Ordered arrangement of gold nanoparticles on an α-cyclodextrin–dodecanethiol inclusion compound produced by magnetron sputtering†

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An ordered self-assembly of gold nanoparticles (AuNPs) onto microcrystal faces of a 2α-cyclodextrin–dodecanethiol (2αCD–DDT) inclusion compound (IC) by means of a magnetron sputtering technique was obtained. The preferential deposition on the (001) plane of the αCD IC crystal occurs because –SH groups from the guest molecules found within the αCD protrude into that plane. These –SH groups form a two-dimensional hexagonal lattice that interacts with the metal NPs, arranging them in an ordered way.

Gold nanoparticles (AuNPs) are fascinating materials owing to their to unique quantum size effect,[1] optical,[2] electronic,[3] magnetic[4] and supramolecular[5,6] properties. In order to explore these potential applications, systematic studies on the controlled assembly of such nanoparticles are needed, for example on polymer surfaces and single atomic monolayers.[7] A novel concept, reported for the first time recently, has been the face selective adhesion of AuNPs onto the crystal faces of organic crystals.[8] Hexagonal single crystals of L-cystine were used, providing different functional groups on the crystal faces. 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 AuNPs: 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 involved 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]

The other preparation method can briefly be described as the sputtering of a high-purity gold target with argon ions, followed by 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 environmentally friendly, since the excess gold is recoverable from the chamber and there is no liquid waste.

As an alternative and even more versatile concept, we introduce in this work the use of cyclodextrin (CD) inclusion compounds (IC). Although unmodified and thiolated α- and β-cyclodextrins have been used for the preparation of colloidal gold nanoparticles[6,12,13] or the phase transfer of nanoparticles in liquids of different polarity,[14,15] the method described here utilizes the well-defined surface functionality of CD inclusion compounds, where the surface –SH functional groups can be adjusted by guest molecules. Hence, two very interesting areas of chemistry converge, *i.e.* the molecular recognition phenomenon applied to CD inclusion compounds and the assembly of metal nanoparticles. As a first result, we describe here the self-assembly of AuNPs produced by sputter deposition onto microcrystal faces of a 2αCD–dodecanethiol inclusion compound (2αCD–DDT).

Fig. 1 shows the diffuse reflection spectroscopy for the sputtered AuNPs on the surface of the αCD IC, showing the characteristic surface plasmon resonance with a maximum absorption around 530 nm. Compared to the maximum extinction of the particles in colloidal solution at around 520 nm,[9] the plasmon band observed here is shifted to longer wavelengths and extremely broadened. The average interparticle spacing is in the order of the particle size (Fig. 2).

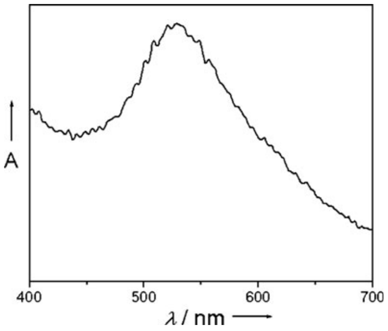

Fig. 1 Optical spectra of AuNPs on the surface of a microcrystal of 2αCD–dodecanethiol complex (recorded in diffuse reflectance).

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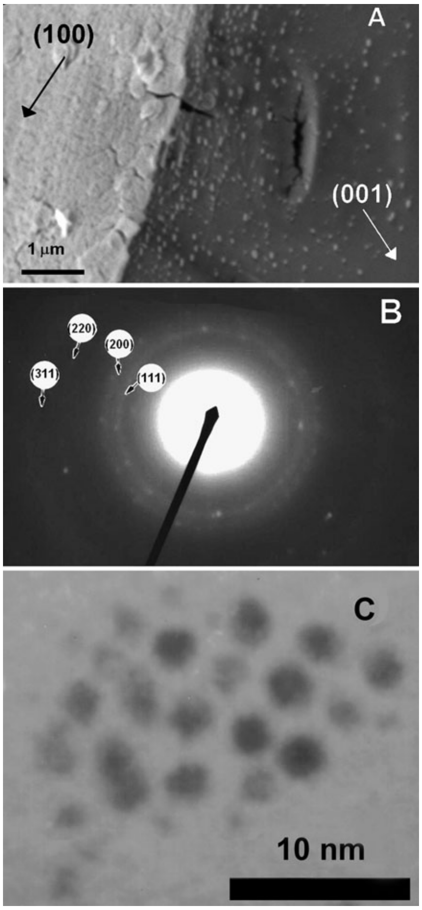

