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# Supramolecular Colloidal Systems of Gold Nanoparticles/Amphiphilic Cyclodextrin: a FE-SEM and XPS Investigation of Nanostructures Assembled onto Solid Surface

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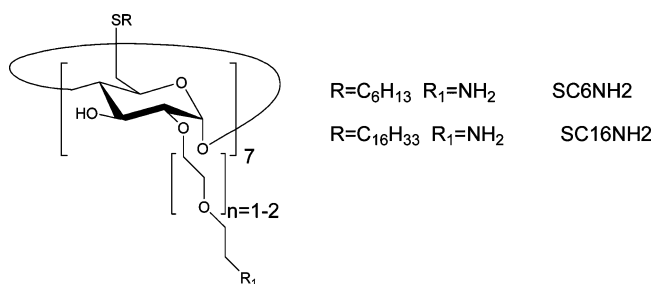
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Properly functionalized amphiphilic cyclodextrins (CDs) can act as capping agents for gold colloids in solution (Mazzaglia, A.; et al. *J. Phys. Chem. C* **2008**, *112*, 6764). In the present work, we report a study on a hybrid gold nanoparticles/amphiphilic CD supramolecular system assembled onto a surface by both field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) techniques. Amphiphilic CDs bearing respectively thioalkyl chains with different length in the primary site (thiohexyl in SC6NH2 and thiohexadecyl in SC16NH2) and oligoethylene amino groups in the secondary ones were drop-cast onto glass and silicon surfaces. FE-SEM pointed out on the mesoscopic scale the presence of CDs aggregates with sizes of about 100–300 nm, mostly displaying the known vesicular aspect. Both CDs can interact closely with gold nanoparticles of 10–20 nm. The binding mode was investigated in detail by XPS pointing to the coordination of CD amino groups with the external thin shell of gold nanoparticles. In the present case, the anchorage of the CDs to the noble metal occurs via the amino groups, which are unexpectedly favored with respect to the less accessible thioether groups. This investigation can potentially open perspectives in the design and control of devices engineered onto surface for biosensing or drug delivery.

## Introduction

The design of surface microenvironments suitable to integrate cells in implantable therapies and build cell-based biosensors,<sup>1</sup> or control the delivery of molecules for therapy and diagnosis,<sup>2</sup> are at the center of a consistent interdisciplinary research effort. Complex hybrid nanoparticles can act as building blocks to assemble new electronic and optical devices<sup>3</sup> or interact with surfaces by spontaneous self-assembly of functional components<sup>4</sup> as an alternative to top-down miniaturization and bottom-up nanofabrication.<sup>5</sup> The stabilization in solution of noble metal nanoparticles with different ligand systems<sup>6</sup> as dendrimers,<sup>7</sup> sugars,<sup>8</sup> micellar copolymer,<sup>9</sup> amphiphiles,<sup>10</sup> and cyclodextrins<sup>11</sup> can address the self-assembly of nanostructures for surfaces modifications. A new generation of amphiphilic cyclodextrins (CD) modified with thioalkyl groups on the upper rim and oligoethylene-glycol on the lower rim<sup>12</sup> are good candidates for the controlled delivery to the site of action of particular molecules such as photosensitizers<sup>13</sup> and anticancer drugs.<sup>14</sup> The selectivity of such amphiphilic CDs toward some specific receptor proteins was demonstrated by grafting receptor targeting groups on the CDs hydrophilic region.<sup>15</sup> Photoresponsive films of CDs embedding porphyrins on glass were proposed as systems displaying hydrophobic–hydrophilic moieties for potential application as local photosensitizer-eluting surfaces in

## SCHEME 1: Sketched Structure of the Investigated Amphiphilic CD



photodynamic therapy of tumors (PDT).<sup>16</sup> Multifunctional carrier systems with photoactivable centers and noble metal core which (simultaneously) generate hyper-reactive species have been developed.<sup>17</sup> Gold nanoparticles (AuNPs) stabilized by CDs in aqueous solutions have been recently described with perspective in photothermal therapy of tumors (PTT).<sup>18a</sup> Here we report an investigation of the nanostructures consisting of gold colloids capped with amphiphilic cationic CD (SC6NH2 and SC16NH2, see Scheme 1) and assembled onto glass and Si surfaces. SC6NH2 and SC16NH2 have been proposed as suitable carrier because their ability to include neutral and ionic drugs in their different portions (hydrophobic and hydrophilic moieties and even in the cavity) and deliver the encapsulated guest into cells, displaying an high internalization efficiency.<sup>13,18a–c</sup>

