A general and efficient method to form self-assembled cucurbit[*n*]uril monolayers on gold surfaces†

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A general protocol based on spontaneous adsorption of cucurbit[*n*]uril (CB[*n*]) molecules through a strong multivalence interaction between CB[*n*] and gold is described, by which the formation of self-assembled CB[*n*] monolayers on gold surfaces can be efficiently achieved.

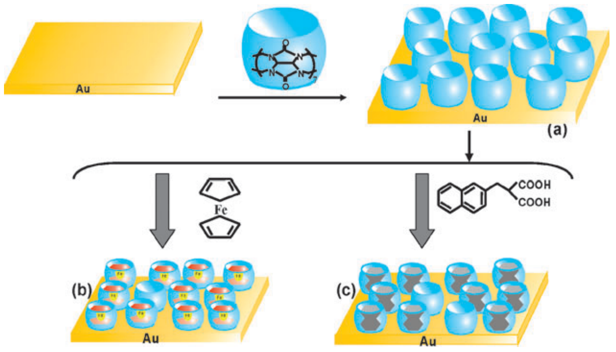
Cucurbit[*n*]urils (CB[*n*]) are pumpkin-shaped macrocyclic molecules which are composed of glycoluril units and each possess a hydrophobic cavity accessible through both identical carbonyl-fringed portals.[1] Due to their unique structure and outstanding multiple recognition properties, the CB[*n*] family holds high potential in the domain of supramolecular chemistry and has presented many exciting research results in recent years.[1] The binding properties of CB[*n*] to various guests as well as their applications for constructing sensors, drug delivery and biomimetic systems *et al.* have been investigated extensively.[1–7]

However, most research work involving CB[*n*] has been conducted in bulk solution.[1] The properties of the surface-confined CB[*n*] moieties, which may differ from those in bulk solution and are essential for many applications such as the development of chemo- or biosensor systems, have rarely been studied. The key factor that impedes such research is the difficulty in arranging CB[*n*] molecules on surfaces because of the difficulty in introducing functional groups in their scaffolds.[8,9] Although CB[*n*] monolayers on solid surfaces have been achieved either by threading CB[*n*] molecules on surface-attached molecules[10] or by employing substituted CB molecules,[8] there still does not exist an efficient approach to obtain self-organized monolayers on surfaces with their cavities free for recognizing guests. Thus, it would be very attractive and highly desirable to develop a simple, convenient and efficient approach to construct CB[*n*] monolayers applicable for all members of the CB[*n*] family. In this work, such an approach is described, by which self-assembled CB[*n*] monolayers can be generally and efficiently constructed on gold surfaces without any modification or special treatment of the CB[*n*] molecules, as shown in Scheme 1.

The new approach described here is based on our previous finding that acetone molecules can bind to the surface of citrate-coated gold nanoparticles (AuNPs) by replacing the ligand through the interaction between carbonyl and gold.[11] Since CB[*n*] are molecules with multiple carbonyl groups, we wondered whether they could also interact with gold. The performed simple experiments with AuNPs and CB[*n*] confirmed our supposition. Upon the addition of a small amount of aqueous CB[*n*] into a colloidal AuNP solution, the CB[*n*] molecules actually act as glue to connect AuNPs together, and finally, the resulting larger gold particle aggregates precipitated from solution, clearly evidenced by TEM observation and UV/Vis measurements (Fig. S1 and S2 in the ESI†). Encouraged by this preliminary result, we immersed a gold substrate into a 0.1 mM aqueous solution of CB[7] (or saturated aqueous CB[6] or CB[8] solution), and after 24 h exposure, were glad to find that a self-assembled CB[*n*] monolayer was really achieved.

The formation of the CB[*n*] SAMs was first detected by Fourier transform IR reflection absorption spectroscopy (FT-IRRAS). In the FT-IRRAS spectrum (Fig. 1), two characteristic peaks of CB[7] at 1751 cm^{-1} and 1474 cm^{-1} corresponding to C=O and C–N stretching vibrations,[10] respectively, were clearly detected. Compared with the spectrum of CB[7] obtained using a bulk KBr pellet (Fig. S3†), the more intense peak at 1751 cm^{-1} (amide I) suggests that CB[7] molecules rest with their carbonyls perpendicular with respect to the gold surface, in accordance with the FT-IRRAS surface selective rule.[12] This configuration indicates that the upright carbonyls contact with the gold surface and may provide the binding force by chelation.

The presence of CB[7] molecules on the gold surface as well as the interaction between the carbonyl groups and gold was further confirmed by comparing the XPS spectra (Fig. 2b1–b3) of a CB[7]-treated gold surface with those (Fig. 2a1–a3) of



Scheme 1 Schematic illustration of the construction of a self-assembled CB[*n*] monolayer on a gold surface (a), and inclusion complexes (b, c).

