparticles (AuNPs) are very special materials owing to their unique optical, electronic, catalytic, and supramolecular properties, promising a wide range of different applications in nanotechnology and biotechnology [31]. Silver nanomaterials exhibit different properties compared to bulk materials, and therefore also extensive new applications [32]. For example, applications are highlighted in microelectronic and bacteriostatic materials [33], catalytic or magnetic recording materials [34], in medical therapy and pharmacology [35]. Silver nanoparticles (AgNPs), can be used as antibacterial materials, and applied as nanopowder in common synthetic textiles [36, 37], antistatic materials, cryogenic superconducting materials [38] biosensor materials [39], and in the electronic industry [40]. The activity of AgNPs depends on their structure, size, shape, distribution, and chemical–physical environment [41, 42], controlled frequently by synthetic conditions [43, 44].

MNPs offer a wide range of applications, and it is therefore of interest to know their behavior when they are deposited stabilizing previously organized surfaces. Fujiki et al. have reported for the first time the face-selective deposition of AuNPs on the crystal faces of organic crystals using hexagonal single crystals of L-cystine [45]. We have recently explored a more versatile face-selective deposition of gold nanoparticles onto α -cyclodextrin/octanethiol and α -cyclodextrin/dodecanethiol ICs [46–49], and this year the adhesion of AgNPs on a montmorillonite surface has been described [50].

We consider it interesting now to contribute to the knowledge of the supramolecular chemistry of urea using primary alkylamines as guest family, and also to study the adhesion phenomena of MNPs onto microcrystals of these inclusion compounds.

Experimental

Preparation of ICs

All chemicals were reagent grade or analytical grade and were used as obtained from commercial sources. The ICs were synthesized directly by mixing 3.0 mmol of each alkylamine [octylamine (OA), decylamine (DA), and dodecylamine (DDA)] with a saturated solution of urea (U) (9.0 mmol) in approximately 40 mL of methanol at room temperature. The guest-to-urea mole ratio used in the experiments was always 1:3. The needle shaped microcrystals obtained after about 4 days were filtered and washed with 10 mL of cold methanol to remove traces of the reacted amine. Finally, the compounds were dried

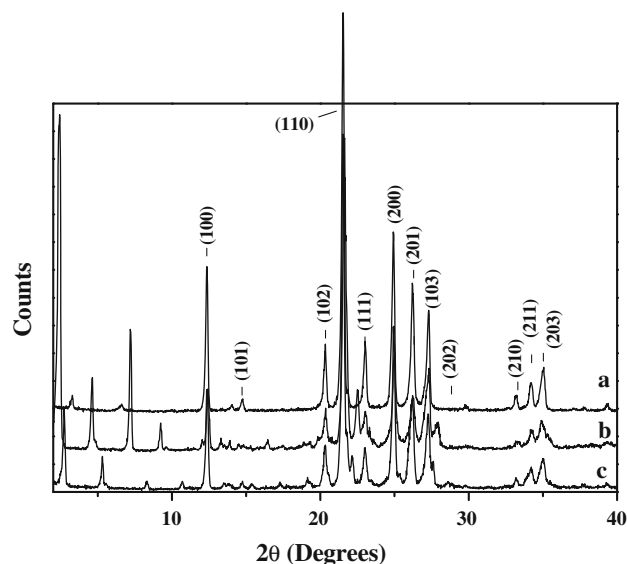


Fig. 1 Indexed powder X-ray diffractograms for the matrix in OA-(6 urea) (a), DDA-(9 urea) (b) and DA-(9 urea) (c)

