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



Yu Wang*, Yibin Sun, Xiaobing Ding, Jinghong Liang, Xiaoyu Cao, Zhong-Qun Tian*

State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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ABSTRACT

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.

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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

http://dx.doi.org/10.1016/j.electacta.2017.06.015 0013-4686/© 2017 Published by Elsevier Ltd. 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.

^{*} Corresponding authors.

E-mail addresses: ywang2@uakron.edu (Y. Wang), zqtian@xmu.edu.cn (Z.-Q. Tian).

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 monolaver 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 photoelectrocatassembler and works repeatedly to produce covalently stabilized 2D assemblies.

2. Experimental

2.1. Chemicals Reagents

Dodecane-1-thiol (DT, \geq 98%) and pentacosa-10,12-diynoic acid (PCDA, \geq 98%) were purchased from Alfa Aesar. Tetrahydrofuran (THF, HPLC-grade) was purchased from Sigma-Aldrich. Si(100) wafer (2 inches, flatness \leq 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 M Ω 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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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 singlecrystal 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 $1 \text{ cm} \times 1 \text{ cm}$ 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 H₂SO₄:H₂O₂) for 10 min, washed by water and dried with nitrogen before used as the assembly substrate of PCDA.

2.4. Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded in CDCl₂ 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 K₃[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.

characterization. Raman spectra were acquired using Renishaw R 1000 confocal microscopic Raman spectrometer under the excitation laser of 633 nm (1% intensity) with an acquirement time of 10 s. The UV-vis absorption of PCDT monolayer was measured by Agilent Cary 5000 UV-Vis-NIR spectrometer in the reflection mode with the clean evaporated Au substrate as reference.

2.5. Calculation

The diacetylene oligomer with four repeated units was used as a simplified structure of polymerized PCDT and PCDA. Structural optimization and Raman intensity computation were carried out in Gaussian 09B [35] by the density functional three-parameter hybrid mode (DFT/B3LYP) with 6-311g(d,p) as basis set. A Lorentzian line-shape broadening was applied for plotting the Raman spectra with full-width at half-maximum (FWHM) of 10 cm⁻¹.

3. Results and discussion

3.1. Photo-electrocatassembly based on PCDT monolayer

The combination of molecular assembly and photo-polymerization is a promising approach to fabricate well-ordered 2D assemblies with strong robustness [36–38]. Linear molecules with diacetylene group, *e.g.*, PCDT, have potential to form 2D assemblies and further be polymerized into functional materials [39,40]. However, in a self-assembly pathway without the assistance from Au substrate (black line in Fig. 2b), the PCDT molecules cannot form a well-ordered monolayer in a dilute solution since this is an energy-increasing process with an extremely high energy barrier. Therefore, although the overall energy decreases in the combined process of self-assembly and photo-polymerization, this combined process would not occur spontaneously.

As an alternative approach, we proposed to substitute the selfassembly method by a photo-electrocatassembly method as shown in Fig. 2a. In this photo-electrocatassembly process, the Au substrate first works as a template to assist PCDT to form a wellordered 2D monolayer, thus facilitating the subsequent polymerization (Fig. 3a). With the assistance of the Au template, the energy barriers of assembly and polymerization would be decreased to a feasible level (blue line in Fig. 2b). Furthermore, the Au substrate also works as an electrode, thus positive or negative potentials could be applied to facilitate the adsorption of PCDT monomer or the desorption of the polymerized PCDT, respectively (red arrows in Fig. 2b). After the potential-controlled desorption of the poly-PCDT, the Au electrode would return to the initial state and help the next cycle of template-assisted assembly, photo-induced polymerization, and electro-controlled desorption. Therefore, the Au substrate could play the role of photo-electrocatassembler in this combined process, working like a photoelectro-driven printer for fabricating 2D assemblies.



Fig. 2. (a) Representative schematic of the photo-electrocatassembly of PCDT through the direct adsorption on Au substrate. (b) Reaction coordinates of the self-assembly pathway (black curve), the template-assisted pathway (dashed blue curve) and the photo-electrocatassembly pathway (red curve).



