Observing Host–Guest Interactions at Molecular Interfaces by Monitoring the Electrochemical Current

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ABSTRACT: Macrocyclic cucurbit[\textit{n}]uril (CB[\textit{n}]) molecules have triggered renewed interest because of their outstanding capabilities as host molecules to selectively interact with a wide range of small guest molecules. Here, CB[7]-based host–guest interactions were investigated for a guest-modified nanoelectrode by monitoring the electrochemical current. A ferrocene (Fc)-terminated molecule immobilized on a gold nanoelectrode (GNE) showed suitable affinity with CB[7] when the effective exposing area of the GNE was between 5.3 and 12 μm² and the bias applied on the GNE was −500 mV. Monitoring the dynamics of nanoparticles (NPs) on a nanoelectrode provides new insights into the host–guest interactions at molecular interfaces.

INTRODUCTION

Supramolecular chemistry is the fastest-growing discipline, crossing a range of subjects from biological chemistry to materials science. It focuses on the noncovalent intermolecular interactions between host and guest molecules, which has broad applications in chemistry, biology, materials science, and nanotechnology.1−6 Of particular note, the macrocyclic cucurbit[\textit{n}]uril (CB[\textit{n}]) family, as an exceptional type of supramolecular host molecules due to their structural rigidity, high chemical stability, and high molecular symmetry, has been extensively investigated in nanoreactors, sensors, and drug delivery systems.7−14 Among various CB[\textit{n}] families, CB[7] has gained much interest due to its good water solubility, interaction with small molecules, and recognition properties, which is of interest for applications including surface-enhanced Raman spectroscopy (SERS),15−16 force microscopy (FM),17 recognition tunneling (RT),18 imaging,19 and electrochemical sensing.20−22 Moreover, CB[7] retains its molecular recognition properties when bound to metallic surfaces.

The dynamic interactions of discrete nanoparticles (NPs) on ultrasmall electrodes (ultramicroelectrode (UME) or nanoelectrode (NE)) have been widely investigated by electrochemical methods, which serve as powerful analytical tools in understanding their molecular chemistry, surface chemistry, and dynamics and these processess processes23−26 are also applied in NP analysis, catalysis, and chemical/biological sensing.27−33 Functional gold nanoparticles (GNPs) moving to the electrode contribute to the interactions between the host molecule and the guest group instead of nanoparticle collision such that gold nanoparticles directly interact with the molecule containing a thiol or amino group at the electrode. Different from traditional analytical methods like nuclear magnetic resonance (NMR), UV−vis, fluorescence, and isothermal titration calorimetry (ITC), observing the dynamics of nanoparticles provides a new opportunity to understand the interactions between the host and guest molecules.

In this report, we described the host–guest interactions at the molecular interfaces of a self-assembled monolayer (SAM)-modified nanoelectrode by monitoring the current (Figure 1A). The gold nanoelectrodes (GNEs) were modified with a SAM of R-terminated molecules that are denoted R1 = ferrocene (Fc), R2 = adamantane (Ad), and R3 = phenyl (Ph),

![Diagram](https://example.com/diagram.png)

Figure 1. (A) Measurement scheme of the electrochemical current. (B) Molecular structures of R-terminated molecules (R1 = Fc, R2 = Ad, R3 = Ph).

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which could interact with the host molecule CB[7]. Negatively charged CB[7]-protected gold nanoparticles tended to move to the electrode due to the positive bias. While no collision events were observed under positive bias, the dynamics of GNPs could be investigated under negative bias.

**RESULTS AND DISCUSSION**

Figure 1A shows the schematic representation of our experimental setup. The modified GNE was immersed in an electrolyte containing 10 nm diameter CB[7]-capped GNPs that were negatively charged in the experimental electrolyte (ζ-potential $-20.4 \pm 0.1$ mV). When positive bias was applied, GNPs were driven by the attractive electrostatic force to more easily move to the positive electrode to have a collision with the GNE. The interaction between the CB[7] molecule and the terminated group of the molecule may bring the current spikes during the collision events, which would be discussed below.

Figure 2 shows the scanning electron microscopy (SEM) image and cyclic voltammetry (CV) curves of the GNE modified with an R1-terminated molecule. The successful modification was confirmed by CV due to a decrease of the diffusion current (see Figure S8 for R2- and R3-terminated molecules in the Supporting Information). We also observed an increase in the water contact angles of the GNE after modifying with the R1-terminated molecule in Figure 2C (i and ii) (see Figure S9 for R2- and R3-terminated molecules in the Supporting Information), which is attributed to the hydrophobic Fc group of the target molecules immobilized on the surface. The SEM image showed the GNPs (marked with the yellow arrow) attached on the GNE after the i-t test. Decreased contact angles were observed Figure 2C (iii and iv) after incubation with CB[7]-capped GNPs (see Figure S9 for R2- and R3-terminated molecules in the Supporting Information) because the surface-bound electronegative carbonyl portals of CB[7] contribute to a more hydrophilic surface, which suggested the successful modification of CB[7]-capped GNPs.