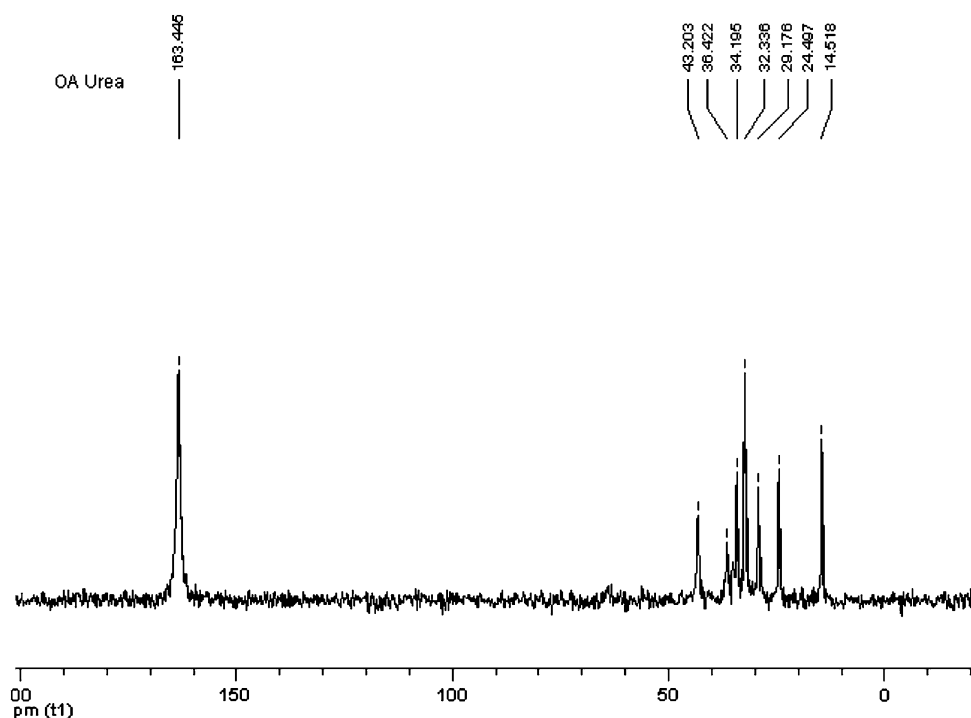
Table 1 Lattice parameters for the hexagonal structure with space group P6₁22 of urea matrix at room temperature, for different inclusion compounds with alkylamines and guests lengths obtained theoretically considering the more extended conformation (zig-zag)

Phase	A (Å)	b (Å)	c (Å)	Guest length (Å)	Guest length/c
Octylamine-(6U)	8.23 (2)	8.23 (2)	11.01 (3)	11.68	1.06
Decylamine-(9U)	8.21 (6)	8.21 (6)	10.99 (9)	14.10	1.28
Dodecylamine-(9U)	8.21 (2)	8.21 (2)	11.01 (3)	16.29	1.48

Table 2 Chemical shifts of octylamine inserted in the urea matrix compared with those of the amine in other media

Assignment	Guest in urea matrix	Reported for the guest*	Reported for the guest in CCl ₄
C- α -1(1)	43.20	42.3	42.51
C-2	36.42	34.4	34.27
C-3	29.18	27.4	27.48
C-4 and C-5	34.19	30.0	32.42
C-6	32.34	32.5	30.09
C-7	24.50	23.1	23.18
C8	14.52	14.0	14.57

* ChemDraw Ultra[®], Chemical Structure Drawing Standard, 1985–2000 CambridgeSoft.Com. and in CCl₄

Fig. 2 ¹³C CP-MAS NMR spectrum of OA-(6 urea) at room temperature and at 100.63 MHz. The urea/alkylamine inclusion compounds have a resonance at about 163.4 ppm due to the carbon in the urea molecule

under vacuum at room temperature for about 5 h. The colorless crystalline products have the composition: octylamine-(6U), decylamine-(9U) and dodecylamine-(9U).

Synthesis of metal nanoparticles

Samples of ICs were ground to a fine powder in order to reduce the likelihood of the crystallites exhibiting a preferred orientation.

