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A combined electro- and photo-chemical approach to repeatedly fabricate two-dimensional molecular assemblies

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A B S T R A C T

To facilitate the design and construction of complex functional materials, the field of molecular assembly can learn from the well-established field of catalysis including its branches such as electrocatalysis and photo-electrocatalysis. In this study, we establish a "photo-electro-catassembly" strategy to repeatedly fabricate two-dimensional molecular assemblies on electrode surface by learning from the concept of photo-electrocatalysis. With the rational design of the linear diacetylene building blocks, Au electrode surface itself and the thiol-functionalized electrode both can assist the formation of two-dimensional assemblies and their subsequent covalent stabilization through the polymerization of diacetylene groups. Nevertheless, when using the Au electrode surface as a direct template, the polymerized product would be hardly removed from the electrode due to the strong synergistical interactions through multivalent Au-S bonds. By contrast, when using the thiol-functionalized electrode as an indirect template, the diacetylene building block forms a well-ordered second layer over the thiol monolayer due to the solvent-phobic and solvent-philic effects. After photo-polymerization, the polymerized product can still be removed from the electrode along the electro-induced removal of the thiol monolayer. Driven by electricity and photoirradiation, the thiol-functionalized electrode assists the combined process of assembly and photo-polymerization as a "photo-electrocatassembler", and it works repeatedly to produce covalently stabilized two-dimensional assemblies.

1. Introduction

Molecular assembly provides an elegant approach to functional materials and systems with biomimetic elements. Starting from simple recognitions of ions and small molecules [1], chemists are committed to push molecular assembly more and more complex to realize advanced functions like what nature does [2]. Despite of substantial achievements on self-assembly methodologies [3–12], artificial chemical systems still pale in comparison to life systems in terms of complexity and efficiency [13]. To endow assembly systems with more functionality and complexity, various kinds of "*assisted assembly*" strategies have been developed to enhance the efficiency and selectivity of assembly systems [5,14–19]. From these strategies, such as "*electro-assisted assembly*" [14,16] and "*photo-assisted assembly*" [5,15,18], one can clearly see the resemblance to the control methods of chemical reaction, such as photo-reaction and electrochemical reaction.

Inspired by the most important control method of chemical reaction, *i.e.*, catalysis, we recently proposed a new mode of assisted assembly and suggested a new term [20,21], "*catassembly*", which combines the Greek root "*cat-*" of "*catalysis*" and the word "*assembly*". Catassembly in molecular assembly is a concept analogous to catalysis in chemical synthesis, referring to the increase in the rate and control of a molecular assembly process. The corresponding "helper" species in a catassembly process is named "*catassembler*". Through multi-site synergistic noncovalent interactions, a catassembler (or a group of catassemblers) increases the efficiency and/or selectivity of an assembly process by dividing it into a cascade of sub-processes. Some of these features have been reflected in a few of primitive examples [22–25], however, new experimental and theoretical methodologies are highly desirable in this infant stage of the field of catassembly. Developments on catassembly will facilitate the design and construction of complex functional systems of molecular assemblies, and promote the field of molecular assembly in a similar way that catalysis does to chemical syntheses.

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To develop new catassembly methodologies, the field of catassembly can learn from the well-established field of catalysis including its branches such as "*electrocatalysis*" [26–28] and "*photo-electrocatalysis*" [29–31]. In an electrocatalysis system, the electrocatalyst usually functions at electrode surface or may be the electrode surface itself, which increases the rate of chemical reactions through facilitating the electron transfers between the electrode, reactants and reaction intermediates [32]. Distinguished from the electron transfers in chemical reactions, the molecular assembly mainly refers to the changes of molecular arrangements and conformations [1]. Therefore, when the concept of "*(photo-)electrocatalysis*" is extended into the field of molecular chemistry, the analogy concept "*(photo-)electrocatassembly*" should refer to using "*(photo-)electrocatassembler*" to increase the formation of molecular assemblies through facilitating the intermolecular arrangements of building blocks. The (photo-)electrocatassembler might be electrode surface itself or the functional materials at electrode surface, driven by suitable working potentials.

Herein, we report a photo-electrocatassembly approach to fabricate two-dimensional (2D) molecular assemblies through the combination of template-assisted assembly, photo-induced polymerization and electro-controlled desorption. 2D molecular assemblies were first formed on the electrode surface, and then were covalently stabilized by the photo-induced polymerization, thereby avoiding the disassembly of building blocks during the electro-controlled desorption. We tried both the electrode surface itself and the functionalized electrode as the photo-electrocatassembler for this combined process, and found that the electrode functionalized with a monolayer of dodecane-1-thiol served as a better photo-electrocatassembler than the bare electrode. Driven by electricity and photoirradiation, the functionalized electrode facilitates the combined process as a photo-electrocatassembler and works repeatedly to produce covalently stabilized 2D assemblies.

2. Experimental

2.1. Chemicals Reagents

Dodecane-1-thiol (DT, ≥ 98%) and pentacosa-10,12-diynoic acid (PCDA, ≥ 98%) were purchased from Alfa Aesar. Tetrahydrofuran (THF, HPLC-grade) was purchased from Sigma-Aldrich. Si(100) wafer (2 inches, flatness ≤ 3 nm) used for preparing Au substrates was purchased from Li Jing Co. (China). Ultrapure water was prepared with a Milli-Q system (resistivity = 18.2 MΩ cm) and used throughout the experiments. Other chemicals were analytical quality and used without further purification.

