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Interfacial Supramolecular Self-Assembled Monolayers of C_{60} by Thiolated β-Cyclodextrin on Gold Surfaces via Monoanionic C_{60}

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Abstract: The supramolecular self-assembled monolayers (SAMs) of C_{60} by thiolated β-cyclodextrin (CD) on gold surfaces were constructed for the first time using C_{60} monoanion. The results indicate that monoanionic C_{60} plays a crucial role in the formation of the C_{60}-containing self-assembled monolayers. The generation of C_{60} monoanion and the formation process of C_{60} SAMs were monitored in-situ by UV−visible and near-IR spectroscopy. The resulting C_{60} SAMs were fully characterized by spectroscopic ellipsometry (SE), cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), and water contact angle measurements. After the immobilization of C_{60} by the SAMs of thiolated β-CD, the film thickness increased by approximately 1 nm from 0.8 to 1.8 nm as determined by SE, demonstrating the formation of the supramolecular self-assembled monolayers of thiolated β-CD/C_{60}. The new C_{60} SAMs exhibited one quasi-reversible redox couple at half wave potential of -0.57 V vs SCE in aqueous solution containing 0.1 M KCl. The surface coverage of C_{60} on the gold surfaces was estimated to be 1.1×10^{-10} mol cm^{-2}. The XPS showed the assembly of C_{60} over the thiolated β-CD SAMs. The surface hydrophobicity increased greatly upon the formation of the C_{60}-containing SAMs as analyzed by water contact angle measurements. The results are in agreement with the formation of 1:1 complex of C_{60} and cyclodextrin on gold surfaces, though it also reveals some non-homogeneous features of the monolayers.

Introduction

Due to the intriguing electronic and dimensional structure, fullerenes have been shown to be promising organic electronic materials for applications in areas such as photoelectric conversion devices,[1] superconductivity,[2] nonlinear optics,[3] ion-selective electrode,[4] single-molecule devices,[5] and organic memory devices.[6] For most of the applications, it requires the preparation of fullerene-containing films on desired surfaces, and the successful application of these devices relies greatly on the degree of the film order. Methods used to prepare fullerene-containing films include solution casting,[7] thermal evaporation,[8] electrochemical deposition,[9] Langmuir and Langmuir−Blodgett films,[7b,10] and self-assembled monolayers (SAMs).[11] The self-assembled monolayers is by far the most effective method to organize a two-dimensional highly ordered fullerene-containing assembly on various substrates. In general, the fullerene self-assembled monolayers can be constructed by either the “direct” method or the “indirect” method.[11a,f] It has been shown that

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the construction of fullerene self-assembled monolayers via the "indirect" method can be achieved by interfacial supramolecular interactions. Echegoyen et al. reported the first example of self-assembly of [60] fullerene derivative driven by the molecular recognition between the crown ethers linked to C_{60} and the ammonium groups attached to the gold surfaces.[11d] Most recently, the work was extended to the noncovalent self-assembly of native C_{60} via the interfacial supramolecular recognition by surface-attached host systems such as cyclotriveratrylene derivatives,[12] calixarene derivatives,[13] and porphyrin derivatives.[14] The utilization of the interfacial supramolecular recognition principles to construct noncovalent fullerene SAMs is of great interest and importance because the self-aggregation of fullerene is inhibited and, at the same time, the inherent electronic properties of fullerene is preserved.

Cyclodextrins, a class of cyclic oligosaccharides with a hydrophobic inner cavity and a hydrophilic outside surface, and a widely used family of host molecules, because they are readily available, economic affordable, and biocompatible, have been shown to be able to form a water-soluble supramolecular inclusion complex with C_{60}.[15−17] Previous works on the inclusion complexation between cyclodextrin and C_{60} are mostly limited to the use of γ-CD,[15] whereas only very few papers appeared for inclusion complex of β-CD/C_{60} and α-CD/C_{60} to date[16,17] probably due to the size compatibility between the cavity size of CD and the van der Waals dimension of C_{60} (γ-CD: 0.84 nm, β-CD: 0.66 nm, α-CD: 0.52 nm,[18] and the C_{60}: 1 nm[19]). The inclusion complex of γ-CD and C_{60} in aqueous solution has displayed many interesting properties such as DNA cleavage,[20a] dinitrogen fixation[20b] as well as C═C, C═O, and $N-N^+$ bonds reduction under mild conditions.[20c] Studies on the solution-casting films of the inclusion complex of γ-CD and C_{60} on glassy carbon electrodes have shown that the compound has electrocatalytic properties toward certain biomolecules.[21] Thiolated cyclodextrins have been proved to be powerful electrode modifiers. They provide a surface layer that can form supramolecular inclusion complexes with various appropriately sized species via noncovalent forces such as van der Waals forces and hydrophobic interactions and are frequently used as templates for the preparation of sensors[22] and molecular devices.[23] The orientation of the cyclodextrin cavity can be controlled to be perpendicular to the substrate surface via the multithiolation of the cyclodextrin molecule, which favors the binding of guest molecules to the surface attached cyclodextrin.[22a,24] It has been reported that thiolated γ-CD or β-CD attached to the surface of gold nanoparticles are able to encapsulate C_{60} molecule and form large network aggregates.[25] However, to the best of our knowledge, no report has appeared on the construction of the interfacial supramolecular self-assembly of C_{60} by surface-attached cyclodextrin on solid surfaces. Recently, we have developed a novel method for the preparation of supramolecular inclusion complex of cyclodextrin and C_{60} using C_{60} monoanion,[17] which is stable and readily generated due to the strong electron-accepting ability of C_{60}.[26] The results indicate that the monoanionic C_{60} has a much better complexing ability than the neutral one toward cyclodextrins in solution. Complexes of γ-CD, β-CD, and even α-CD with C_{60} have been prepared by this protocol.[17] Herein we report the first C_{60} interfacial supramolecular self-assembled monolayers by thiolated β-cyclodextrin on gold surfaces via monoanionic C_{60}. The obtained C_{60}-containing monolayers were characterized by spectroscopic ellipsometry, cyclic voltammetry, XPS, and water contact angle measurements.

