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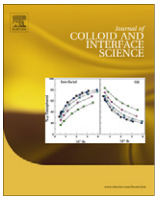

Selective nanodecoration of modified cyclodextrin crystals with gold nanorods

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ABSTRACT

Gold nanorods (AuNRs) stabilized by cetyltrimethylammonium bromide (CTAB) were deposited onto crystals of α-cyclodextrin (α-CD) inclusion compounds (ICs) that contained octanethiol (OT) as guest molecules. The nanodecoration was produced specifically at the {001} crystal planes through interaction between the –SH groups of the ICs and the AuNRs.

1. Introduction

Cyclodextrins (CDs) are water-soluble doughnut-shaped cyclic oligosaccharides with principally 6, 7, or 8 glucose units, and a central hydrophobic cavity that can enclose one or more molecules through noncovalent interactions [1,2]. CDs are widely used in the pharmaceutical sciences [3], technological separations [4], catalysis [5], and more recently in the field of chemical nanostructures [6]. In the CD molecule (Fig. 1A), the hydroxyl groups of the C2 and C3 carbon atoms are located around the larger opening, while the hydroxyl group of the C6 carbon atoms are aligned around the smaller opening [7]. The secondary hydroxyl groups of the C2 and C3 carbon atoms can interact with through hydrogen bonding due to their proximity within the cavity, whereas the hydroxyl groups of the C6 carbon atoms are free, which enables the groups to interact with guest molecules such as octanethiol [8]. These interactions are several of the driving forces that lead to the formation of CD IC. Other forces that govern the formation of CD IC with guest molecules possessing alkyl chains (e.g., OT) are hydrophobic and van der Waals interactions between the inner surface of the CD ring and the hydrophobic tail of the guest [1].

Structural studies of single crystals using X-ray diffraction (XRD) of the CD ICs with alkylated guest molecules have a basic structure: a type channel with two α-cyclodextrins (α-CDs) aligned head to head with alkylated guest molecule in a stretched conformation within the cavities [6] (Fig. 1B). However, high mobility of the guest molecule, even at low temperatures, causes the determination of the specific sites occupied by the guest molecule in the cavities of α-CD molecules to be difficult [6]. Proton nuclear magnetic resonance (^{1}H NMR) experiments, which were previously reported, by our group demonstrated that the CD IC existed in solution and maintained the basic dimeric structure with the guest molecule enclosed. The analysis of the results for the IC formed by α-CD with OT (α-CD/OT IC) indicated that the alkyl chain of this guest interacted in the following manner (see Fig. 1A): the proton of the –SH group formed hydrogen bonds with the hydroxyl groups of the C6 carbon atom located at the smaller opening of the first α-CD unit. The protons attached to the C4 to C7 carbon of the chain interacted with the H3 and H5 protons and were determined to be inside the first α-CD unit, while the protons of the $–CH_3$ group of the guest interacted with the H3 proton inside the second α-CD unit [7]. This assignment indicated that the guest was stretched across the canal generated by the α-CD molecules.

Solid states studies indicate that α-CD/OT ICs can form supramolecular self-assemblies, which can crystallize in anisotropic polyhedra with sizes that range from the nanometer to micrometer scale (Fig. 1C) [7,8].

The α-CD/OT IC has a triclinic structure, and the OT molecule is ordered along the *c* axis; therefore, the preferential Miller plane is assumed to be {001} [6–8]. α-CD IC crystals are insoluble in water because the hydroxyl groups are participate in the supramolecular self-assembly, which causes the crystal surface to be hydrophobic. However, the {001} plane of the surface of the crystal is hydrophilic due of the presence of –SH and –OH6 groups.

The presence of anisotropic interfaces in the α-CD IC crystals that exhibit different chemical properties can be used for selective