Au/SC6NH2 and Au/SC16NH2 have been investigated by combination of field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS). FE-SEM has revealed the organization of CD-bounded AuNPs,

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displaying the formation of CD nanoaggregates which closely interact with metal clusters. XPS is a powerful technique to study the physical and chemical phenomena on the surface of solids. Relevant biomedical problems have been approached by using XPS<sup>2,19</sup> since it allows to gain detailed information on the interactions between molecular and metal components in biologically inspired surfaces, providing relevant information on free and complexed metal nanoparticles. Since the interactions in Au/CDs nanoassemblies can depend on the nature of the CD-Au bond, we have deeply explored by XPS their surface chemical composition. To the best of our knowledge, this is the first investigation reporting preferential coordination of gold by amino rather than thioether groups for a ligand containing both functionalities. This experimental evidence is in line with a lower availability of the sulfur donor atom due to the steric hindrance imposed by hydrophobic interactions driving the nanoassemblies formation.

## Experimental Section

**Materials and Methods.** Heptakis(2- $\omega$ -amino-oligo(ethylene glycol)-6-deoxy-6-hexyl-thio)- $\beta$ -CD (SC6NH2) and heptakis(2- $\omega$ -amino-oligo(ethyleneglycol)-6-deoxy-6-hexadecyl-thio)- $\beta$ -CD (SC16NH2) were synthesized as chloride salt (SC6NH3<sup>+</sup>Cl<sup>-</sup> and SC16NH3<sup>+</sup>Cl<sup>-</sup>) according to the general procedures.<sup>12c</sup> The solvents used were purified and dried by standard techniques. All the other reagents were of the highest commercial grade available and were used as received or were purified by distillation or recrystallization when necessary.

**Casting of Au/SC6NH2 and Au/SC16NH2 on Glass and Si Surface.** Preparation of CDs nanoaggregates was carried out by using conventional procedures.<sup>13</sup> CDs solutions in CHCl<sub>3</sub> (330  $\mu$ M) were first slowly evaporated overnight to form thin films that were subsequently hydrated, sonicated for 20 min in a bath sonicator, and eventually equilibrated overnight.

AuNPs were prepared in water by reducing a solution of tetraethyl ammonium tetrachloroaurate (III) [Et<sub>4</sub>N][AuCl<sub>4</sub>] (1.4 mM) with citric acid by a slight modification of the typical procedure.<sup>20</sup> The obtained gold colloidal solution (1 mL) was mixed with the amphiphilic CDs solutions (SC6NH2 and SC16NH2) according to the reported procedure in the presence of Et<sub>3</sub>N to form Au/SC6NH2 and Au/SC16NH2, respectively.<sup>18</sup> Also samples of SC6NH3<sup>+</sup> and SC16NH3<sup>+</sup> were prepared without Et<sub>3</sub>N, thus as specified. Samples of AuNPs/CDs were drop-cast onto glass and Si (100) surface and dried. The supports were previously treated with a mixture NH<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O at 1:1:4 molar ratio and rinsed with ethanol and ultrapure water. Solutions of free AuNPs, SC6NH2 and SC16NH2 were also drop-cast on the same comparison. All the samples were analyzed, 1–2 days after overnight evaporation of the solvent at room temperature.

**Field Emission Scanning Electron Microscopy (FE-SEM).** The micro and nanomorphology of the deposited samples was investigated by using a high brilliance LEO 1530 (FE-SEM) apparatus equipped with an energy dispersive X-ray spectrometer (EDS) model INCA 450 and a back scattered electron detector. The images were recorded both in the secondary electron image (SEI) and back scattered image (BSD) mode at different acceleration voltage ranging from 20 to 1 kV.

The samples have been graphite-coated in order to avoid charging effects. The coating was deposited by using a sputter coater unit at a pressure of  $1 \times 10^{-5}$  mbar in order to produce a carbon film with a nearly constant thickness less than 1.0 nm.