Experimental Section

Materials. C_{60} (99.9%) was purchased from SES Research, Houston, U.S.A., and used as received. 1-Methylnaphthalene (98%) was purchased from Aldrich and used as received. β-Cyclodextrin, sodium, iodine, KCl, and all other reagents are of analytical grade and purchased from Sinopharm Group Chemical Reagent Company Ltd., Shanghai, China. DMF was distilled over $MgSO_4$ under vacuum at 25 °C. Milli-Q water (18 MΩ cm^{-1}) was used for the preparation of solutions. Alumina powders (diameter, 0.3 and 0.05 micron) were purchased from CH Instruments Inc. Ultrahigh pure argon was purchased from Juyang Gas Company, Changchun, China.

Pretreatment of Gold Electrodes and Substrates. Gold electrodes for self-assembly and electrochemistry measurements were polished successively with 0.3 and 0.05 micron alumina slurry, then ultrasonicated in water, and electrochemically cleaned in 0.05 M H_2SO_4 with a potential cycling from −0.4 to +1.5 V (vs SCE) for more than 10 circles at a scan rate of 100 mV/s, and finally blown dry with Ar stream after being washed with water. The geometric areas of the gold electrodes (A_g) were obtained from cyclic voltammetric data of $K_3Fe(CN)_6$ using the Randles−Sevcik equation.[27] The real surface areas of

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the gold electrodes (A_r) were determined in deaerated 0.05 M H_2SO_4 from the charge required for the reduction of the gold oxide using a value of 420 μC cm^{-2} for the reduction of a monolayer of chemisorbed oxygen on polycrystalline gold.[28] The roughness factor R_f for the electrode was calculated according to $R_f = A_r/A_g$.

Gold substrates for X-ray photoelectron spectroscopy (XPS) and water contact angle (CA) measurements were prepared by thermal evaporation of 200 nm gold on polished glass slides (26 mm × 76 mm) with a 5 nm chromium layer as an adhesion promoter. They were kept under nitrogen for storage and were cut to appropriately sized pieces and annealed with a H_2 flame prior to use. For spectroscopic ellipsometry (SE) experiments, 1.4 cm × 1.1 cm gold-coated mica substrates with 1500 angstroms of Au (111) covering 1.0 cm × 1.1 cm purchased from Agilent Technologies were used.

Synthesis of Per-6-Thio-β-Cyclodextrin. This compound was prepared according to previous method[22a] and characterized by ESI-Ion-Trap MS, FT−IR, and Raman spectra. ESI-Ion-Trap MS, *m/z* 1245 ([M − H]$^-$, calcd for $C_{42}H_{70}O_{28}S_7$, 1246). FT−IR, 2565 cm^{-1} (S−H, weak). Raman spectra, 2575 cm^{-1} (S−H, strong).

Self-Assembled Mononlayers of Per-6-Thio-β-Cyclodextrin on Gold Surfaces (Thiolated β-CD SAMs). The self-assembled monolayers of per-6-thio-β-cyclodextrin on gold surfaces was constructed in a mixture of DMSO/H_2O (60:40 v/v) containing a 1.0 mM solution of the thiolated β-CD for more than 2 days under argon atmosphere in the dark. The modified electrodes or substrates were washed with DMSO and H_2O alternately for more than 5 times and blown dry under stream of Ar before the next step.[22a]

Supramolecular Self-Assembly of C_{60} by Thiolated β-Cyclodextrin on Gold Surfaces (C_{60}/thiolated β-CD SAMs) via Monoanionic C_{60}. C_{60} monoanion was generated by 10-fold molar equivalent of 1-methylnaphthalene radical anion in freshly distilled DMF similar to previous method.[29] Typically, 3.5 mg (0.15 mmol) sodium was added to a deaerated DMF solution of 1.5 equiv of 1-methylnaphthalene; the reaction was allowed to proceed until the sodium was completely dissolved. The 1-methylnaphthalene radical anion solution was then transferred into a suspension of C_{60} (10.8 mg 0.015 mmol) in deaerated DMF and stirred for more than 3 h. After that, the cyclodextrin SAMs modified gold electrode or substrates were immersed in the C_{60} monoanion (approximately 1.0 mM) solution for about 24 h. Finally, iodine was introduced to the system to oxidize $C_{60}^{\bullet-}$ back to neutral. The modified electrode or substrates were thoroughly washed with DMF and water and blown dry with Ar.