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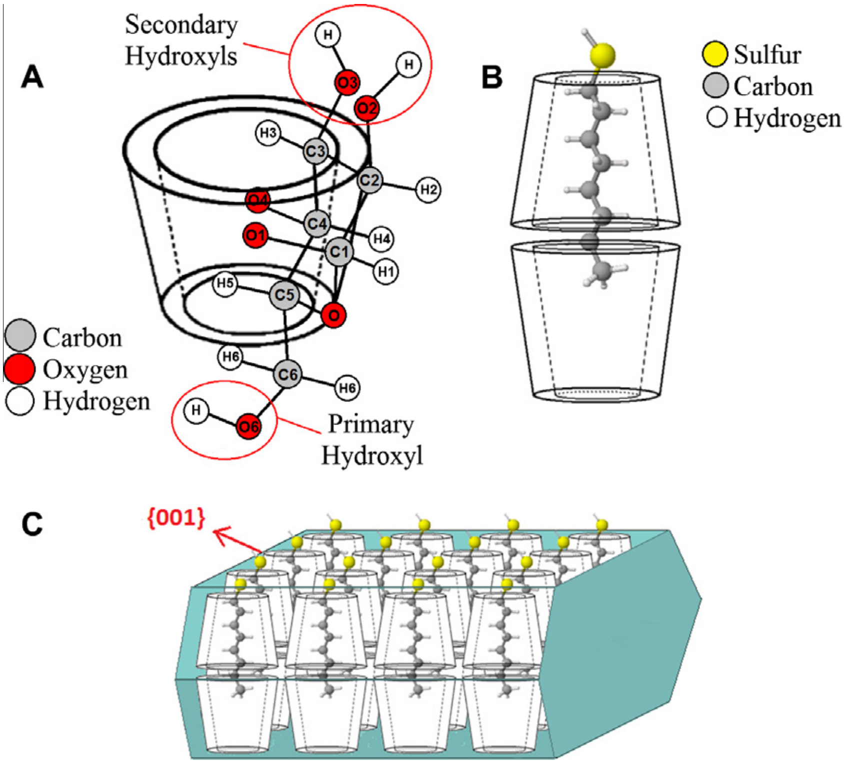

Fig. 1. Schematic representation of: (A) Glucopyranose unit that conform the doughnut-shaped α-CD structure, (B) dimer structure that form α-CD/OT IC, and (C) {001} crystal plane of a α-CD/OT IC crystal (B), (C) and (D).

surface decoration of single crystals [8,9]. Recently, we reported that citrate-stabilized gold nanoparticles (AuNPs) can be preferentially deposited onto α-CD/OT IC crystals [10]. In that case, the attachments of the AuNPs were caused by replacing the citrate shell of the AuNPs with the free –SH groups of the guest molecule that protruded from that particular plane of the crystal. Therefore, these ICs can be used as reservoirs of nanostructures such as AuNRs.

The AuNRs have two surface plasmon absorption bands: a band that occurs at approximately 520 nm due to transverse electronic oscillations and a strong band that occurs at 800 nm due to longitudinal oscillation of the electrons, which is very sensitive to the size of the nanorods. As the aspect ratio (length/width) of the nanorods increases, the longitudinal absorption maximum bathochromically shifts [11]. This phenomenon leads to interesting optical properties, which can be exploited by the functionalization of surface with this type of nanostructure.

In this paper, we reported for the first time the selective nanodecoration of α-CD/OT IC crystal plane with AuNRs by the action of dynamic functionalized surface, where the –SH groups of the guest molecule, that protruded from that particular plane of the crystal, act as a pivot [12], partially displaced the CTAB molecules of AuNRs. This produces a single coating of AuNRs onto crystal surface that allows the study of individual optical properties, which are of the great important in nanochemistry and interface phenomenon.

2. Experimental

2.1. Materials

Alpha-cyclodextrin, octanethiol, and all reagents used in the AuNRs synthesis were purchased from Sigma–Aldrich and were used as received without further purification. Milli-Q water was used as the solvent.

2.2. Experimental procedures

The AuNRs were prepared according to the seed-mediated approach [13,14], with several slight modifications. Briefly, a seed solution was prepared reducing $HAuCl_4$ solution with $NaBH_4$ solution. Subsequently, the growth solution was prepared by mixing ascorbic acid, $AgNO_3$, CTAB, $HAuCl_4$, and HCl solutions. To this solution, the seed solution previously prepared was added. The mixture was kept reacting and then centrifuged. Finally, supernatant was eliminated and the pellet was re-suspended in MilliQ water (Supporting information).

The IC was obtained by mixing octanethiol (Sigma–Aldrich, 98.5%, USA) with a saturated solution of α-CD (Sigma–Aldrich, ⩾98.0%, Germany) in water at room temperature in a 3:1 M ratio, respectively. The immediate precipitation of a white solid indicated the formation of the IC. After 72 h, the IC microcrystals were filtered and dried under a vacuum.

Addition of the α-CD/OT IC crystals into a dispersion of AuNRs resulted in the immediate deposition of AuNRs onto the α-CD/OT IC crystals. Immersion of the colorless α-CD/OT IC microcrystals into a dispersion of AuNRs caused the color of the crystal to immediately change to pink, and the color remained after the sample was washed (Fig. S1, Supporting information).