**X-ray Photoelectron Spectroscopy.** XPS experiments were carried out by using an ESCALAB MkII (VG Scientific Ltd.,

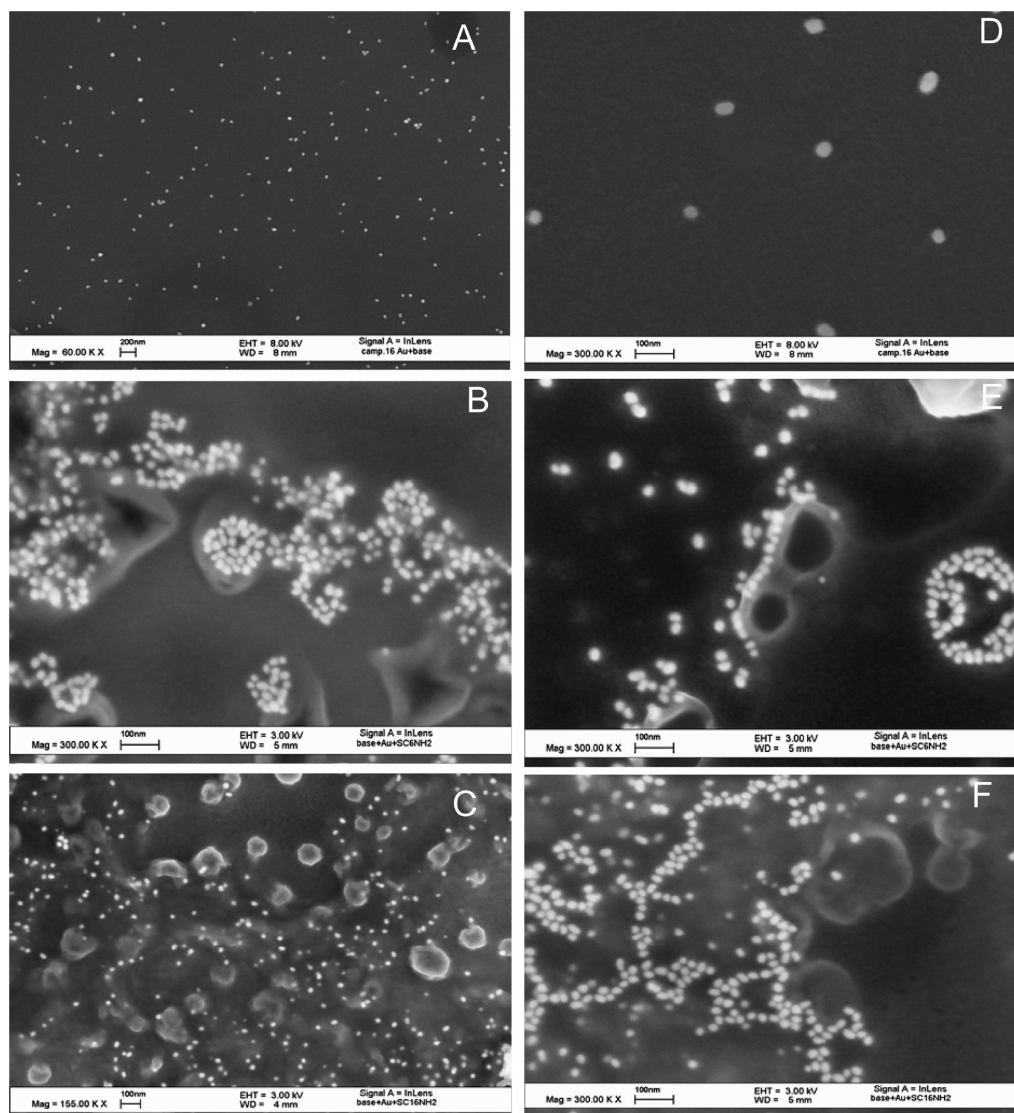
U.K.) spectrometer, equipped with a standard Al K $\alpha$  excitation source and a 5-channeltron detection system. Photoelectron spectra were collected at 20 eV constant pass energy of the analyzer and a base pressure in analysis chamber of  $10^{-8}$  Pa. The binding energy (BE) scale was calibrated by measuring the C 1s peak (BE = 285.0 eV) from the surface contamination and Au 4f<sub>7/2</sub> peak (BE = 84.0 eV) from AuNPs. However, before investigating the samples, the energy scale was precalibrated by measuring sputter-cleaned Au 99.99% foil and setting Au 4f<sub>7/2</sub> peak to BE = 84.0 eV. The accuracy of experimental BE scale was  $\pm 0.1$  eV. More experimental details on XPS technique have been reported elsewhere.<sup>21</sup> The spectra were processed by the CasaXPS v. 2.2.84 software, using a peak-fitting routine with symmetrical Gaussian–Lorentzian functions. The background was subtracted from the photoelectron spectra by using Shirley method.