The generation and the encapsulation processes of C_{60} monoanion were further monitored by UV−vis−NIR spectroscopy as shown in Figure 1. Immediately after the injection of 10 equiv of 1-methylnaphthalene radial anion to the deaerated DMF suspension of C_{60} under argon atmosphere in a quartz cuvette, there appeared the representative electronic absorptions of $C_{60}^{\bullet-}$ at 1074, 992, and 930 nm.[26b,30] The absorption intensity of $C_{60}^{\bullet-}$ approached to the maximum slowly, and no C_{60}^{2-} was formed under the experimental conditions. The thiolated β-CD modified gold substrate was kept in the $C_{60}^{\bullet-}$ solution for about 24 h. Finally, after iodine was introduced to the system, the characteristic absorption bands of $C_{60}^{\bullet-}$ disappeared quickly accompanied by the appearance of the spike at 405 nm,[31] indicating that $C_{60}^{\bullet-}$ was oxidized to neutral C_{60}.

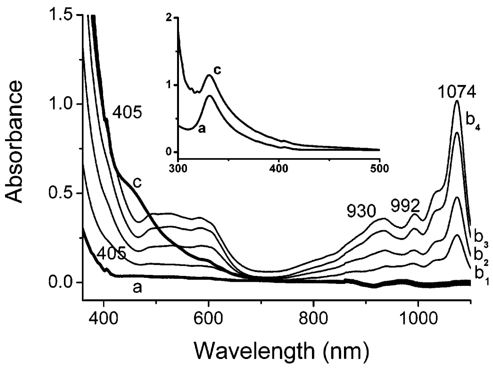
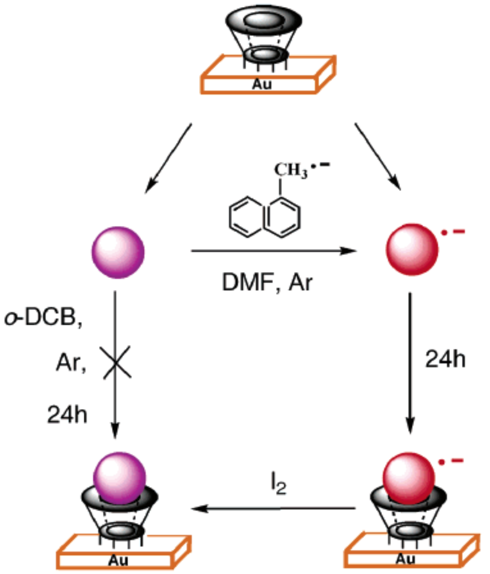


Figure 1. Electronic absorption spectra observed in the supramolecular self-assembly of C_{60} with thiolated β-cyclodextrin on gold surfaces via monoanionic C_{60}. (a) Unreacted C_{60} suspension in deaerated DMF. (b_1−b_4) Generation of C_{60} monoanion at different time intervals, $t_{b1} = 5$ min, $t_{b2} = 1$ h, $t_{b3} = 8$ h, $t_{b4} = 27$ h. (c) Oxidation of $C_{60}^{\bullet-}$ to C_{60} after the addition of iodine.

Scheme 1. Schematic Illustration of Supramolecular Self-Assembled Monolayers of C_{60} by Thiolated β-Cyclodextrin SAMs on Gold Surfaces via Monoanionic C_{60}



Control experiments were performed where *o*-DCB (1,2-dichlorobenzene) solution of neutral C_{60} was used to construct the monolayers under similar conditions; however, no C_{60} containing self-assembled monolayers could be obtained.

The self-assembly of C_{60} by thiolated β-cyclodextrin on gold surfaces is illustrated in Scheme 1.

Instrumentation. Spectroscopic ellipsometry measurements were performed over a wavelength range of 550−800 nm at a fixed incident angle of 70° using a UVISEL spectroscopic ellipsometer (Jobin Yvon, France). The SE spectra were obtained on three separate substrates with at least three different spots on each substrate being measured. Film thicknesses were determined by fitting the SE spectra to a two-phase optical model (SAMs/Au), and an average value at the 95% level of confidence is reported. Cyclic voltammetry was carried out on a CHI 630B potentiostat (CH Instruments Inc., Austin, TX) using a conventional three-electrode cell with bare or modified gold electrode as the working electrode, a platinum wire as the counter electrode, and a KCl-saturated calomel electrode (SCE) as the reference electrode. UV−visible and near-IR spectroscopy (UV−vis−NIR) measurements were performed using a Perkin-Elmer Lambda 900 UV−vis−NIR spectrometer. X-ray photoelectron spectroscopy (XPS) was measured using a Thermo ESCALAB 250 instrument with a monochromatic Al Kα source ($h\nu = 1486.6$ eV) at 2.2 × 10^{-9} Torr. XPS data were collected from a spot size of 500 μm with a pass energy window of 20 eV, and