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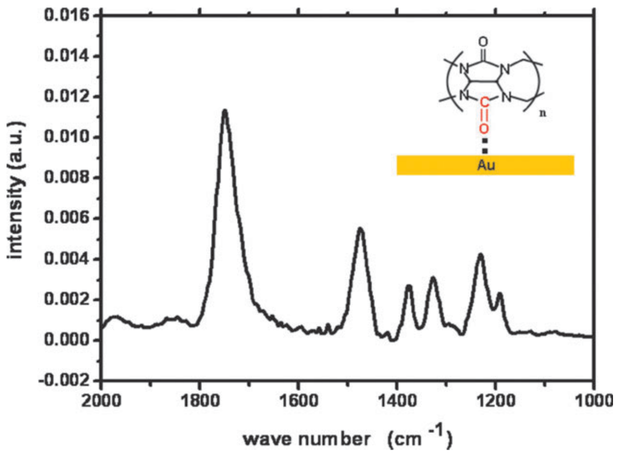

Fig. 1 FT-IRRAS spectrum of the CB[7] monolayer on a gold surface.

CB[7] deposited on an inert silicon surface, on which no interaction should exist. Apparently, the peak corresponding to O 1s broadens and moves to a higher binding energy region in the sample of CB[7]-treated gold. This result fits well with our argument that the O atoms of one carbonyl-fringed portal should interact with gold and bear a higher binding energy. The overlap of the spectrum of interacting O atoms (532.5 eV) upon that of the regular ones (531.9 eV) of another carbonyl-fringed portal broadens the peak (Fig. 2b3). The peak corresponding to the C 1s region was also influenced. The regular C 1s spectrum comprises three distinct peaks (Fig. 2a1), corresponding to contamination (285.0 eV), C in C–N (287.5 eV) and C in the C═O bond (289.1 eV), respectively. While in the spectrum of surface-attached CB[7], the figure of the peaks is blurred, which may be due to the change of oxidation state of the C atom in the surface-attached C═O bond. Detailed explanation of this change demands further investigation. The peak corresponding to the N 1s region stays identical with that of the regular ones. Based on these results, it is reasonable to assume that the CB[7] molecules orient themselves normal relative to the surface, as demonstrated in Scheme 1, and the strong interaction of one of the carbonyl ports of CB with the gold surface induces the additional carbon and oxygen species, as shown in the C 1s and O 1s spectra.

Electrochemical data further support the efficient formation of a CB[*n*] monolayer on gold. A CB[*n*]-modified gold electrode was obtained by immersing a clean gold electrode in a 1 mM aqueous solution of CB[7] (or a saturated aqueous solution of CB[6] or CB[8]) for 24 h. After the incubation process, the electrode was washed with deionized water and dried with nitrogen. Fig. 3 gives the capacitances of gold electrodes before and after CB[*n*] modification measured by cyclic voltammetry (CV)[13] in the following order: bare electrode > CB[8]-modified > CB[7]-modified > CB[6]-modified electrode, indicative of the attachment of CB[*n*] molecules on the gold surface. It is reasonable that the CB[6]-modified electrode bears the largest capacitance drop, since CB[6] molecules have the smallest cavities which serve as pinholes on the surface. What is more, the uncovered space of the electrode surface among CB[6] molecules would be the narrowest due to its smallest molecular scale among these three kinds of CB[*n*]. More importantly, the hydrophobic cavities of the attached CB[*n*] are accessible and their unique recognition capability is maintained. When a CB[7]-modified electrode was exposed to a 5 mM acetonitrile solution of ferrocene for 6 h, the typical and well-defined redox signal of trapped ferrocene was detected after thoroughly washing (Fig. 4b). The linear relationship between scan rates and peak currents indicates that the ferrocene molecules were confined to the electrode surface. In contrast, due to the lack of a specific binding force,[1] CB[6]-modified electrodes following the same incubation process could not exhibit the similar response to ferrocene molecule, as expected (Fig. S4†). In the case of CB[8], however, a trace signal of ferrocene was detected after the same washing process (Fig. S4†), indicating that the trapped ferrocene molecules in CB[8] are easily removable, due to the larger cavity of CB[8].

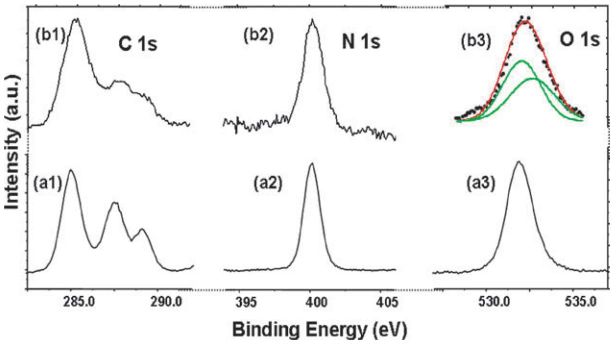

Fig. 2 High-resolution XPS spectra for C 1s, N 1s and O 1s. (a1–a3): CB[7] deposited on Si substrate; (b1–b3): self-assembled CB[7] on gold.