Fine gold (or silver) target cathodes were utilized in the sputtering equipment. A glass sample-holder containing the evenly distributed IC fine powder was introduced in the sputtering camera. Subsequently a vacuum of 0.5 mbar and an Ar flux was introduced. A current of 30 mA was used to ionize the Ar. The Au (or Ag) atoms present in the plasma were deposited on the ICs apparently in an epitaxial form, leading to the formation of metal nanoparticles. During the process, the IC crystals were stirred manually in

the equipment to facilitate the deposition of MNPs on a possible preferential plane.

Characterization

The formation of the urea-alkylamine ICs The formation of urea-alkylamine ICs was demonstrated by the observation of visible and characteristic motions that accompany its decomposition in water, reported by us [51] and the stoichiometry of the compounds was determined by elemental analysis.

XRD data were collected at room temperature on a Siemens D 5000 powder diffractometer, with Cu K α radiation in the $2^\circ < 2\theta^\circ < 80^\circ$ range (40 kV, 30 mA) and a graphite monochromator (1.540598 Å). The lattice parameters and refinement were calculated by the ITO method, which is the basis of the theoretical powder X-ray computer program.

The UV–visible absorption spectra of the MNPs deposited onto the ICs were measured at room temperature in a Shimadzu UV-2450 spectrophotometer.

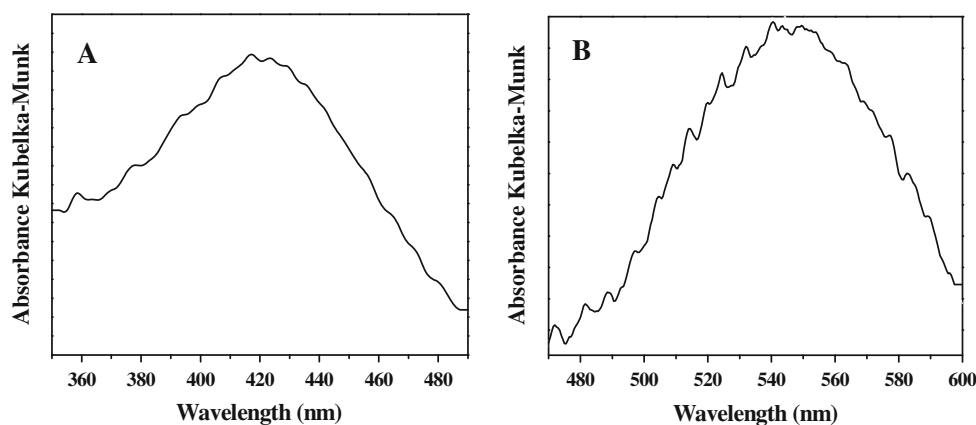
The size distribution of the nanoparticles was obtained by a transmission electron microscope, TEM, (Zeiss EM109). TEM images of nanoparticles were obtained by preparing an isopropyl alcohol suspension of substrate on carbon-coated copper grid disks and evaporating the solvent in air. The TEM images of all samples were measured with a maximum acceleration voltage of 50 kV.

SEM images were obtained on LEO 1420VP equipment.

IR measurements were carried out on a Perkin Elmer System 2000 using KBr pellets or films.

^{13}C - cross-polarization magic angle spinning (CP-MAS) NMR spectra were recorded on a Bruker MSL-100 at a frequency of 100.63 MHz. The polycrystalline powder sample was spun at a frequency of 4 kHz. The number of the scan was 5,000. The chemical shifts are given relative to TMS.

Fig. 3 Absorption spectra of AgNPs onto DA-(9 urea) (a) and AuNPs onto OA-(6 urea) (b), and 25-s exposure for the sputtering



Results and discussion

Characterization of the inclusion compounds

Alkylamine-urea stoichiometric ratios in all cases satisfy the relationship $1:3n$ ($n = 2$ for octylamine and 3 for decylamine and dodecylamine); determined by quantitative elemental analysis.

