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Electro-Induced Copper-Catalyzed Surface Modification with Monolayer and Polymer Brush

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4.1 Introduction

There is an increasing demand for polymer-based thin films with well-defined spatial control in the field of biology and modern chemistry.^{1,2} Polymers at surfaces can be designed with many interesting properties that are a consequence of conformation changes of polymer chains, which have potential applications as functional materials.^{3–6} In the past few decades, chemists have made great progress with regard to the assembly of an impressive wide range of molecules onto surfaces. For example, Langmuir–Blodgett deposition, layer-by-layer assembly, and electrostatic or hydrophobic adsorption are commonly

used and well established. However, most of these technologies require specific chemical or physical substrate properties.

The two methods named “grafting to” and “grafting from” are mostly used to assemble small molecules or polymers onto surfaces, either through physisorption or chemisorption techniques.^{7,8} However, covalent immobilizations yield polymers on surfaces with higher stability than physisorbed polymers and are less prone to degradation. The *grafting-to* technique consists of adsorbing polymers that is induced by various anchor groups to form a covalent bond with a complementary surface functionality, but the film thickness and graft density are quite limited due to the steric effect of polymer chains. The *grafting-from* approach involves *in situ* initiation of surface polymerization from an initiator-decorated substrate and has been widely used to generate polymeric films with high grafting densities and various functional groups, however, disadvantages of this technique include such as rigorous synthetic protocols and limited controllability to the polymerization process.

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There is a continuous search for new, versatile, and more controllable mediating means for surface-induced reactions. Electrochemistry offers many benefits including the generation of a dynamic solution, and its ability to provide temporal and spatial control over the reaction process and also compatibility

with automation. The objective of this chapter is to provide a status report on synthetic strategies and mechanistic aspects of electrochemically induced Cu(I)-catalyzed chemical reactions for surface modifications from reactive self-assembled monolayers (SAMs). The main focus is in particular on electrochemically induced Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC or “e-click” chemistry) and surface-initiated atom transfer radical polymerization (SI-eATRP), for the two different chemical reactions are both Cu(I)-catalyzed reactions that have the potential to provide refined control of the reaction parameters and surface structures electrochemically. eATRP is also applicable to a wide variety of material surfaces and compatible well with “click” chemistry and photolithography techniques that can be used as a new route to surface functionalization in aqueous solution.

4.2 “Electro-Click” Chemistry

SAMs are playing a key role in many surface modifications methods. As constitute a very important class of two-dimensional (2D) materials which are versatile in tuning surface/interface properties.^{9–11} Recently, a range of new approaches to surface reactions have been applied to precision surface functionalization, with the aim of increasing efficiency and controllability in space and time in a high-throughput manner at surfaces. In particular, CuAAC or “click” chemistry reactions between azides and terminal alkynes have become the most popular “click” reactions in the selective modification of reactive surfaces, and “electro-click” reactions offer new opportunities to expand the function and to tailor the properties of surfaces.^{12–14}

“e-Click” Chemistry Directed by Scanning Electrochemical Microscopy. Scanning electrochemical microscopy (SECM) is a powerful tool to surface modifications and surface patterning, allows both local mediating of surface-initiated systems from reactive moieties, and the analysis of the surface morphology at micrometer scales, as well as the tuning and optimization of experimental parameters *in situ*.¹⁵

Bard and co-workers demonstrated an electrochemically induced “click” chemistry to immobilize fluorescent molecules onto azido moieties coated glass substrate (Figure 4.1).¹⁶ A gold microelectrode directed by SECM was brought close to the azido-terminated monolayer on a glass substrate, the catalytically active Cu^{I} was locally generated via electrochemical reduction of a Cu^{II} salt and was employed to immobilize alkyne-functionalized fluorescent molecules via the “e-click” reaction. This study offered a feasible surface

