PREPARATION OF CYCLODEXTRIN-IRON NANOSTRUCTURES

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1. Introduction

Nanoparticles can be defined as particles that are sized between approximately 1 and 100 nm and they show properties that are not shared by non-nanoscale particles with the same chemical composition. They belong to currently the most studied branch of material science, and have a variety of applications in electronics, optics, diagnostics, and catalysis [1, 2]. There are several approaches how to prepare metallic nanoparticles, where a use of surfactant, e.g. micelle or microemulsions, is most widely utilized[3]. The preparation of metallic nanoparticles from "water-in-oil" microemulsion leads to the suspension of nanoparticles, which are chemically reduced and stabilized by surfactant. In order to have a bare metallic nanoparticle, a focus is on laser ablation. The laser ablation is using a metallic target, e.g. gold, silver, iron, zinc or platinum [4], exposed to a laser pulse generating plasma, where the metal is deposited on a substrate placed in the plasma impact. The preparation of metallic nanoparticles in a cyclodextrin (CD) solution is also one popular method to obtain stabilized nanoparticles [5].

CD molecules are cyclic oligosaccharides that consist of (α-1,4)-linked α-D-glucopyranose units and have a hydrophobic cavity and hydrophilic outer surface. Owing to the cavity, CDs are widely used as host molecules in host–guest supramolecular chemistry. CDs can not only form host–guest complexes, but also adducts [6].The adductis defined for attachment on the outer surface of the CD cavity.Molecules of CD are widely used also in the supramolecular self-assembly. The self-assembling process leads to the formation of self-assembled monolayer (SAM)[7].SAMis formed by adsorption of surfactant from solution on solid surface. Molecules of CDs are widely used, which can be immobilized on different surfaces after their chemical modification. The typical modification is thiolated CD(CD-SH), which forms more SAM-like film due to the structure of CD-SH.

Our system consists of the host molecule of monothiolated β-CD chemically adsorbed on Au surface through the S-Au bond (Au-S-CD) and of Fe species incorporated as the guest. Secondary ion mass spectrometry (SIMS) is used to study the formation and the composition of these surface supramolecular nanostructures.

2. Experimental Details

2.1 Preparation of Self-Assembled Monolayer-like

SAM-like were prepared using thiolated cyclodextrin (CD-SH) as 6-monodeoxy-6-monothio-β-cyclodextrin (CYCLOLAB) and an Au surface (ARRANDEE). CD-SH was used without further purification as a solution with a concentration of approximately 10^{-3}mol.dm^{-3}. Distilled water was used as the solvent. The Au surface was immersed in a 5 ml solution of CD-SH for 1 hour. A prepared SAM-like film was rinsed with water and dried in air at room

temperature. This SAM-like film was used as a surface substrate for the preparation of nanostructures.

2.2 Preparation of Surface Nanostructures

A pulsed-laser beam from an amplified femtosecond laser system (COHERENT LEGEND DUO USP) with a central wavelength of 800 nm, a pulse energy of 3.3 mJ, a repetition rate of 3 kHz, and a pulse duration of 100 fs was passed through a f=100 mm focusing lens (f15). It was focused such that the laser beam waist was located approximately 2 mm below the sample surface. The ablation process was limited to 100 seconds. Two types of samples were prepared: 300 µl of a reaction medium was dropped on a SAM-like film with or without rinsing with water. All samples were dried in air at room temperature.

2.3 Mass Spectrometry

Mass spectrometry measurements were performed by using a ToF-SIMS IV (ION-TOF) reflectron-type time-of-flight mass spectrometer equipped with a Bi ion gun. Pulsed 25 keV Bi_3^+ were used as primary ions with an ion current of 0.24 pA. Secondary ion mass spectra were measured by scanning over a selected 100x100 μm^2 analysis area. Note that due to the spectral significance, only positive polarity spectra are shown.