Characterization of the ICs by X-Ray powder diffraction clearly shows that octylamine, decylamine and dodecylamine can be accommodated by the urea to form stable inclusion compounds with channel structures at room temperature (296 K), which are similar to those obtained from the inclusion of other guest [16, 52]. The products crystallize as hexagonal prisms which are easily distinguished from pure urea, which crystallizes as tetragonal prisms [53]. The diffractograms of the ICs indicated the absence of any crystalline phases other than those of the reported inclusion compounds. The crystals obtained are typically a few tenths of a millimeter in cross-section and several tenths of a millimeter in length. The cross-sectional shape of most crystals of the synthesized amine derivatives are practically perfect, regular hexagons. Moreover, the synthesized urea ICs behave under the polarizing micro-

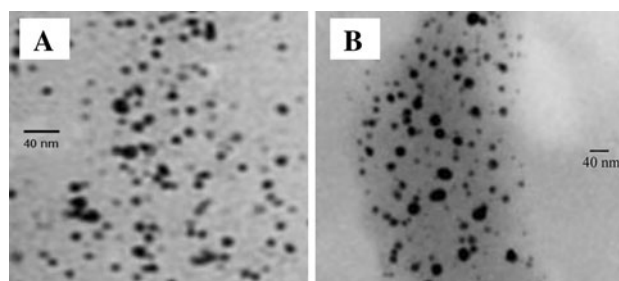


Fig. 4 TEM micrographs of AuNPs supported on DA-(9 urea) (a), and AgNPs supported on DA-(9 urea) (b)

Fig. 5 Size distributions of AuNPs supported onto DA-(9 urea) (a) and AgNPs onto DA-(9 urea) (b)

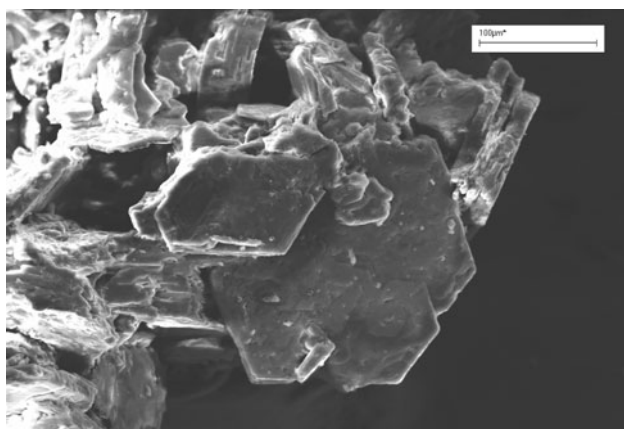
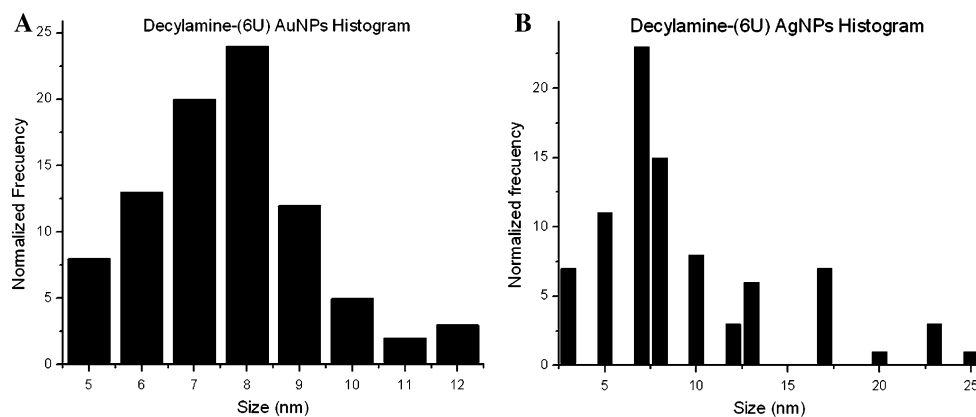
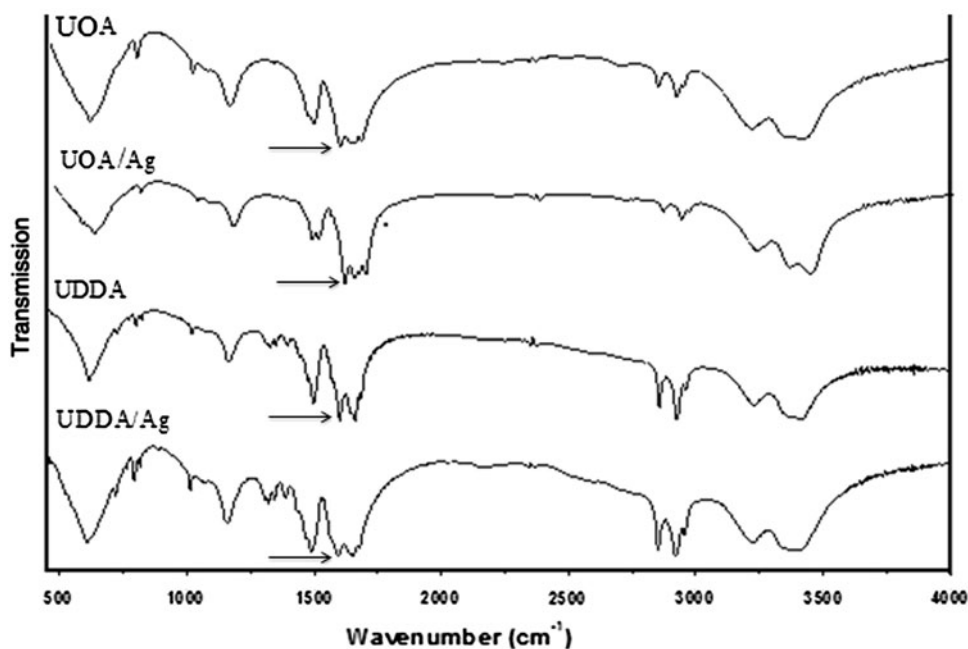