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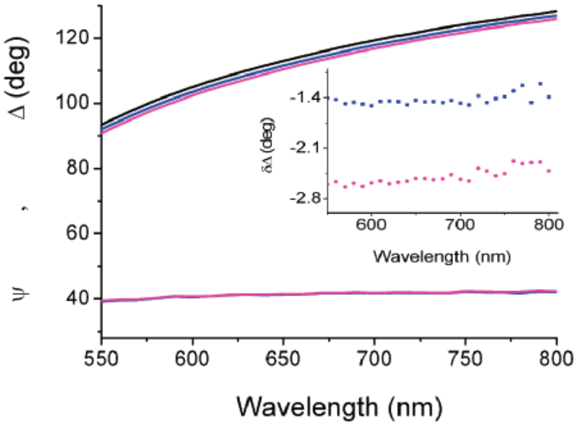

Figure 2. Experimental Ψ and Δ spectra obtained on bare gold substrate (black line), thiolated β-CD SAMs (blue line), and C_{60}/thiolated β-CD SAMs (magenta line). (Inset) Difference spectra ($\Delta_{SAM/Au}-\Delta_{Au}$) obtained from SE data: [$\Delta_{\text{thiolated }\beta\text{-CD SAMs}}-\Delta_{Au}$] (blue dots), [$\Delta_{\text{C60/thiolated }\beta\text{-CD SAMs}}-\Delta_{Au}$] (magenta dots).

a takeoff angle of 90° was employed for each sample. The binding energies were referenced to C1s at 284.6 eV. The area intensities were obtained following the spectral fitting. The atom percentage values are averaged from five separate measurements. Static water CA were determined using a Krüss DSA10-MK2 (Germany) CA measuring system under ambient conditions. The probe fluid was deionized water with a droplet volume of 3 μL. The reported CA value was the average result of three separate substrates with five different measurements at different positions on each substrate. ESI-ion-trap MS was carried out on a Finnigan MAT LCQ electrospray ionization ion trap mass spectrometer. FT−IR spectra were obtained with a Bruker IFS-66v/S (Germany) FT−IR spectrometer. FT−Raman spectra were measured with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.).

Results and Discussion

Ellipsometry has been shown to be an important method for the characterization of ultrathin film such as fullerene SAMs.[11f,32] It measures the polarization changes of the light that is reflected from the surface of a sample, which can then be used to determine the thickness of the film. The polarization changes can be expressed in terms of complex reflection coefficient (ρ) according to the equation:

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)\, e^{i\Delta}$$

in which R_p and R_s are the Fresnel reflection coefficients for p and s-polarized light, and Ψ and Δ are the measured ellipsometric angles. Figure 2 shows the Ψ and Δ spectra for bare gold substrates, thiolated β-CD SAMs and C_{60}/thiolated β-CD SAMs. With respect to ultrathin films, Δ is very sensitive to thickness, and the difference of Δ between the film and the substrate roughly indicates the film thickness.[33] As is shown from the figure, Δ decreases slightly but distinctly in the sequence of $\Delta_{Au} > \Delta_{\text{thiolated }\beta\text{-CD SAMs}} > \Delta_{\text{C60/thiolated }\beta\text{-CD SAMs}}$, and $|\Delta_{\text{thiolated }\beta\text{-CD SAMs}}-\Delta_{Au}| < |\Delta_{\text{C60/thiolated }\beta\text{-CD SAMs}}-\Delta_{Au}|$ can be clearly seen from the difference spectra of Δ in the inset of Figure 2. Therefore, it can be deduced that the film thickness increases after the assembly of C_{60} on the SAMs of thiolated β-CD.

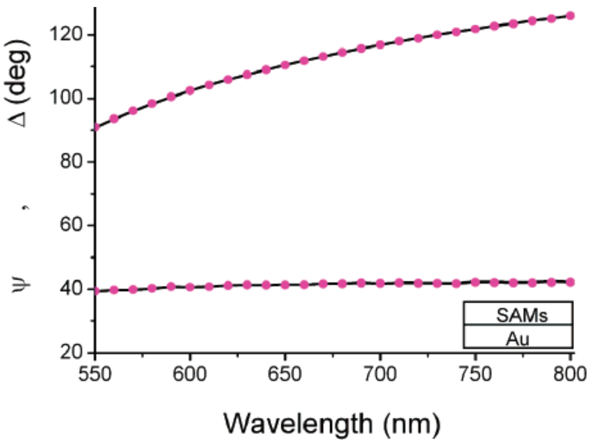

Figure 3. Ψ and Δ spectra for C_{60}/thiolated β-CD SAMs. Experimental data (black line) and generated data obtained using two-phase model (magenta dots).