Fig. 2 A: SEM image reveals the selective deposition of AuNPs on the (001) plane with respect to the (100) plane of the CD IC. B: Diffraction pattern of AuNPs. C: TEM image showing the hexagonal arrangement of the AuNPs on the 2αCD–DDT.

The broadening, together with the red-shift of the plasmon peak, can be assigned to a dipolar coupling between closely neighboring particles and to a change of dielectric environment.[16]

Scanning electron microscopy (SEM) shows that the AuNPs were deposited preferentially on a crystal face. A representative SEM image of the microcrystal is shown in Fig. 2. Self-assembly of AuNPs can be seen on the surface of the inclusion complexes. The absence of any sizeable non-crystalline particles indicates that the NPs present in the sample must be bound to the microcrystal surface. The gold deposits were prepared in a short time (5–10 s). The size of the deposited AuNPs 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 AuNPs are located preferentially on selected faces of the crystal. A transmission electron microscopy (TEM) image is presented in Fig. 2. Several linear arrangements of the microcrystal surface are observed, leading to partial hexagonal ordering in some areas (40% approximately). The diffraction pattern shown in Fig. 2 demonstrates the presence of Au, with the corresponding (111), (200), (220) and (311) planes for the fcc metal phase.

Taking into account that the 2αCD–DDT complex structure presents a hexagonal structure and the DDT molecules are ordered along the *c* axis, the preferential plane is assumed to be the (001) Miller plane (Fig. 3). The lattice parameters are approximately $a = b = 25$ Å and $c = 16$ Å.[17] TEM shows an average inter-AuNP spacing of 50 Å, twice the CD unit's distance, indicating that the AuNPs are located in an alternated form on the CDs in the supramolecular structure.

The immobilization of AuNPs is due to the formation of an Au–S bond with the free-dangling –SH groups of the guest molecule, located at the entrance to the cavity of the αCD ((001) crystal plane). This leads to the stabilization of the particles on the surface. Therefore, the crystal provides a convenient way of storing the NPs in the solid state without aggregation. Fig. 4 shows the Raman spectra of 2αCD–DDT and αCD–DDT-AuNPs. It is seen that the S–H stretching peak appearing at 2575 cm^{-1} in 2αCD–DDT is practically absent in 2αCD–DDT-AuNPs due to deprotonation of the thiol group[18] of the DDT guest located at the entrance of the cavity of the αCD. The preferential deposition on the (001) plane of the CD inclusion compound crystal occurs because –SH groups from the guest molecules found within the CD protrude into that plane. These –SH groups form a two-dimensional hexagonal lattice that interacts with the metal NPs, arranging them in an ordered way.

Experiments performed in pure CD lead to the formation of AuNP aggregates and sporadic nanorods in a non-selective way on the crystal planes (ESI†).