Fig. 3. (a) Structures of the PCDT monolayer on Au substrate and the polymerized monolayer after UV irradiation. (b) Cyclic voltammetry of the electrochemical probe $[Fe(CN)_6]^{3-}$ on the clean Au electrode (black curve), the PCDT modified electrode (red curve), and the poly-PCDT modified electrode (blue curve). (c) UV-vis absorption spectra of the PCDT monolayer under UV irradiation for different minutes. (d) Raman spectra of the PCDT monolayer before (black line) and after UV irradiation (red line), after the application of negative potential of -1.4 vs (Ag/AgCl)/V for 5 min (blue line), and the DFT-calculated spectrum of PCDT (green line).

To test the feasibility of this photo-electrocatassembly method, we first assembled the PCDT molecules onto the evaporated Au(111) electrode in a 1 mM PCDT solution in THF for 24 hours. $[Fe(CN)_6]^{3-}$ was used as an electrochemical probe to examine the formation of PCDT monolayer. As shown in Fig. 3b, the reduction and oxidation currents of the $[Fe(CN)_6]^{3-}$ probe remarkably decreased after the Au electrode being assembled in PCDT solution, suggesting the formation of PCDT monolayer on electrode surface. After the PCDT monolayer was irradiated under the UV light (254 nm), the UV-vis reflection analysis showed the appearance of the absorption peaks at

630 nm and 685 nm (Fig. 3c), indicating the formation of poly-PCDT with a well-ordered conjugated structure in "blue phase" [41]. The intensity of these two absorption peaks increased upon irradiation time and reach the maximum at 10 minutes, indicating the photopolymerization was accomplished quickly. Raman spectroscopy provided a better way to monitor the polymerization of PCDT on the single-crystal Au(111) substrate in the electrochemical cell, and showed a distinct resonance Raman spectrum of the poly-PCDT after UV irradiation (red line in Fig. 3d). DFT calculation confirmed the conjugated structure with interlaced C=C double bonds and C \equiv C



Fig. 4. Representative schematic of the photo-electrocatassembly of PCDT through the co-assembled PCDA and DT double layers.

triple bonds (green line in Fig. 3d). In addition, the peak at 1451 cm⁻¹ was attributed to the stretching vibrations of C=C double bonds, the peaks at 2080 and 2149 cm⁻¹ were attributed to the stretching vibrations of C = C triple bonds, the peaks at 1086 and 1334 cm⁻¹ were attributed to the bending mode of side alkyl chains, and the peaks at 695, 1187, 1215 and 1241 cm⁻¹ are attributed to in-plane bending mode of the conjugated backbone (Details in Supplementary Data).

So far, the template-assisted assembly and photo-polymerization sub-processes worked as proposed in Fig. 2a, however, the potentialcontrolled desorption did not occur as expected. After applied a -1.4vs (Ag/AgCl)/V on the electrode with poly-PCDT for 5 min, the Raman spectrum remained the similar intensity, suggesting the poly-PCDT was not removed by the application of negative potential. Similar phenomenon has also been found in a similar poly-diacetylene selfassembled monolayer [42,43]. We conjecture that the multivalent Au-S bonds synergistically increase the interaction between the poly-PCDT and the Au electrode and dramatically increase the energy barrier of desorption. Therefore, although the energy barrier of the desorption of poly-PCDT was lowered by the application of negative potentials, it is still too high to occur.

3.2. Photo-electrocatassembly based on co-assembled PCDA and DT double layers

To overcome the strong multi-covalent interaction between the poly-diacetylene and the Au electrode, we adopted an alternative photo-electrocatassembly method based on the co-assembled double layers of PCDA and DT (Fig. 4).