We found that the baseline current originated from the redox reaction of the redox mediator ferrocyanide. Before the addition of GNPs, no events were observed. Furthermore, we applied different positive biases from $+100$ to $+800$ mV into the electrolyte solution after the addition of CB[7]-capped GNPs to see whether any kind of molecular event occurs in the solution. Neither the bare GNEs without any molecule modification nor the three molecule-modified GNEs showed detectable current changes under positive bias (see Figure S10 in the Supporting Information). Additionally, no events were observed with the absence of GNPs in the solution as well, which led to the following assumptions: First, there may be a very small current during NP collision events due to electron transfer resistance because of the relatively long molecule length.34–36 Second, the small-sized GNPs could not efficiently facilitate electron tunneling through the insulating layer. Third, fast adsorption of GNPs makes it hard to observe a detectable current change. Fourth, a few adsorbed GNPs on the GNE go against the free GNPs in the solution, which move to the GNE because of the steric hindrance effect.

To better investigate the dynamics of the adsorbed GNPs, we refreshed the buffer solution without GNPs. Figure 3B shows i-t traces of the GNE modified with the R1-terminated molecule with the absence of GNPs in the electrolyte solution under negative bias. Downward current spikes were observed. As shown in Figure 3D, the electrons continuously flow from the GNP–GNE geometry to the other electrode under bias. The GNP served as an intermediate electron reservoir, which continuously charges up by acquiring electrons from the GNP–GNE geometry, and then provided electrons for the mass transport. When negative bias was applied, negatively charged GNPs were forced to move away from the GNEs. The dynamics of the landed GNPs led to the interactions between the CB[7] molecule and the Fc group. Moreover, the suitable affinity between the CB[7] molecule and the Fc group also contributes to electron transfer, which triggered the current spikes. To confirm these events, we also checked the bare GNE (without modifying any R-terminated molecule) after incubation with the GNP solution. CB[7]-capped GNPs could be immobilized on the gold tip because of the interaction between the carbonyl group and gold.37 No events were observed for the bare GNE with the absence of GNPs in electrolyte solution under different negative biases (see Figure S11 in the Supporting Information). This suggested that the events come from the interactions between the host and guest molecules instead of the interactions between CB[7] and the gold electrode. No events were observed for the R2- and R3-terminated molecules with the absence of GNPs even under high negative bias (see Figure S12 in the Supporting Information), which suggested that the R1-terminated molecule immobilized on a gold nanoelectrode showed suitable affinity with CB[7] under these conditions.

We further studied the bias effect on the current spikes of this R1-terminated molecule–modified GNE. Figure 4 shows that the current spikes gradually appeared when the bias was at $-500$ mV. The interactions between the CB[7] molecule and the Fc group were interfered with by the applied bias. The current spike amplitude increased with the increase of applied negative bias magnitude, which suggested that the electrons need to overcome enough barrier to complete the electron transfer process.

We then investigated the GNEs with larger sizes between 27 and 45 μm² ($i_d$ range from 90 to 120 nA). Figure S13 shows...
the i−t traces of the larger GNEs modified with the R1-, R2-, and R3-terminated molecules. The effectively exposed area of the GNEs was 44 μm² (i_d = 115 nA), 30 μm² (i_d = 95 nA), and 27 μm² (i_d = 90 nA) for GNE A, B, and C, respectively. Compared to the sizes between 5.3 and 12 μm² (i_d range from 40 to 60 nA), the larger-sized GNE showed the same tendency of events. Only the GNE modified with the R1-terminated molecule showed the current spikes with the absence of GNPs in the solution when negative bias was applied. Moreover, some events could be observed at −400 mV. More molecules and GNPs could be attached on the GNE with a larger size, which led to weaker binding of GNPs due to the repulsion of carbonyl portals of the GNP-surface-bound CB[7]. This brought the possibility to observe current events at a lower negative bias.

To confirm the size effect, we further investigated the larger-sized ultramicroelectrode (UME) modified with R1-, R2-, and R3-terminated molecules (see Figure S14 in the Supporting Information). Here, the sizes of R1-, R2-, and R3-terminated molecule—modified electrodes were 87.5 μm² (i_d = 162 nA), 190 μm² (i_d = 240 nA), and 133 μm² (i_d = 200 nA), respectively. It is easier to observe events for the R1-terminated molecule—modified electrode. A few events could be observed for the R2-terminated molecule—modified electrode under a negative bias of −500 mV because of the strongest interactions between CB[7] and the R2 group in our study. As for the R3-terminated molecule, a very small number of GNPs could effectively adsorb onto the electrode because of the weakest interactions between CB[7] and the R3 group in our study. Therefore, it was difficult to observe leaving events for the R3-terminated molecule.