Fig. 6 SEM micrograph of DA-(9 urea) microcrystals decorated with silver nanoparticles

scope in a manner which is consistent with the assignments to the hexagonal crystal system.

The X-ray diffraction analysis of polycrystalline samples of the products shows that most of the peaks in the diffractograms can be indexed on the basis of the hexagonal lattice parameters: $a = b = 8.2 \text{ \AA}$, $c = 11.0 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, which correspond to a basic host structure. Some low intensity peaks cannot be indexed on this basis and probably belong to reflections of the guests. Typical diffractograms of the products OA-(6 urea), DA-(9 urea) and DDA-(9 urea) are shown in Fig. 1. Table 1 shows the corresponding lattice parameters for the matrix urea with hexagonal structure for the synthesized ICs. From the amine/urea stoichiometric ratios with $1/3n$ ($n = 2, 3$) it follows that an amine guest molecule, depending on its molecular length, in its most extended

Fig. 7 IR spectra of OA-(6 urea), DDA-(9 urea) and the IR spectra of these inclusion compounds interacting with Ag nanoparticles



linear conformation, must occupy either 1 or 2 channel units repeat. Moreover, these features correspond to a two dimensional array of hexagonal channels along which the translation repeat unit (c) of about 11 Å is always the same, independent of the size of the guests, agreeing therefore with the basic host structure observed for urea–hydrocarbon inclusion compounds [13]. The basic hexagonal structure remains unchanged when the inclusion compounds interact with AuNPs and AgNPs, showing additional peaks of relatively low intensities characteristic of the fcc phase of the metals.

The ^{13}C CP-MAS NMR spectra of the urea inclusion compounds at room temperature show a pattern which is similar to those of the same amine as a pure liquid or dissolved in an organic solvent or simulated. High-amplitude motions of the amine guest molecules in the channels average the residual dipolar interactions between ^{13}C and ^{14}N to less than 25 Hz. ^{13}C - ^{14}N residual dipolar interaction is not averaged to zero by MAS. The axis of quantization of the ^{14}N nucleus is tilted from the direction of the static magnetic field as a consequence of the interaction between the ^{14}N nuclear quadrupole moment and the electric field gradient at the ^{14}N nucleus [15]. In Table 2 are reported the chemical shifts of octylamine inserted in the urea matrix with those of the amine in other media. Figure 2 reproduces the ^{13}C CP-MAS NMR spectrum of OA-(6 urea).