In the first step of template-assisted assembly of PCDA, the single crystal Au(111) electrode was dipped in the ethanol solution containing 20 mM PCDA, 40 μ M DT and 0.1 M KOH for 12 hours. Due to the presence of a high concentration of KOH, PCDA was in the form of conjugate base with a high polarity end of carboxylate ion and a low polarity end of alkyl chain (Fig. 5a). The DT molecules would form the first layer on Au electrode through the strong covalent Au-S bonds. The alkyl tails of DT layer have a low polarity and hence are solvent-phobic to the KOH/EtOH solvent. To lower the interfacial energy between the solvent-phobic tail of DT and the solvent, a second molecular layer with high polarity ends towards the solution phase has to be formed. Because PCDA has a much larger concentration than DT and it has a longer alkyl chain to form a more compact second layer, the second layer is mainly formed by PCDA as showed in Fig. 5a.

Before UV irradiation, the co-assembled double layers of PCDA and DT showed no resonance Raman signal (black line in Fig. 5b). Nevertheless, Raman spectrum with strong intensity was observed after the co-assembled double layers was irradiated for 10 min (red line in Fig. 5b), indicating the successes of the co-assembly and the subsequent photo-polymerization.

Although the second layer of PCDA was polymerized, DT molecules in the first layer still connect with Au electrode by individual Au-S bonds, making its removal much easier than the removal of multivalently connected poly-PCDT. Cyclic



Fig. 5. (a) Structures of the co-assembled double layers of PCDA and DT on Au substrate and the polymerized double layers after UV irradiation. (b) Cyclic voltammetry of the desorption of the co-assembled double layers. (c) Resonance Raman spectra of the co-assembled double layers before and after UV irradiation, after potential-controlled desorption, and in the second and third cycles of photo-electrocatassembly.

voltammetry indicated the DT layer could be removed under negative potential lower than -1.0 V (Fig. 5c). After applying a -1.2vs (Ag/AgCl)/V negative potential on the electrode for 5 min, Raman spectroscopy confirmed the completely removal of poly-PCDA layer (blue line in Fig. 5b) along with the removal of DT.

Therefore, a complete cycle of photo-electrocatassembly has been realized by using the assembled monolayer of DT as the template for the second layer of PCDA, applying photo-irradiation to induce the polymerization of diacetylene groups, and applying negative potential to induce desorption of the product poly-PCDA. The photo-electrocatassemblers, *i.e.*, the electrode and the DT molecules, assisted the fabrication of poly-PCDA by taking parts in the assembly and polymerization sub-processes, yet were restored in the last sub-process of potential-controlled desorption. Thus, the electrode and the DT molecules could be further used in the next cycles of photo-electrocatassembly. As shown in Fig. 5c, the poly-PCDA produced in the second and third cycles have extremely similar Raman spectra to that in the first cycles, indicating the sustainability of the photo-electrocatassemblers.

4. Conclusions

We have proposed two strategies to realize the combined photoelectrocatassembly and photo-polymerization for fabricating robust two-dimensional (2D) molecular assemblies. Using the electrode surface itself as the photo-electrocatassembler, the templateassisted assembly and photo-polymerization sub-processes worked as expected, however, the potential-controlled desorption did not occur due to the strong synergistically interaction between poly-PCDT and Au substrate through multivalent Au-S bonds. This problem was overcome by using the electrode surface functionalized with DT monolayer as the photo-electrocatassembler. PCDA building blocks formed a well-ordered second layer over the DT monolayer due to the solvent-phobic and solvent-philic effects. After photopolymerization, the poly-PCDA can still be removed from the electrode along the removal of DT molecules. Driven by electricity and photoirradiation, the functionalized electrode assisted the combined process as a photo-electrocatassembler and it works repeatedly to produce 2D assemblies.

The photo-electrocatassembly product in this study was realized by the random-walk polymerization of the relatively simple diacetylene building blocks, therefore, the structural order of the product does not achieve an impressive level compared to graphene. Nevertheless, this study mainly aims to provide a photo-electrocatassembly strategy to achieve repeatable formation and removal of 2D assemblies, and this strategy could be applied to the building blocks with three or more functional groups and thus to form 2D crystal lattices with square or hexagonal symmetries [36–38]. We are optimistic that, development of photo-electrocatassembly will enhance our understanding of molecular assembly on surface, and will promote new discoveries and fabrications of complex 2D functional materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2017. 06.015.

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