We also studied the small-sized GNEs modified with the R1-, R2-, and R3-terminated molecules. i−t traces are shown in Figure S15 in the Supporting Information. Here, the sizes of R1-, R2-, and R3-terminated molecules—modified electrodes were 1.65 (i_d = 24 nA), 3.12 μm² (i_d = 30 nA), and 4.32 μm² (i_d = 35 nA), respectively. Only few events could be observed under −900 mV for the R1-terminated GNE. They may need more energy to force GNPs to move away from the GNE.

We focused on the GNEs used in our experiments, in which the effective exposing area was between 5.3 and 12 μm² (i_d = 40−70 nA). Moreover, the GNEs modified with the R1-terminated molecules showed current events (for more examples, see Figure S16 in the Supporting Information). More negative bias was needed to observe the detectable events if the size was too small. If the electrode was of large size, both R1- and R2-terminated molecules showed events under normal negative bias. In addition, the electrode with a large exposing area should not be a nanoelectrode but an ultramicroelectrode.
CONCLUSIONS

In summary, we investigated the host–guest interactions at the molecular interfaces of an SAM-modified nanoelectrode by monitoring the current. Transient intermediate states of the interactions between CB[7] and ferrocene (Fc), adamantane (Ad) and phenyl (Ph) group-terminated molecules on the gold nanoelectrode were revealed with the absence of GNPs in the solution under negative bias. The size of the GNE and the applied bias have an effect on the transient current. An Fc-terminated molecule immobilized on the gold nanoelectrode showed suitable affinity with CB[7] when the effective exposing area of the GNE was between 5.3 and 12 μm² and the bias applied on the GNE was −500 mV. We believe that the reported results will provide new insights into our understanding of the process of interactions for supramolecular systems.

EXPERIMENTAL SECTION

Chemicals. Cucurbit[7]uril (CB[7]) and R-terminated molecules were synthesized and fully characterized by our lab (Figures S1–S6). Gold wire, pyrrolidine, potassium ferrocyanide, potassium chloride, potassium dihydrogen phosphate, dibasic sodium phosphate, and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the purchased chemicals were used directly without further purification. Deionized water from a Milli-Q water purifying system was used to prepare all of the solutions (18.2 MΩ).

GNE Fabrication and Modification. GNEs were fabricated by following previous reports. First, a gold wire was electrochemically etched and cleaned by immersion in piranha solution (H₂SO₄/H₂O₂ = 3:1, by volume), rinsed with copious amounts of deionized water, and blown dry with argon. Second, the gold tip was insulated with high-density polyethylene (HDPE) to expose only the tip apex.

A 5 mM solution of R-terminated molecules (R-SAc) in ethanol solution (2.5 mL) was treated with pyrrolidine (0.2 mL) to remove the thiol-protecting group. Fresh GNEs were immersed in this solution overnight at room temperature. The modified GNEs were washed with copious amounts of ethanol and deionized water, dried with argon gas, and used immediately.

Preparation and Characterization of CB[7]-Capped GNPs. Gold nanoparticles were prepared by following our reported procedure, by mixing solutions of KAuCl₄ and CB[7] in the presence of NaOH at room temperature. Figure S7 shows the TEM image of GNPs. The ζ-potential of CB[7]-capped GNPs was measured by Zetasizer Nano ZS ZEN3600 (Malvern, UK). The ζ-potential was −20.4 ± 0.1 mV under experimental conditions (2.17 mg/mL).

CV Measurements. CVs were recorded in a three-electrode system with a CHI 660c electrochemical analyzer. A platinum wire was used as the counter electrode, and an Ag/AgCl3 M KCl electrode was used as the reference electrode. The cyclic voltammograms (CVs) of GNEs before and after modification were measured and recorded in 1 M KCl solution containing 100 mM potassium ferrocyanide by cycling the electrode potentials (50 mV/s). All of the CV measurements were performed in a Faraday cage.

Contact Angle of SAMs. Water contact angles were measured using a goniometer (OCA15EC, Germany) immediately after the addition of 4.0 μL of water droplets on R-terminated molecule–modified gold substrates before and after immersion with CB[7]-capped GNP solution for 2h.

I–t measurements. Electrochemical current measurements were achieved by the current recording instrument Axon Digitada 1440B. An Axon 200B patch-clamp amplifier (Molecular Devices Inc., CA) in the voltage-clamp mode was used to supply the bias and amplify the current. A 5 kHz Bessel low-pass filter was typically used for current measurements. The GNE was used as the working electrode. The Ag/AgCl electrode was grounded and used as the quasi-reference electrode. The GNE was placed in a 5 mM phosphate buffer solution (PBS, pH = 7.4) with 3 mM potassium ferrocyanide. The concentration of CB[7]-capped GNPs was 2.17 mg/L. All of the measurements were performed in a Faraday cage at room temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01077.

Molecules’ preparation, 1H NMR and 13C NMR spectra of molecules; TEM image of CB[7]-capped GNPs; CV measurements of R2- and R3-terminated molecule-modified GNEs; contact angle of SAMs; I–t measurements; size effect (PDF)

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Notes

The authors declare no competing financial interest.
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