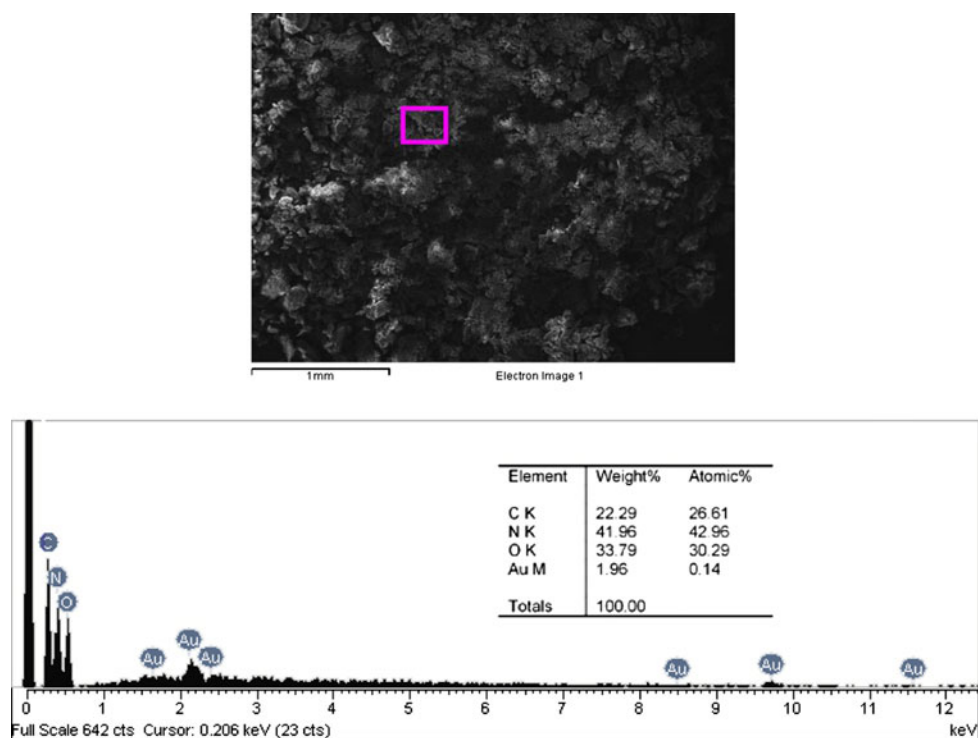
The behavior of organic molecules placed in environments such as those occurring within clathrate cavities is expected, in general, to differ from those of the same

molecule in other phases [54–56]. In this work, the ^{13}C -NMR behavior of octylamine was analyzed in some detail. Indeed, the effect of the amine autoassociation on the chemical shifts can be appreciated by observing the shifts on going from the pure amine liquid to a dilute solution in CCl_4 . Interestingly, the ^{13}C chemical shifts of octylamine included in the urea correspond to the free amine or at least to an amine undergoing weaker interaction with the medium than the amine dissolved in an inert solvent. Urea channels appear to be a perfect van der Waals cavity.

Deposition of metal nanoparticles

The gold and silver NPs deposits onto the ICs were prepared in a short optimal time (25 s), determined from optical studies for exposure to sputtering. Increased efficiency is obtained in sequential exposure of 5 s due to the statistical presentation of the crystal faces. The size of the deposited AuNPs and AgNPs could be estimated from the exposure time of the substrate. This indicates that the particles are not formed in the plasma phase before landing, but that they are formed on the ICs. The MNPs are located almost certainly preferentially on selected faces (100) of the crystal. The immobilization of AuNPs and AgNPs can be attributed to the interaction of Au-NH_2 or Ag-NH_2 with the free-dangling $-\text{NH}_2$ groups of the guest molecule located at the entrance to the cavity of the urea matrix [(001) crystal plane]. This would lead to the stabilization of the particles on the surface of the ICs.