Quantitative analysis of the SE spectra to determine the optical thickness of the monolayers was conducted by fitting the measured SE data to a two-phase optical model (SAMs/Au). An appropriate dielectric model for the Au substrates was determined first from the SE measurements of bare gold substrates, and it was used as the substrate model for the determination of thickness of the upper SAMs. The measurement was carried out in the range of 550−800 nm because the absorption of both cyclodextrin and C_{60} is negligible in this region.[34] The real refractive indexes for the SAMs of thiolated β-CD and C_{60}/thiolated β-CD were assumed to be 1.50[24,35] and 1.55,[11f,36] respectively, and their imaginary refractive indexes were held at 0. These treatments are comparable with the thickness analysis of organic molecular monolayers in a similar way.[11f,35−37] As shown in Figure 3, the generated Ψ and Δ for the SAMs of C_{60}/thiolated β-CD obtained using the two-phase model actually overlap with the experimental data, and the same consistency between the fitting and experimental data is also obtained for the SAMs of thiolated β-CD.

The experimental thickness determined by SE spectra fitting and the calculated theoretical thickness are listed in Table 1. The theoretical thickness of the SAMs of thiolated β-CD is estimated to be 1.0 nm (the reported height of cyclodextrin molecules is about 0.8 nm from the S atom,[22a,38] and the Au−S bond is 0.236 nm[11f]) with the *Cn* axis of the cyclocextrin torus perpendicular to the gold surface.[22a,24] The theoretical thickness of the SAMs of C_{60}/thiolated β-CD is 2.0 nm, assuming that C_{60} (van der Waals dimension of 1 nm[19]) is standing right over the torus cavity of β-CD. The SE measurement results show that the film thickness for the SAMs of thiolated β-CD is 0.8 nm, whereas it changes to 1.8 nm upon the immobilization of

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Table 1. Theoretical Thickness and Experimental Thickness Determined by Spectroscopic Ellipsometry for the SAMs of Thiolated β-CD and C_{60}/Thiolated β-CD

monolayers	theoretical thickness (nm)	experimental thickness (nm)
thiolated β-CD	1.0	0.8[a]
C_{60}/thiolated β-CD	2.0	1.8[a]

[a] The value measured by SE with an error of ± 0.2 nm.

C_{60} by the SAMs of thiolated β-CD, suggesting that C_{60} was assembled right over the β-CD at van der Waals distance. The measured ellipometric thicknesses of the SAMs are in reasonably good agreement with the theoretical values considering that ellipometry is only accurate with ± 0.2 nm.[39] In summary, the SE results support the formation of the interfacial supramolecular self-assembled monolayers of C_{60} over the thiolated β-cyclodextrin SAMs on gold surfaces.

The thiolated β-CD SAMs and C_{60}/thiolated β-CD SAMs were further characterized by cyclic voltammetry measurements. The self-assembly of thiolated β-CD on gold electrode was confirmed by the blocking effect on the cyclic voltammetric response of $K_3Fe(CN)_6$ in 1 M KCl aqueous solution, and the reductive desorption wave of thiolated β-CD in 0.5 M KOH aqueous solution (Figure 4). As shown in Figure 4a, after the modification with thiolated β-CD, the peak potential separation ΔE_p increased from 62 to 117 mV, and peak current decreased with $i_p^c\,(\mathrm{CD}) / i_p^c\,(\mathrm{Au}) = 0.74$. The presence of relatively large peak currents indicates that the SAMs is imperfect as observed by Kaifer et al. previously.[22a] When cyclic voltammetric scans were conducted on thiolated β-CD SAMs in 0.5 M KOH aqueous solution in the range between 0 and −1.2 V, there appeared a desorption wave at −0.95 V vs SCE, which is attributed to the reductive desorption of the thiolated β-CD attached to gold surfaces. The results are consistent with the previous report[22a] and confirm the formation of cyclodextrin self-assembled monolayers on gold surface.

Figure 5 shows the cyclic voltammograms of the thiolated β-CD SAMs and C_{60}/thiolated β-CD SAMs in 0.1 M potassium chloride aqueous solution. After the self-assembly of C_{60} by thiolated β-CD SAMs, one quasi-reversible redox couple is observed at $E_{1/2}$ of −0.57 V vs SCE, which corresponds to the first redox process of C_{60}. The potential value matches well with the reported first reduction potential of γ-CD/C_{60} complex[15c] in aqueous solution. Because the water-soluble β-CD/C_{60} inclusion complex shows no CV response in aqueous solution probably due to the formation of aggregate,[17] the observation of the CV response of C_{60}/thiolated β-CD SAMs indicates that the aggregation of C_{60} is effectively inhibited in the film.

The surface coverage of C_{60} estimated by integrating the current under the cathodic wave at scan rate of 0.1 V/s after the correction of surface roughness ($R_f \approx 1.5$) is about 1.1×10^{-10} mol cm^{-2}, thereby the occupied area per molecule of C_{60} is calculated to be about 150 Å^2, which is larger than that of the fcc packing of pristine C_{60} (100 Å^2 molecule^{-1}) on gold,[40] though smaller than the estimated molecular surface of 180 Å^2 molecule^{-1} for thiolated β-CD.[22a]