3. Results and Discussion

The focus is on the preparation of supramolecular complexes based on Au-S-CD and Fe species by using laser ablation in the liquid phase. The laser ablation of bulk Fe was performed by a pulsed laser in water. The experiment is based on dropping a water solution of the ablated Fe species on the Au-S-CD film. Using the SIMS technique, an ideal scenario could be to observe an intact CD-S molecular ion. In the approach of the dropping, the masses of 1173 m/z and 1189 m/z were determined and assigned as $C_{42}H_{69}O_{34}SNa^+$ and $C_{42}H_{69}O_{34}SK^+$, supporting the presence of CD-S on the Au surface after adsorption and the SAM-like formation. Since the focus is on the supramolecular complex formation, the next region of interest is approximately 56 m/z, the mass of Fe, higher.The relevant mass peaks in this region were at 1227 m/z and 1243 m/z and were assigned as $C_{42}H_{68}O_{34}SNa\text{-}Fe^+$, as shown in Fig. 1, and $C_{42}H_{68}O_{34}SK\text{-}Fe^+$, as shown in Fig. 2.
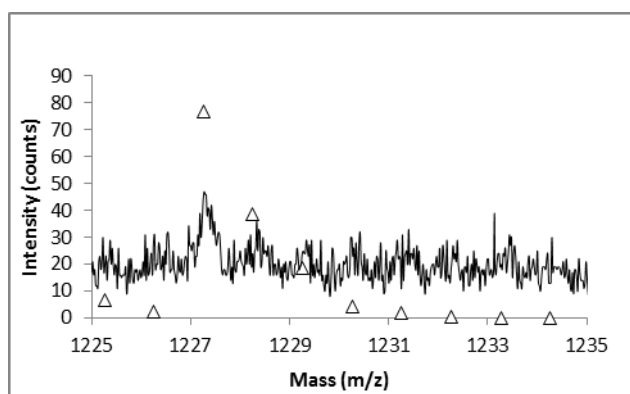

Fig.1: *Secondary ion mass spectrum of Na cationized complex between Au-S-CD and Fe with the relevant isotope distribution.*

These masses provide the relevant molecular formulas of the surface supramolecular complex between the Au-S-CD and one Fe atom. This observation suggests the formation of a surface supramolecular Au-S-CD-Fe complex, presumably with a 1:1 Au-S-CD:Fe ratio. Nevertheless the mass peak at 1243 m/z as shown in Fig. 2 also corresponds to the molecular

formula of $C_{42}H_{68}O_{34}SNa\text{-}FeO^+$. The next relevant mass peak in this region is at 1260 m/z and was also assigned as $C_{42}H_{68}O_{34}SK\text{-}FeO^+$, as shown in Fig. 3. These masses with the relevant formulas suggest also the formation of cyclodextrin based Au-S-CD-FeO adducts, presumably with a 1:1 Au-S-CD:FeO ratio.
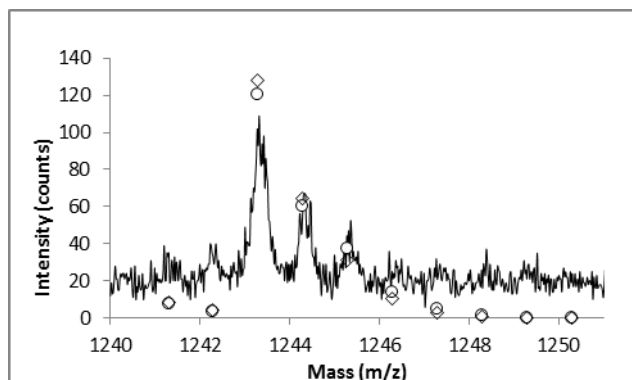

Fig.2: *Secondary ion mass spectra of cationized complex of Au-S-CD with Fe and adduct of Au-S-CD with FeO with the relevant isotope distributions.*
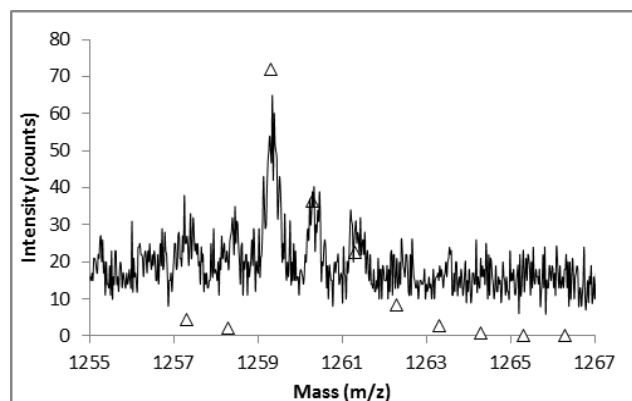

Fig.3: *Secondary ion mass spectrum of K cationized adduct between Au-S-CD and FeO with the relevant isotope distribution.*