The shell thickness of AuNPs was approximately estimated by calculating the relative concentration of positive gold species from Au 4f spectra and putting the obtained value in the computed graphics reported by Gillet and Meunier.<sup>22</sup>

## Results and Discussions

Recently, we have successfully used SC6NH2 as capping agents for AuNPs in aqueous solution.<sup>18</sup> The capping reaction was carried out in solution in the presence of a slight excess of ligand aiming to an effective CD coverage of the AuNPs surface. The plasmon resonance band of AuNPs stabilized with citrate was affected by the interaction with SC6NH2. An increase of the AuNPs size was also confirmed by Quasi Elastic Light Scattering (QELS). In particular, we hypothesized that an electrostatic interaction between the negative citrate and the cationic charges of the CDs could further stabilize gold colloids. However, the unprotonated SC6NH2 can efficiently interact with Au surface affording nanoparticles having hydrodynamic radii of 2 and 25 nm in aqueous solution which were tentatively ascribed to Au/CDs hybrid systems. A similar behavior was found for Au/SC16NH2 system (data not reported). In aqueous solutions the detection of CDs aggregates by QELS was prevented by the marked contrast due to the much larger refractive index of gold with respect to the organic capping reagent. Recently, FE-SEM has been used to investigate the morphology of a powdered sample of a unmodified  $\alpha$ -cyclodextrin and its self-assembly with guest molecules.<sup>23</sup> When the aggregates are supported on solid substrate, FE-SEM affords additive information with respect to the results in solution. Figure 1 shows AuNPs of 10–20 nm diameter (A and D) agglomerated nearby SC6NH2 nanoassemblies. These latter exhibit a vesicular aspect and an average diameter of about 200 nm (Figure 1B). Some of the Au clusters are covering the smallest CD nanoassemblies or are located in the enclosure of the aggregates (Figure 1B) or around the external surface (Figure 1E). In all the images free agglomerates of AuNPs and free CD nanoassemblies are clearly detectable due to the high tendency of both unbound gold colloids<sup>24</sup> and free CD amphiphiles,<sup>12c</sup> respectively, to self-aggregate.

The vesicular aspect of the hollow aggregates of Au/SC6NH2 (sample freshly prepared and evaporated overnight) is probably due to the slow solvent evaporation which could stratify layers of CD material from the interior of the microdroplets to the periphery. Besides the morphological aspect of the CD aggregates can be affected by the nonionic headgroups<sup>25</sup> which would exhibit a reduced repulsive interactions with respect to the charged form.<sup>12c</sup> Differently, FE-SEM investigation on a SC6NH2 sample aged 5–7 days displays the typical micellar



**Figure 1.** Representative FE-SEM images at different magnification of free AuNPs (A, bar = 200 nm; D, bar = 100 nm) and AuNPs interacting with SC6NH2 and SC16NH2: Au/SC6NH2 (B, bar = 100 nm; E, bar = 100 nm); Au/SC16NH2 (C, bar = 100 nm; F, bar = 100 nm).

cluster structures (not shown). In the case of the Au/SC16NH2 system, AuNPs are distributed in the surroundings of the CD vesicles (Figure 1C). A magnified analysis of this sample (Figure 1F) shows that some of these Au nanoparticles can form clusters which closely interact with CD aggregates. SC16NH2 vesicles can coalesce onto the surface after 5–7 days from sample preparation, even if they could maintain their clear vesicular morphology (not shown).