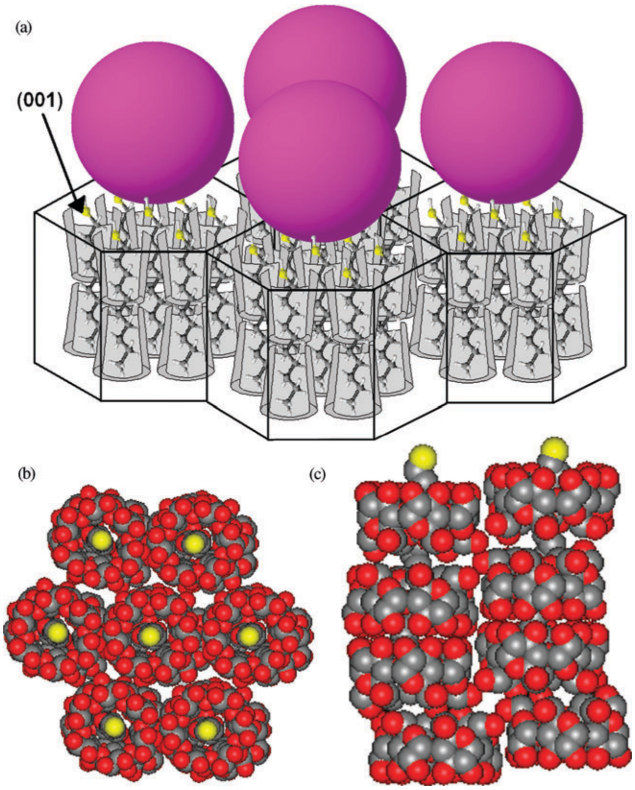

Fig. 3 A: Schematic representation of AuNP deposition on the (001) crystal plane of the 2αCD–DDT inclusion compound. B: Frontal and C: perpendicular view of the channel on the hexagonal structure of 2αCD–DDT.

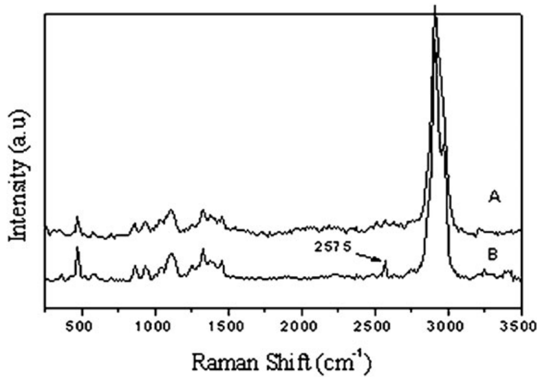

Fig. 4 Raman spectra of AuNPs on A: 2αCD–DDT and B: pure 2αCD–DDT in a powdered state.

In conclusion, the self-assembly of gold nanoparticles (AuNPs) onto the microcrystal faces of a α-cyclodextrin–dodecanethiol inclusion compound by means of a magnetron sputtering technique was achieved. Preferential deposition on the (001) plane of the αCD IC crystal occurs because –SH groups from the guest molecules found within the αCD protrude into this plane. These –SH 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 AuNPs has several advantages, such as the lack of waste stream and scalability, that make it attractive for industrial applications.

This work gives the first evidence of nanoparticle assemblies mediated by a guest molecule in a supramolecular structure. The wide variation of surfactant guest and metal nanoparticles should provide various composite materials coated by self-assembled nanoparticles.

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Experimental

The IC was obtained directly by mixing DDT (0.10 mL, 0.42 mmol) with a saturated solution of αCD (0.50 g, 0.51 mmol) in water at room temperature. The immediate formation of a white precipitate demonstrates the formation of the IC. The DDT : αCD molar ratio used in the experiment is somewhat greater than the stoichiometric 1 : 2 determined by ^{1}H NMR and elemental analysis.[19,20] Microcrystals were separated after 24 h, washed with hot acetone and dried under vacuum at 50 °C.

Microcrystals of the inclusion compound were spread on a glass surface to form a homogeneous layer prior to being exposed to sputtering. Gold was deposited onto the substrate in an inert atmosphere at room temperature.

Powder X-ray diffraction studies showed indistinguishable diffraction patterns for αCD–DDT and αCD–DDT-AuNP samples. All peaks in the diffractograms could be indexed on the basis of a hexagonal lattice with parameter values close to $a = b \approx 27$ Å, $c \approx 16$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$ for αCD.[19]

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