Figure 6 shows the cyclic voltammograms of the C_{60}/thiolated β-CD SAMs at different scan rates from 0.1 to 1.0 V/s. The cathodic peak current is shown to be proportional to the scan rate, implying that the electrochemical redox reaction of C_{60} is a surface-confined process. However, as compared with those for γ-CD/C_{60},[15c] C_{60} in solution,[26a] and the SAMs of a C_{60} derivative with rigid molecular tripod,[11f] the redox waves of C_{60}/thiolated β-CD SAMs are much broader with a large peak-to-peak separation and seem to be a combination of waves, indicating that the monolayers are non-homogeneous with the existence of multiple interaction modes of C_{60} molecules.[11f,12,13,41] Tour et al. have shown that fullerene interactions have a great effect on the electrochemistry of the monolayers.[11f] They used a C_{60} derivative with a rigid molecular tripod and a large footprint of about 4.4 nm^2 to remove such interactions and obtained an "ideal" electrochemical behavior for the monolayers. However, for the C_{60}/thiolated β-CD SAMs, the average area for the molecule is only 150 Å^2, which is much smaller and might not be enough to remove the fullerene interactions completely within the monolayers; as a result, it might lead to nonideal electrochemical behaviors such as peak broadening for the monolayers. It is also possible that in addition to the assembly of C_{60} over thiolated β-CD SAMs, C_{60} molecules might be trapped between the loosely packed thiolated β-CD,[11f,12,13] as indicated by the average molecular area of the C_{60}/thiolated β-CD SAMs, and this will also lead to the broadness of the voltammetric response wave of the monolayers. Furthermore, C_{60} might even directly bond to the gold surface due to the strong interactions between them;[42] however, such direct deposition will not show voltammetric response of C_{60} around −0.57 V vs SCE in aqueous solution as reported previously.[43]

As for the large peak-to-peak separation (110 mV at scan rate of 0.1V/s), it is probably due to the slow electron-transfer caused by the resistance effect of the insulating barrier of the thiolated β-CD.[41b,44] Kitano et al. have shown that the peak-to-peak separation for the voltammetric response of surface-confined hydroquinone increases significantly on a thiolated cyclodextrin modified Au electrode, while at the same time, a linear relationship between the peak current and scan rate is observed.[44] In addition, the large peak separation might also be caused by the slower electron-transfer kinetics between the C_{60} and the gold surface due to the structural constraint of C_{60} and the partial inhibition of the transportation of counterions within the monolayers.[11b,f, 41b,e,f,45]

The C_{60}-containing films can stand continuous scans for a long time with little change, suggesting that the C_{60}/thiolated

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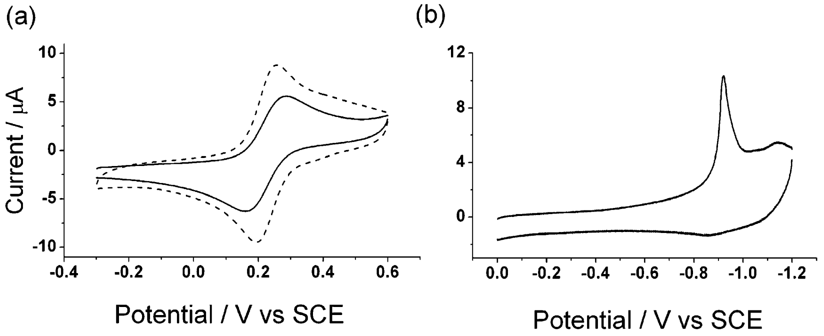

Figure 4. (a) CV of 1.0 mM $K_3Fe(CN)_6$ in 1.0 M aqueous KCl for bare Au (dashed line) and thiolated β-CD SAMs (solid line), and (b) electrochemical desorption of thiolated β-CD SAMs in deaerated 0.5 M KOH aqueous solution.

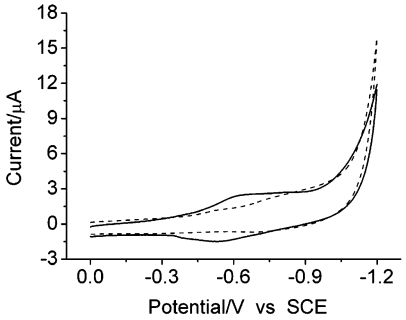

Figure 5. Cyclic voltammograms of thiolated β-CD SAMs (dashed line) and C_{60}/thiolated β-CD SAMs (solid line) in aqueous solution containing 0.1 M KCl at scan rate of 0.1 V/s.

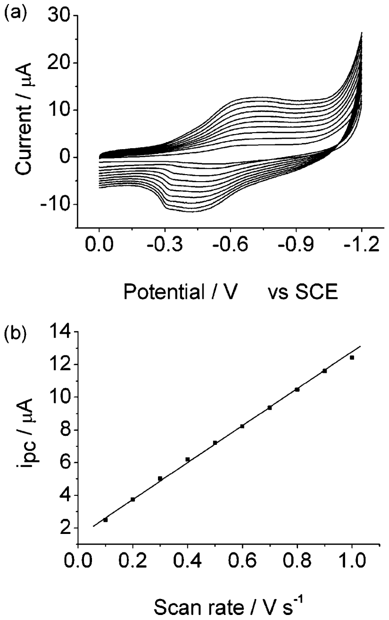

Figure 6. (a) Cyclic voltammograms of C_{60}/thiolated β-CD SAMs in aqueous solution containing 0.1 M KCl at different scan rates (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 V/s), and (b) plot of i_{pc} vs scan rates for C_{60}/thiolated β-CD SAMs.