2.3. Characterization

The typical morphology of the AuNRs was determined by transmission electron microscopy (TEM), and an aspect ratio (length/width) of 4 was determined (Fig. S2, Supporting information). The TEM images were acquired using a JEOL 200KV microscope. Scanning electron microscope (SEM) images were acquired with a NanoSEM NPE67, which was fitted with a field emission source and operated at 5 kV. UV–visible absorption spectra were recorded at room temperature with a UV–visible 2501PC Shimadzu spectrophotometer. Reflectance diffuse spectroscopy was measured using

$BaSO_4$ as a standard on a UV–visible UV-2450 Shimadzu spectrophotometer. Proton nuclear magnetic resonance (^1H NMR) spectroscopy was performed using Bruker AC/200 MHz spectrometer, with TMS as an internal reference and DMSO-d6 as the solvent (Fig. S5–S8, Supporting information). X-ray powder diffraction (XRD) patterns were acquired using a D8 Advanced XRD diffractometer with Cu Kα radiation (Fig. S8, Supporting information).

3. Results and discussion

3.1. SEM and EDS analysis

SEM micrographs and EDS analysis of the colored α-CD/OT IC crystals indicated that AuNRs were present, which exclusively decorated the {001} crystal plane of the α-CD/OT IC (Fig. 2). EDS analysis indicated that gold and sulfur were present, which were attributed to AuNRs and free –SH groups of the guest molecule that protruded from the crystallographic plane, respectively. Under these conditions, the deposition of AuNRs onto the α-CD/OT IC crystals was governed by interactions with the –SH groups.

In this experiment, the CTAB concentration in a colloidal dispersion of AuNRs was 8.19×10^{-4} mol/L (Supporting information), this concentration is sufficient to form a bilayered structure around each AuNRs [13]. Additionally, the critical micelle concentration (CMC) of CTAB is $4.8 \pm 0.3 \times 10^{-4}$ mol/L [11]; therefore, in this experiment, the CTAB formed a bilayer, which stabilized the nanostructure [15] and interacted with the IC surface. CTAB molecules will be replaced in the presence of other gold-binding ligands, (e.g., thiols [16] or other quaternary ammonium cationic surfactants [17]).

In this work, the CTAB molecules were partially displaced from the surface of the AuNRs because the –SH groups outside the {001} crystal plane of the α-CD/OT IC interacted with the surface of the AuNRs, which disrupted the CTAB bilayer and immobilized the AuNRs along the plane.

Remarkably, a laterally aligned pattern of AuNRs was formed on the surface of the IC due to the lateral interaction of the CTAB molecules that tend to a self-assemble [18] (see Fig. 2).

In the SEM micrographs, a single coat deposit of AuNRs on the crystal surface is observed. This is probably due to the greatest interaction between the IC and AuNRs, (produced by the chemisorption of AuNRs and –SH groups of the pivot guest molecules [12]) compared with the van der Waals forces between CTAB molecules surrounding AuNRs. After the process of washing, the crystals remain in the surface only AuNRs that are interacting with –SH groups of preferential plane of the crystal.

3.2. UV–visible spectroscopic analysis

The UV–visible spectroscopic study of α-CD/OT IC nanodecorated crystals confirmed that above-described mechanism caused the AuNRs to be adsorbed onto the α-CD/OT IC crystals. Fig. 3 shows the UV–visible spectrum in the reflection mode for the AuNRs onto α-CD/OT IC crystals. Two maxima were observed at 520 and 850 nm, which were assigned to the transversal and longitudinal absorption bands, respectively. Notably, the UV–visible spectra of the AuNRs-CTAB acquired in solution in the transmission mode had two absorption bands centered at 510 and 800 nm, which corresponded to the transverse and longitudinal localized surface plasmon resonances characteristic of AuNRs with a size of 40 nm of length and 10 nm of wide, approximately, that is, with an aspect ratio of 4 (see Supporting information) [11,13]. Remarkably, the longitudinal absorption maxima of the AuNRs bathochromically shifted as they absorbed onto the α-CD/OT IC crystals. Bathochromic shifts of longitudinal plasmon resonances are caused by changes in the dielectric environment, which result by rods that are close together [19]. In addition, UV–visible analysis of AuNRs onto α-CD/OT IC indicated that no aggregation of nanomaterials occurred because the absorption band did not widen: the morphology and optical properties on the surface were the same as those in solution [20].

3.3. ^1H NMR analysis

Detailed information regarding the nature of the interactions between the AuNRs and α-CD/OT IC was obtained from NMR measurements. ^1H NMR spectra of a solution prepared from nanodecorated IC showed that only a trace amount of CTAB was present, which indicated that the surfactant was displaced by the –SH groups of the IC.