2.2. Synthesis of pentacosa-10,12-diyne-1-thiol

Penatcosa-10,12-diynoic acid (PCDA) was reduced into pentacosa-10,12-diyne-1-ol and the latter was further brominated to form 1-bromopentacosa-10,12-diyne by following the literature report [33]. 1-Bromopentacosa-10,12-diyne (1 g, 2.4 mmol), sodium hydrogen sulfide (1.3 g, 24 mmol) and absolute ethanol (100 mL) was added to a flask under nitrogen atmosphere and sonicated at 50 °C. After 10 hours, the reaction was diluted with 300 mL dichloromethane, washed with hydrochloric acid and dried over magnesium sulfate. After evaporation of solvents, the mixture was recrystallized from hexane to give product pentacosa-10,12-diyne-1-thiol (PCDT) as a yellow solid (0.45 g, 50%).

^1H NMR (400 MHz, $CDCl_3$, ppm, δ): 2.674 (t, $J = 8.00$ Hz, 2H), 2.239 (t, $J = 7.60$ Hz, 4H), 1.665 (dt, $J_1 = 14.40$ Hz, $J_2 = 8.00$ Hz, 2H), 1.509 (dt, $J_1 = 15.20$ Hz, $J_2 = 6.40$ Hz, 4H), 1.430–1.220 (m, 28H), 0.880 (t, $J = 5.20$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 77.58, 77.46, 65.31, 65.24, 39.16, 31.93, 29.66, 29.65, 29.62, 29.50, 29.36, 29.33, 29.21, 29.18, 29.12, 29.03, 28.87, 28.81, 28.50, 28.37, 28.33, 22.70, 19.22, 19.21, 14.14.

2.3. Experimental setup

The template-assisted assembly, photo-induced polymerization, and electro-controlled desorption of PCDT and PCDA were carried out in a home-made electrochemical cell with a transparent quartz window for the UV irradiation and Raman characterization (Fig. 1). A platinum wire was sealed in the cell as the counter electrode, and saturated calomel electrode or Ag/AgCl electrode were used as reference. Evaporated Au(111) electrode and single-crystal Au(111) electrode were used as the assembly substrates of PCDT and PCDA, respectively. Evaporated Au(111) electrode was prepared by thermal evaporation of 100 nm Au over a 20 nm titanium adhesion layer confined to a flat silicon wafer by a Temescal FC-20359 system with an evaporation rate of 0.1 Å/s. The evaporated Au(111) substrates were cut into 1 cm × 1 cm pieces, annealed under butane flame for 1 min, cleaned in sulfuric acid (98%) for 10 min, washed by water and dried with nitrogen before used as the assembly substrate of PCDT. Single-crystal Au electrode was prepared by the Clavilier method [34], cleaned in piranha solution (7:3 H_2SO_4:H_2O_2) for 10 min, washed by water and dried with nitrogen before used as the assembly substrate of PCDA.

2.4. Characterization

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a Bruker AV-400 spectrometer (400 MHz and 100 MHz, respectively) at 298 K and are reported relative to residual solvent signals. Cyclic voltammetry and electro-controlled desorption were preformed on CHI-631B. For probing the assembled monolayer of PCDT, the evaporated Au substrate was used as the working electrode in an aqueous electrolyte solution containing 2 mM $K_3[Fe(CN)_6]$ as electrochemical prober and 1 M KCl as electrolyte with a saturated calomel reference electrode. For electro-controlled desorption of the co-assembled double layers of PCDA and DT, the single-crystal Au substrate was used as working electrode in an ethanol electrolyte solution containing 0.1 M KOH with a Ag/AgCl reference electrode. Photo-induced polymerization was achieved by the irradiation of a 11 W UV lamp (254 nm) from 3 cm above the Au electrode for 10 min. Au electrodes assembled with PCDT monolayer and PCDA/DT double layers were washed with pure ethanol and 1 M KOH ethanol solution, respectively, and both were dried under flowing nitrogen before spectroscopic

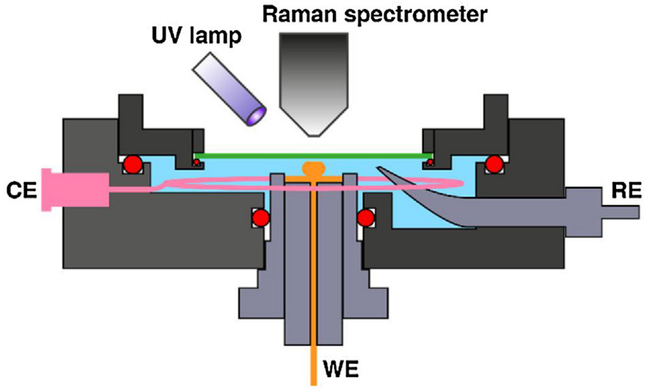

Fig. 1. Schematic illustration of the electrochemical cell for template-assisted assembly, photo-induced polymerization, and electro-controlled desorption. Quartz window (green) allows the penetration of UV irradiation and the excitation and emission of Raman light. Gasket rings (red) prevent the electrolyte (cyan) from leaking or being oxidized by air.