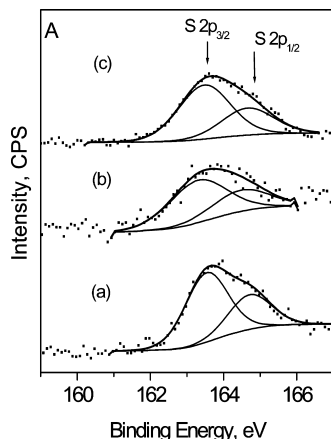
**XPS Analysis of Au/SC6NH2 Sample.** The molecular structure of a single modified  $\beta$ -CD (Scheme 1) suggests that gold nanoparticles could be bound to different donor atoms, such as S in thioalkyl- or N in amino-terminal groups. As it is well-known, Au exhibits a very strong affinity for sulfur that is frequently exploited to modify nanostructured materials. Although Au–S is stronger than Au–N interaction, when a molecule contains both S and N donor atoms, in line of principle it can be bonded to Au by different links. In order to solve this uncertainty and to disclose which kind of interactions drives the assembling process, the anchorage typology of cyclodextrins to inorganic nanoparticles was investigated by using XPS.

Surface chemical composition and BE of the main XPS peaks of the Au/SC6NH2 sample were compared with those of the SC6NH2 samples without AuNPs. Since during the capping

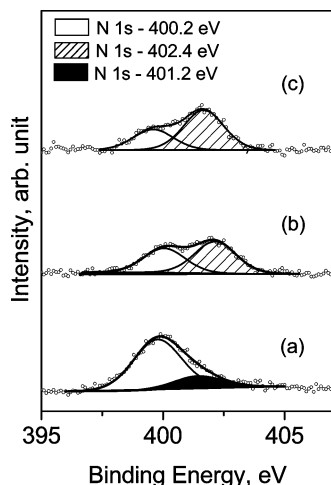
reaction, the pH solution was adjusted to 11 by adding  $\text{Et}_3\text{N}$ , this step could modify the shape and intensity of N 1s signal. Therefore, aiming to reduce perturbation of the XPS measurements, Au/SC6NH2 samples were also prepared in acidic environment (pH = 3). Moreover, in order to avoid the superimposition of Au 4f peak with the Si 2p satellites produced by the nonmonochromatic X-ray source, all the investigated samples were also supported on a glass substrate. Since the chemical shift of the Si 2p signal is about 3–4 eV from  $\text{Si}^0$  to  $\text{Si}^{4+}$ , the satellite peaks, generated at 10 eV below to the main peak, fall out of the Au 4f region when the glass substrate is used.

Figure 2 shows S 2p spectra of the investigated samples, that consist of a typical spin–orbit doublet  $2p_{3/2}$  and  $2p_{1/2}$  separated in energy by 1.1 eV. The deconvolution of the signals revealed that only single chemical species of sulfur were present in the samples. The S  $2p_{3/2}$  synthetic peak was centered at BE = 163.5 eV, that is the characteristic value of free thiol group. Such an assignment is supported by the work of Reinhoudt et al.,<sup>11a</sup> that reported a BE value of 163.4 eV for the unbonded sulfur while Au–S bond should give a contribution at 161.9 eV, which is absent in the spectra of analyzed sample.





**Figure 2.** S 2p spectra for the samples of (a) free SC6NH<sub>2</sub>, (b) Au/SC6NH<sub>2</sub>, and (c) Au/SC6NH<sub>3</sub><sup>+</sup> (sample not treated with Et<sub>3</sub>N).



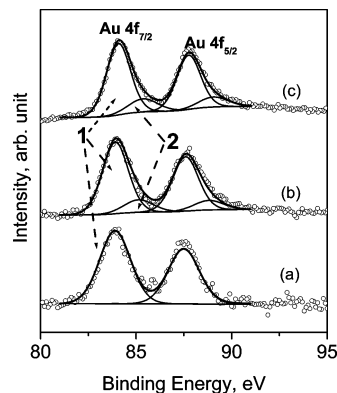
**Figure 3.** Comparison of the N 1s spectra for the samples of (a) free SC6NH<sub>2</sub>, (b) Au/SC6NH<sub>2</sub>, and (c) Au/SC6NH<sub>3</sub><sup>+</sup>.

Therefore the S 2p spectrum can be safely assigned to C–S–C bond, ruling out the sulfur binding to AuNPs.

Figure 3 shows a comparison of N 1s spectra registered for different samples. The N 1s spectrum of the SC6NH<sub>2</sub> sample was fitted by introducing two synthetic peaks, positioned at BE = 400.2 and 401.2 eV, respectively. As reported in the literature,<sup>26</sup> the lower energy component can be assigned to amine group and the higher one to ammonium groups. The shape of the signal shows a dominant contribution of amine groups in the SC6NH<sub>2</sub> sample.