Fig. 8 SEM image and EDAX analysis after the adhesion of Au-NPs onto the urea inclusion compound containing octylamine as guest



Verification of the deposition of the metal nanoparticles on the supramolecular substrate was obtained by diffuse reflectance spectroscopy. The UV/visible spectra show the characteristic surface plasmon resonance peaks at 520 nm for Au and 420 nm for Ag [46].

Figure 3 show the surface plasmon resonance of spherical AuNPs on OA-(6 urea) with maximum absorptions at 545 and 420 nm for DA-(9 urea). No significant differences were observed for the absorption of the other AuNPs-ICs and AgNPs-ICs systems. With longer time, 60 s for example, decreased absorbance or a shift toward longer wavelengths of surface plasmon resonance of the MNPs, are observed. Probably a single exposure for a longer time would generate larger size nanoparticles.

The AuNPs and AgNPs were characterized by transmission electron microscopy (TEM). Spherical Au and Ag nanoparticles with low size dispersion were observed, in a size range between 8 and 25 nm for gold, and between 8 and 40 nm for silver. Figure 4 shows the corresponding TEM images of the AuNPs onto DA-(9 urea) and Ag onto DA-(9 urea) systems.

Figure 5 shows histograms for the AuNPs onto OA-(6 urea) and Ag onto DA-(9 urea) systems with a nanoparticles average size for all the systems of around 8 nm for Au and 7 nm for Ag.

SEM images demonstrate clearly the hexagonal structure of the microcrystal decorated previously with Au- and AgNPs (Fig. 6). EDAX shows the presence of gold or silver in the corresponding decorated crystals.

Comparison of the IR spectra obtained for the synthesized ICs and for ICs interacting with AuNPs and AgNPs shows that they are basically unchanged. Furthermore, the spectra also present some increased broadening and intensities of the characteristic NH_2 bending frequencies at $1,597\text{ cm}^{-1}$ for the inclusion compounds interacting with the metal nanoparticles (Fig. 7).

The $-\text{NH}_2$ groups, at one end of the channels out of the urea matrix, could act as surfactant groups stabilizing the MNPs, being possible a preferential deposition on the (001) plane of the urea ICs crystals and forming a 2D hexagonal lattice. EDAX analysis of AuNPs onto OA-(6 urea) shows the presence of gold and other elements of the compound (Fig. 8).

The amino groups of the guests can emerge from the entrance of the inclusion compound cavities attracted by the metallic nanoparticles, in opposition to the restoring van der Waals interactions present inside the channels, which increase with increasing chain length of the guest molecules.

Conclusions

The use of urea IC substrates with a surface modified for the deposition of nanoparticles is an efficient method for

obtaining Au- and AgNPs with low size dispersion. This is probably due to the high affinity between the $-\text{NH}_2$ functional group of the surfactant guest with the metal, considering that the $-\text{NH}_2$ groups that are located at one end of the channels out of the urea matrix may interact with the MNPs, possibly with preferential deposition on a plane of the urea IC crystals. These $-\text{NH}_2$ groups can allow the formation of a two-dimensional hexagonal lattice that stabilizes and arranges the MPs in an ordered way. In some cases, partially hexagonal arrangements of the MNPs were observed.

These urea inclusion compounds provide a convenient way of storing the NPs in the solid state without aggregation.

The magnetron sputtering technique used to prepare ordered NPs has several advantages, such as scalability, that make it attractive for industrial applications.

Furthermore, the studied amines have a high tendency to hydrolyze, but their inclusion also has a practical interest considering the stability shown by them when they are included in urea, allowing them to stay for a long time in contact with the atmosphere without decomposition.

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