Based on the number of surface-confined ferrocene molecules, which is indicated by the area of the redox peak, the surface density of CB[7] molecules on the gold electrode was estimated to be at least 2.41×10^{13} molecules cm^{-2}. Taking the large molecular size of CB[7] into consideration, the surface density is satisfied by comparison with that of a monolayer formed from alkanethiol (*ca.* 4.5×10^{14} molecules cm^{-2}), especially thiolated cyclodextrin molecules on a gold surface.[13,15] From the surface coverage, the degree of packing

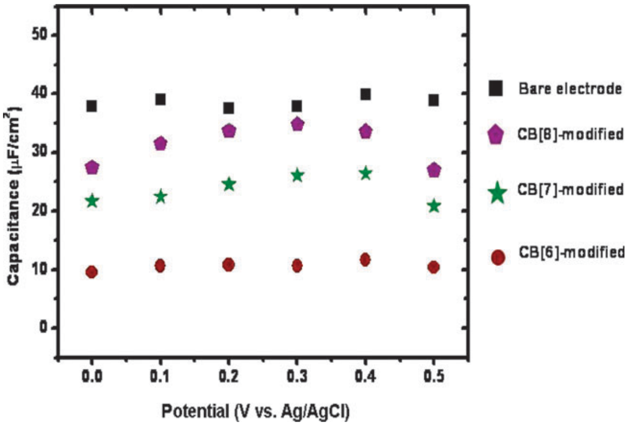

Fig. 3 Capacitances of gold electrodes before and after modification using CB[6], CB[7] or CB[8].

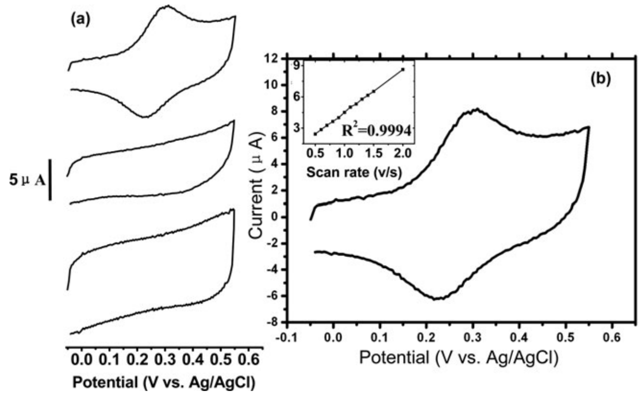

Fig. 4 (a) CVs of a bar Au electrode (below), CB[7] modified electrode (middle) and Fc@CB[7] modified electrode (top) at 1.0 V s^{-1} in 0.1 M aqueous solution; (b) CV of Fc@CB[7] modified electrode at 1.0 V s^{-1}. Inset: anodic peak current *vs.* scan rate plot for the modified electrode. Electrolyte: 0.1 M Na_2SO_4 aqueous solution without any electroactive species.

of the CB[7] SAM was estimated. It was found that 48% of the gold electrode surface was covered by CB[7] molecules, indicating an imperfect monolayer. However, we believe our data cannot reflect the molecular surface density accurately. Since the inclusion of ferrocene into attached CB[7] is a dynamic process,[14] association and dissociation take place at all times. It is reasonable to believe that there exists a fraction of CB[7] molecules whose cavities are not occupied by ferrocene molecules. Thus, the real surface density of self-assembled CB[7] molecules as well as the degree of packing should be larger than the value calculated. This promising result prompts us to employ the attached CB[*n*] molecules as anchor sites for modification of electrode surfaces. In this respect, carboxyl group-substituted naphthalene was bound to surface-confined CB[7] (Scheme 1), and detected by impedance spectroscopy (Fig. S5†). It was also found that, probably due to cooperative interaction of multiple carbonyl groups with gold, the formed CB[*n*] monolayers are stable enough for recognition processes. Upon washing with different solvents, desorption of CB[*n*] from the gold surface was not detected.

In summary, we report the first facile and efficient method for forming self-assembled CB[*n*] monolayers on gold surfaces. This method is based on the spontaneous adsorption of CB[*n*] molecules through the discovered interaction between CB[*n*] and gold, does not require any prior modification or special treatment of CB[*n*] molecules, and is applicable for all members of the CB[*n*] family, at least CB[6–8]. The surface-attached CB[*n*] molecules are uniform in orientation and hold their carbonyls perpendicular with respect to the gold surface and their cavities open to the outer atmosphere or solution. This arrangement maintains the recognition properties of CB[*n*] and facilitates guest molecules to approach the cavities and be recognized. To the best of our knowledge, this is the first time that such a kind of interaction between CB[*n*] molecules and gold has been discovered and applied. We believe that this finding might extend the understanding of CB[*n*] chemistry and promises great potential in the construction of CB[*n*]-based supramolecular structures or assemblies on solid substrates.

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