The same peak for amine group at BE = 400.2 eV was observed in the Au/SC6NH<sub>2</sub> samples in the presence and in the absence of the base, together with a new peak located at BE = 402.4 eV. The observed shift of the second component in the N 1s spectra is indicative of coordination of CDs with AuNPs. Moreover, it can also be noted that in samples with AuNPs (see Figure 3, panels b and c) this second component becomes dominant, pointing to a quite strong interaction.

Furthermore, when the AuNPs interact with CDs, the shape of Au 4f signal is modified as evidenced by the spectra comparison displayed in Figure 4. Au 4f<sub>7/2</sub> peak was fitted by using two synthetic peaks positioned at BE = 84.0 and 85.2 eV. The first contribution was assigned to elemental gold (Au<sup>0</sup>), while the second one was related to the stable state of Au<sup>+</sup>. This result indicates the presence of two different Au species, that can be interpreted by the model of a metallic core covered with a positively charged shell.<sup>27</sup>



**Figure 4.** Comparison of the Au 4f spectra for the samples of (a) AuNPs, (b) Au/SC6NH<sub>3</sub><sup>+</sup>, and (c) Au/SC6NH<sub>2</sub>. The arrows indicate the two Au 4f<sub>7/2</sub> components positioned at 84.0 eV (1) and 85.2 eV (2), respectively.

Several authors have analyzed the relationship between the intensity of photoelectron peak of a nanoparticle and the size of its core and shell.<sup>22</sup> By applying the same procedure and using the intensity ratio  $Au^0/Au^+ = 4/1$ , calculated from experimental Au 4f<sub>7/2</sub> components, we determined the thickness of the shell of a gold nanoparticle, which was equal approximately to 0.3 nm. This thickness of positive charged shell corresponds to about one or two atomic layers of Au. Very similar result (thickness ~0.4 nm) was obtained also by using the XPS thickogram<sup>28</sup> that is based on the flat sample model with thin and homogeneous surface overlayer, not describing accurately rounded nanoparticles.

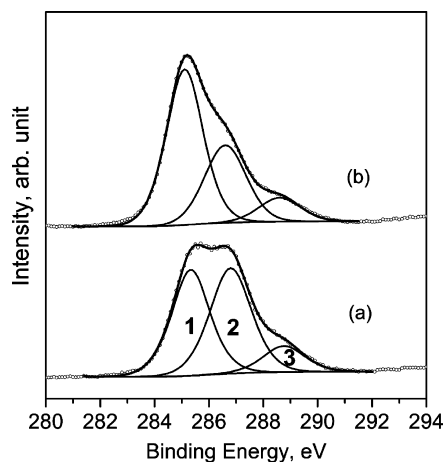
Altogether XPS results proved that AuNPs can preferentially coordinate to the amino-CDs ligands both in charged and in uncharged form (that is in absence or in presence of Et<sub>3</sub>N, respectively), confirming our previous hypothesis on the supramolecular Au/CD assemblies investigated in solution.<sup>18a</sup> In particular our experimental results demonstrate that amino groups of CD can coordinate the positively charged shell of Au nanoparticles. The formation of this bond in which the positive charge is possibly delocalized between metal and nitrogen donor groups can further be stabilized by the counterions (i.e., citrate ions).

**XPS Analysis of Au/SC16NH<sub>2</sub> Sample.** The XPS characterization offered an opportunity to obtain a fingerprint of the investigated cyclodextrins. In fact, the length of the aliphatic chain was identified from the comparison of C 1s spectra of different CDs samples. As it is depicted in Figure 5, the component due to the C–C bond (BE = 285.0 eV) augments together with the length of the aliphatic chain. This increase is modifies the shape of C 1s spectrum (Figure 5b) and the ratios of the component (1) with (2) and (3).

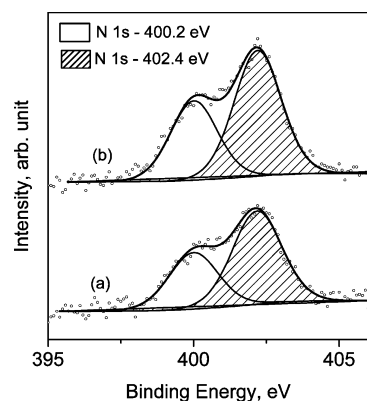
Our findings prove the ability of XPS technique to obtain qualitative information on organic compounds. Both spectra were processed by a peak-fitting routine including three components, positioned at BE = 285.0, 286.8, and 288.7 eV and assigned to C–C, C–O, O–C–O, or N–C–O bonds,<sup>29</sup> respectively.