In the presence of AuNRs, some changes in the chemical environment of the OT and α-CD molecules of the IC were observed. The chemical shifts of OT and α-CD were observed to shift to slightly higher fields with respect to the same molecules of the

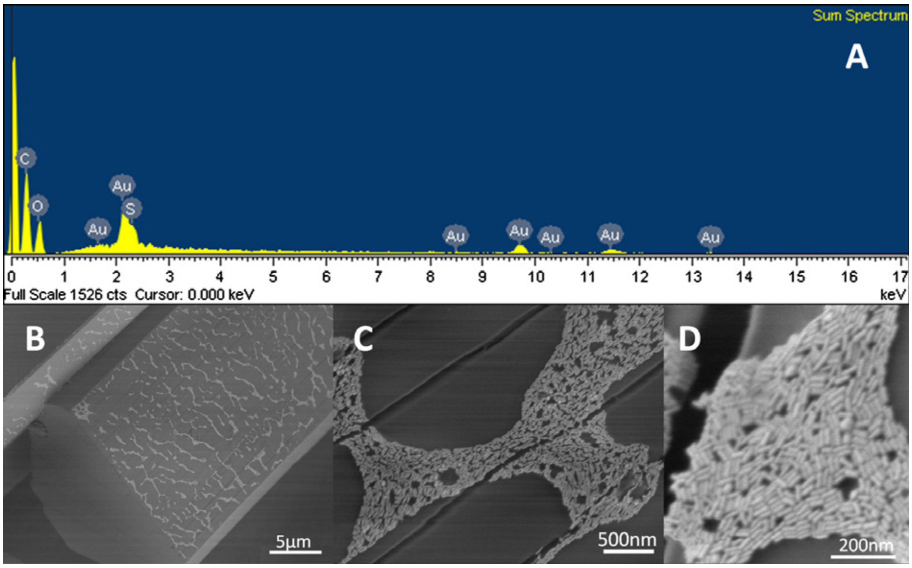

Fig. 2. EDS analysis of α-CD/OT IC surface nanodecorated with AuNRs (A), SEM micrographs of AuNRs deposited onto the {001} crystal plane of a α-CD/OT IC crystal.

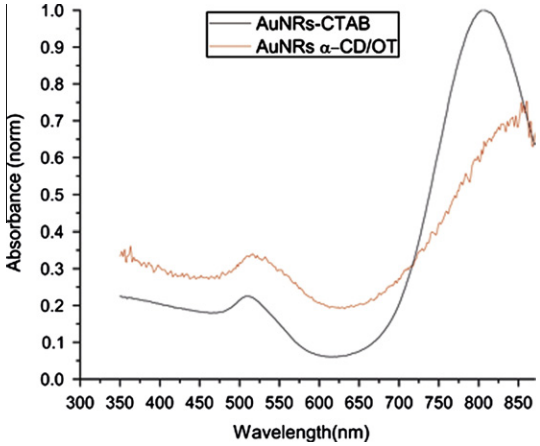

Fig. 3. UV–Vis spectra of AuNRs onto the α-CD/OT IC surface (red) and AuNRs stabilized in CTAB solution (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ICs in the absence of AuNRs. Notably, the proton signal corresponding to the –SH group was observed to shift to a higher field with respect to the same molecule in the IC in the absence of AuNRs. The gold nanostructures gives electron density to the –SH group which eventually caused the hydrogen bonds between the –SH and –OH6 groups to break (see Fig. 1A). The protons of –OH2, –OH3, H3, and H5 of the α-CD molecules did not exhibit a significant shift in the presence of AuNRs, which demonstrated that the integrity of the IC remained (Tables 2 and 3, Supporting information). Because the IC structure was conserved in solution, the NMR solution measurements can probably be extrapolated to the solid state; therefore, the data can explain what occurred when the α-CD/OT IC crystals were nanodecorated.

4. Conclusions

In summary, the experiments provided insight regarding the adsorption of AuNRs onto the {001} crystal plane of IC. The experiments suggest interesting prospects for nanodecoration as a tool to reveal interfacial and structural details of supramolecular structures, such as the CD IC used here [8]. These compounds could be used as new way to store AuNRs in the solid state, which preserve the integrity of both the supramolecular compound and the metal nanostructures.

The use of functionalized surface of supramolecular crystals that have the ability to direct their functional groups to the proximity of a nanostructure [12] allows attachment of a single surface coat of AuNRs facilitating studies of their individual optical properties in solid state [20]. AuNRs have plasmon resonant absorption and scattering in near infrared region, making them attractive probes for *in vitro* and *in vivo* imaging [21]. These properties can be enhanced when AuNRs are arranged in anisotropic organic crystals.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jcis.2012.08.027.

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