β-CD SAMs are stable in aqueous solution under N_2 atmosphere and $C_{60}^{\bullet-}$ complexes well with the surface-attached β-CD host molecules.

To get a better understanding of the formation of C_{60}/thiolated β-CD SAMs by monoanionic C_{60}, several control experiments were conducted. One is directly immersing the thiolated β-CD modified gold electrode into 6 mM C_{60} toluene or 1,2-dichlorobenzene (*o*-DCB) solution for about 24 h for the self-assembly of C_{60}; the other is directly immersing a bare gold electrode into the C_{60} monoanion solution for about 24 h and reoxidizing the solution back to neutral by iodine. However, no redox wave corresponding to C_{60} appeared under the same electrochemical conditions, indicating that monoanionic C_{60} plays a crucial role in the self-assembly of C_{60} by thiolated β-CD on gold surfaces.

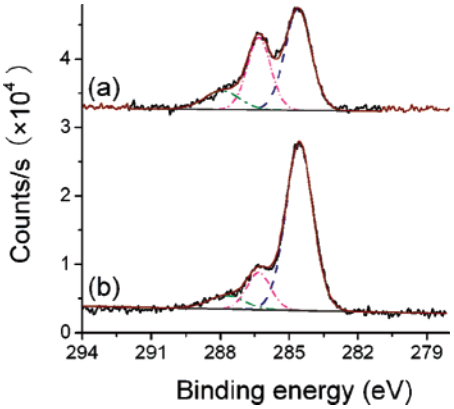

Figure 7. XPS (C1s) spectra for (a) thiolated β-CD SAMs and (b) C_{60}/thiolated β-CD SAMs.

XPS is proved to be a powerful tool for surface analysis that provides diverse information on surface layers of materials. Figure 7 shows the C1s spectra of thiolated β-CD SAMs and C_{60}/thiolated β-CD SAMs. After spectral fitting, different C1s peaks resulting from β-CD are clearly observed in the spectrum of thiolated β-CD SAMs at 284.6 eV (C−C−C), 286.3 eV (C−O/C−S), 287.7 eV (O−C−O).[46] After the incorporation of C_{60}, the C1s of C_{60}/thiolated β-CD SAMs changed dramatically as compared with that of thiolated β-CD SAMs; the peak intensity of C1s at 284.6 eV increased considerably as expected because C_{60} was encapsulated by the CD SAMs,[47] whereas the intensities for peaks corresponding to C−O/C−S and O−C−O of the thiolated β-CD decreased moderately, which is in agreement with the assembly of C_{60} monolayers over the thiolated β-CD SAMs.

Figure 8 shows the S2p spectra of thiolated β-CD SAMs and C_{60}/thiolated β-CD SAMs. The experimental S2p spectra of thiolated β-CD SAMs were fitted to four peaks with fixed $S2p_{3/2}$/

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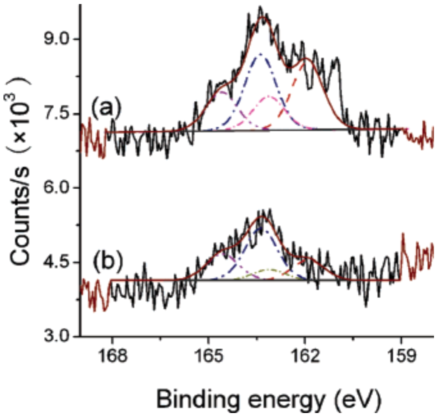

Figure 8. XPS (S2p) spectra for (a) thiolated β-CD SAMs and (b) C_{60}/thiolated β-CD SAMs.

Table 2. Atomic Percentage of SAMs of Thiolated β-CD and C_{60}/Thiolated β-CD Estimated by XPS (%)

	C		O		S	
monolayers	obsd	calcd	obsd	calcd	obsd	calcd
thiolated β-CD	62.3	54.5	30.9	36.4	6.8	9.1
C_{60}/thiolated β-CD	73.5	74.5 (1:1)	21.9	20.4 (1:1)	4.6	5.1 (1:1)

$S2p_{1/2}$ intensity ratio of 2 and peak separation of 1.2 eV.[48] When the thiol sulfur is chemisorbed onto the gold surfaces, the binding energy of S2p is shifted negatively by about 1.5 eV, from 163.4 (unbound $S2p_{3/2}$) to 161.9 eV (bound $S2p_{3/2}$), and from 164.6 (unbound $S2p_{1/2}$) to 163.1 eV (bound $S2p_{1/2}$). These results demonstrate the formation of thiolated β-CD SAMs on gold and show that only about 47% thiols are attached to the gold surfaces. Similar observations have been reported previously.[11f,46] Similar to the observations for the C1s of C−O/C−S and O−C−O of the monolayers, the peak intensity of S2p decreases as the film thickness increases by the assembly of C_{60} as shown in Figure 8b. It is noteworthy that the relative intensity of the bound S2p goes slightly down upon the immobilization of C_{60}, indicating that small amount of C_{60} might compete with the sulfur atoms and directly assemble on the gold surface due to strong interaction between them.[42]