The hydrophobic/hydrophilic balance in CDs could change the availability of the various binding sites and consequently could influence the formation of Au/SC6NH<sub>2</sub> and Au/SC16NH<sub>2</sub> assemblies.

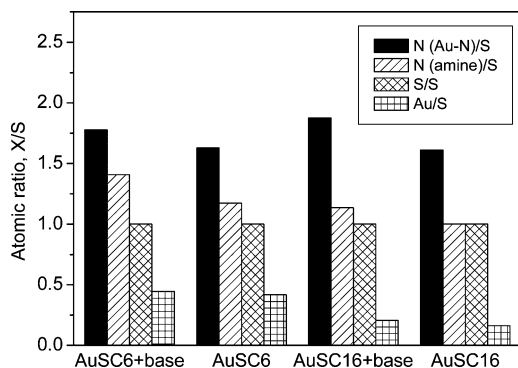
Figure 6 reports a comparison of the N 1s XPS spectra for both systems. The close similarity of the data confirms that, independently of the length of the alkyl chain, CDs bind to AuNPs through the terminal amino groups.



**Figure 5.** Comparison of the C 1s spectra for the samples of Au/SC6NH2 (a) and Au/SC16NH2 (b). Three components of peak fitting are positioned at (1) 285.0, (2) 286.8, and (3) 288.7 eV.



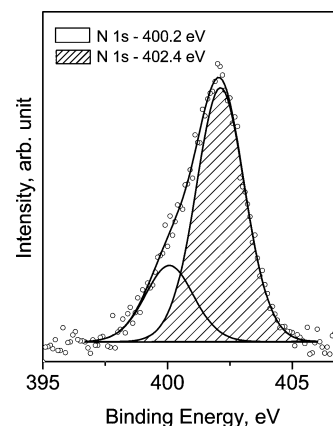
**Figure 6.** Comparison of the N 1s spectra for the samples prepared with base of (a) Au/SC6NH2 and (b) Au/SC16NH2.



**Figure 7.** Relative surface chemical composition of different samples. Elemental peak areas are normalized to the signal of S 2p.

Moreover XPS quantitative analysis revealed that the chemical composition of all the samples is very similar (Figure 7). Only some small changes in the elemental concentrations were observed for the samples prepared without the organic base. Obviously, their chemical composition reflected a lower nitrogen content, especially of the amine contribution. A lower Au/S ratio, observed in the Au/SC16NH2 samples, may be caused by the steric hindrance limiting the number of CDs in the neighborhoods of Au NPs.

Finally, in order to compare directly the samples investigated by XPS and FE-SEM, a sample assembled on Si substrate was also analyzed by XPS. N 1s spectrum of this sample, presented in Figure 8, consists of the same components already discussed above.



**Figure 8.** N 1s spectrum of the Au/SC6NH2 on Si (100) surface.

It is interesting to note that the intensity ratio of these components is higher than that obtained for the sample on glass substrate, indicating a higher content of N coordinated to Au. This result can be interpreted as a different capability of Si substrate to assemble the nanoaggregates of CDs and AuNPs.

## Conclusions

This paper reports a detailed investigation on the morphology and chemical properties of nanostructured material onto solid support, moving from the mesoscopic to the molecular-scale. After our recent results on Au/amphiphilic CD systems investigated in solution<sup>18a</sup> and the perspectives in cancer photothermal therapy, the hybrid nanoaggregates were studied onto surface by FE-SEM and XPS. These two techniques are very informative on the morphology and the nature of the interaction of SC6NH2 and SC16NH2 with Au nanoparticles onto silicon surface. Gold clusters decorate the smallest CD nanoaggregates or interact with the external surface or in the proximity of the larger ones. The interaction has been proven at molecular-level by XPS which points to the coordination by amino groups of CD with the positive external thin shell of gold, ruling out the involvement of the less accessible sulfur atom. These investigation could be useful as starting point to analyze bioinspired surfaces engineered with amphiphilic carriers and inorganic particles for biomedical applications.

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