To support the interpretation of the higher mass ions, natural isotope distributions were employed in calculating theoretical expected peak intensity profiles for several multiatom combinations. The comparisons of these correlated distributions are shown in Fig. 1, 2, and 3 with symbols of triangle for $C_{42}H_{68}O_{34}SNa\text{-}Fe^+$, circle for $C_{42}H_{68}O_{34}SNa\text{-}FeO^+$, rhombus for $C_{42}H_{68}O_{34}SK\text{-}Fe^+$, and triangle for $C_{42}H_{68}O_{34}SK\text{-}FeO^+$. The experimental data indicate the presence of the complexes between Au-S-CD and Fe species and the adducts between Au-S-CD and FeO.

To exclude the supramolecular complex formation in the process of generating secondary ions in SIMS, the SIMS spectra of CD-SH only dropped onto the pure Fe surface were also measured. The masses of 1174 m/z and 1190 m/z correspond to $C_{42}H_{70}O_{34}SNa^+$ and $C_{42}H_{70}O_{34}SK^+$, respectively, representing cationized molecular ions of CD-SH as an intact molecule. The relevant mass peaks in the form of CD-SH+Fe and the $C_{42}H_{68}O_{34}SNa\text{-}Fe^+$, $C_{42}H_{68}O_{34}SK\text{-}Fe^+$, $C_{42}H_{68}O_{34}SNa\text{-}FeO^+$, and $C_{42}H_{68}O_{34}SK\text{-}FeO^+$ were not observed. This result excludes the formation of the relevant complexes and adducts as a consequence of the SIMS collision mechanism. Moreover, the stability of the Au-S-CD film and also of the Au-S-CD-Fe and Au-S-CD-FeO nanostructured films was tested by comparing the SIMS spectral

intensities. The stability was confirmed for the systems prepared by dropping, where the films were measured as native or rinsed with water. The differences between the SIMS spectra with or without rinsing with water were only in the intensity of relevant mass peaks. The mass peaks intensities ratio for the with/without approaches was approximately 1:4 suggesting the SAM-like film without SAM regularity.

4. Conclusion

The goal was to investigate the preparation and formation of supramolecular surface complexes between CD-SH on the Au surface and the Fe species, determining ideally the intact molecular ion of Au-S-CD. The Fe species were prepared by pulsed laser ablation of bulk Fe in water. The solution of Fe species was dropped onto an Au-S-CD SAM-like film and analyzed with SIMS. The relevant mass peaks were at 1227 m/z, 1243 m/z and 1260 m/z and were assigned as $C_{42}H_{68}O_{34}SNa\text{-}Fe^+$, $C_{42}H_{68}O_{34}SK\text{-}Fe^+$, $C_{42}H_{68}O_{34}SNa\text{-}FeO^+$ and $C_{42}H_{68}O_{34}SK\text{-}FeO^+$, which can be interpreted as supramolecular complexes with Fe as $C_{42}H_{68}O_{34}SNa\text{-}Fe$ and $C_{42}H_{68}O_{34}SK\text{-}Fe$ or adducts with FeO as $C_{42}H_{68}O_{34}SNa\text{-}FeO$ and $C_{42}H_{68}O_{34}SK\text{-}FeO$, respectively. The comparison of isotope distributions with the experimental data supported the presence of a supramolecular host-guest complex between the Au-S-CD and the Fe species and the adduct between Au-S-CD and FeO.

References:
[1]   S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. J. Frechet, D. Poulikakos: *Nanotechnology*, **18**, 345202 (2007).
[2]   C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorf, J. Gao, L. Gou, S. E. Hunaydi, T. Li: *J. Phys. Chem. B*, **109**, 13857 (2005).
[3]   S. M. I. Morsy: *Int. J. Curr. Microbiol. App. Sci.*, **3**, 237 (2014).
[4]   F. Mafune, J. Kohno, Y. Takeda, T. Kondow, H. Sawabe: *J. Phys. Chem. B*, **105**, 5114 (2001).
[5]   A. V. Kabashin, M. Meunier, Ch. Kingston, J. H. T. Luong: *J. Phys. Chem. B*, **107**, 4527 (2004).
[6]   S. S. Petrova, A. I. Kruppa, T. V. Leshina: *Chem Phys Lett.*, **385**, 40 (2004).
[7]   J. Ch. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides: *Chem. Rev.*, **105**, 1103 (2005).