To provide more direct information of the elemental composition of the monolayers, the atomic percentage of C, O, and S is estimated semiquantitatively by XPS, and the results are listed in Table 2. The observed values are in agreement with the theoretical values for the formation of inclusion complex of C_{60}/thiolated β-CD with 1:1 molar ratio, suggesting the formation of C_{60} monolayers over the thiolated β-CD SAMs, and are consistent with the SE results. The observed larger deviations for the thiolated β-CD SAMs are probably because the hydrophilic surface is much more susceptible to be contaminated under ambient conditions than the hydrophobic surface.[49]

Wetting CA measurements are widely used as sensitive probes for the hydrophilicity or hydrophobicity of the surface. Static contact angles of drops of water on the modified gold substrates were measured, and the results are shown in Figure 9. The contact angle for the cyclodextrin modified gold substrates is 36 ± 2°, indicating a hydrophilic surface, which agrees with the fact that cyclodextrin has a hydrophilic outside surface.[24] After C_{60} is encapsulated by the thiolated β-CD SAMs on the gold substrates, the CA value increases significantly to 77 ± 2°, which is consistent with the hydrophobic property of C_{60} and is similar to the previously reported value of C_{60} SAMs.[11a,50] For comparison, the contact angle of self-assembled monolayers of pentanethiol on gold was also measured. The observed CA value of 103 ± 1° is in good agreement with the corresponding value in the references.[51]

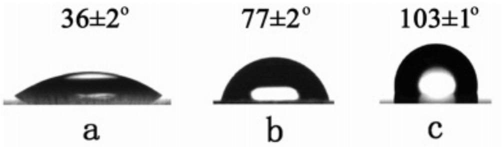

Figure 9. Static water contact angle measurements for modified gold substrates. (a) thiolated β-CD SAMs, (b) C_{60}/thiolated β-CD SAMs, and (c) $Au-S-(CH_2)_4CH_3$.

It has been shown that monoanionic C_{60} exhibited a better complexation ability with α-, β-, and γ-cyclodextrin than neutral C_{60} in solution, and the induction and dispersion forces are considered to be the major driving forces during the formation of the inclusion complex of cyclodextrin and $C_{60}^{\bullet-}$.[17] The anionic C_{60} carries more electron density and thus has greater polarizability to enhance the induction and dispersion forces, which in turn results in a stronger interaction with cyclodextrin.[18] As for the interfacial complexation between C_{60} and surface-attached β-cyclodextrin, again the monoanionic C_{60} demonstrates much better complexation ability than the neutral one, indicating that the same mechanism holds for the interfacial complexation as occurs in solution. In addition, C_{60} monoanion is very soluble in DMF,[26b,52] and the negative charge on it helps to reduce the formation of aggregate in solution; both are favorable for the formation of the $C_{60}^{\bullet-}$/thiolated β-CD SAMs, as it has been demonstrated that good solubility of fullerene or fullerene derivatives are required to achieve fullerene self-assembled monolayers of high quality.[11f] After the formation of $C_{60}^{\bullet-}$/thiolated β-CD SAMs, the negative charge was removed by iodine. The resulting noncovalent bonding SAMs is then probably stabilized by the interactions between the n-donor of the CD oxygen atoms and C_{60} as proposed previously for the complex of γ-CD/C_{60}.[15b]

Studies on the supramolecular inclusion complex of cyclodextrin and C_{60} have shown that the obtained water-soluble complexes are favored with a 2:1 stoichiometry of cyclodextrin and C_{60}.[15b,d,e] However, for the C_{60}/thiolated β-CD SAMs, because the complexation occurred at the interface of thiolated β-CD SAMs and $C_{60}^{\bullet-}$, it is reasonable that the resulted C_{60}/thiolated β-CD SAMs has a 1:1 stoichiometry of C_{60} and β-CD. The cavity dimension of β-CD is much smaller than the diameter of C_{60}; thus, it is not possible for β-CD to fully encapsulate

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C_{60}; instead, it is likely to form a shallow inclusion complex at van der Waals contact distance like that for the inclusion complex between cyclotriveratrylene (CTV) and C_{60}, where C_{60} adopts a position at van der Waals contact distance above the concave surface of the CTV macrocycle as shown by the X-ray structure.[53]

Conclusions

The interfacial supramolecular self-assembled monolayers of C_{60} by thiolated β-cyclodextrin SAMs on gold surfaces using C_{60} monoanion have been prepared. The formation process was monitored by UV−visible and near-IR spectroscopy. The obtained thiolated β-cyclodextrin and C_{60}/thiolated β-cyclodextrin SAMs are characterized by spectroscopic ellipsometry, cyclic voltammetry, XPS, and water contact angle measurements. The results indicate that the monoanion of C_{60} plays an important role in the formation of the monolayers, and the induction and dispersion forces between cyclodextrin and anionic C_{60} are believed to be the major driving forces during the formation process of the monolayers. The use of anionic C_{60} offers new convenient methods for the construction of fullerene-containing SAMs. Studies on more detailed mechanism of the formation of the monolayers and the photoelectrochemical properties of the monolayers are currently in progress.

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