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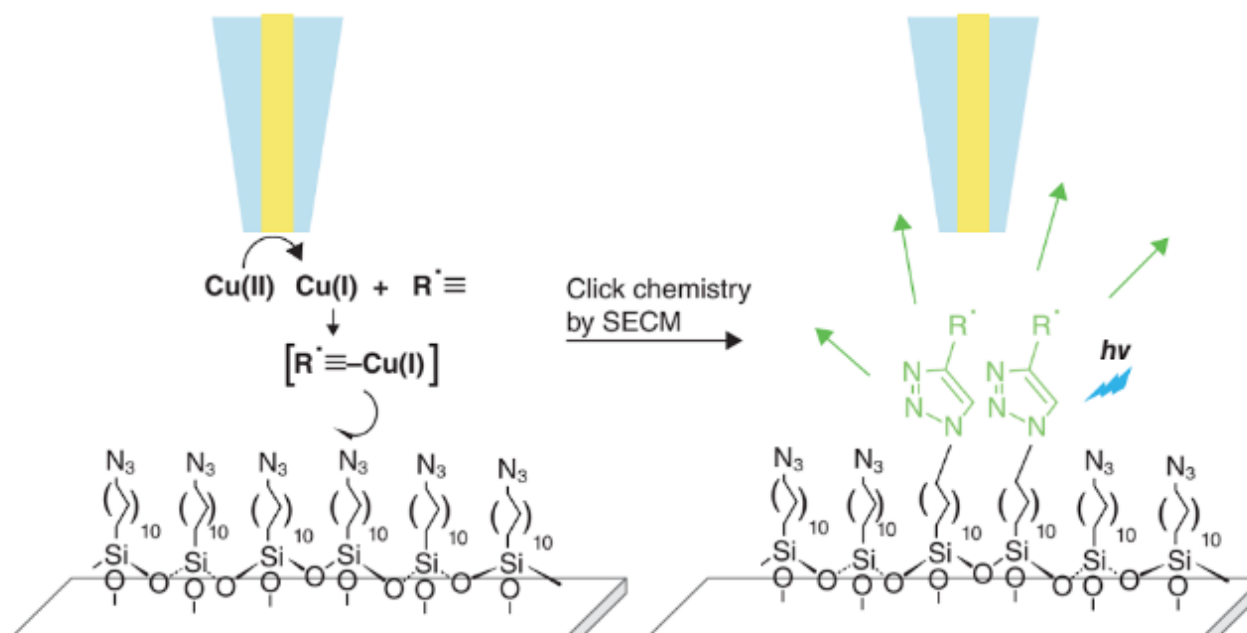


Figure 4.1 Electrochemically reduction of Cu^{II} to Cu^{I} at a gold microelectrode to catalyze the CuAAC reaction via the SECM technique. *Source:* Ku et al. 2008.¹⁶ Reproduced with permission of American Chemical Society.

patterning method via SECM; it was believed that the featured pattern size and shape could be controllable by selecting the tip size and the relative distance between the tip and the substrate.

Stenciled “e-Click” Chemistry. Larsen et al. demonstrated a method for fast production of gradients on an electrically conductive surface (poly-3,4-(1-azidomethylethylene)-dioxothiophene, PEDOT- N_3) using stenciled electro-click chemistry (Figure 4.2). Catalytic Cu^{I} was generated locally through electrochemical reduction of the Cu^{II} complex, and the amount of catalyst generated was determined by the spatial confinement of the active electrodes. Surface gradients were formed by covalently bound alkyne-bearing molecules onto azide-terminated conductive polymers, a stencil on the counter-electrode defined the shape and multiplicity of the gradient on the conducting polymer substrate, the reaction areas and the gradient patterns were controlled by the geometry of the exposed counter electrode (Figures 4.2d and 4.2e). Furthermore, it was proved that the catalyst concentration, geometry of the setup, electrical potential, and reaction time had a strong effect on the gradient formation.

“e-Click” Reaction on a Bipolar Electrode. A bipolar electrode (BPE) is widely used to electro-synthesize novel materials for a wide variety of applications. Electrochemical generation of Cu^{I} species at or near the electrode surface can be utilized immediately to catalyze surface reactions. BPE, with a potential gradient across the surface of the electrode, the Cu^{I} catalyst should be generated at the cathodic side of the BPE with a concentration gradient across the reactive SAMs surface, which would affect the outcome of the surface reaction. Inagi

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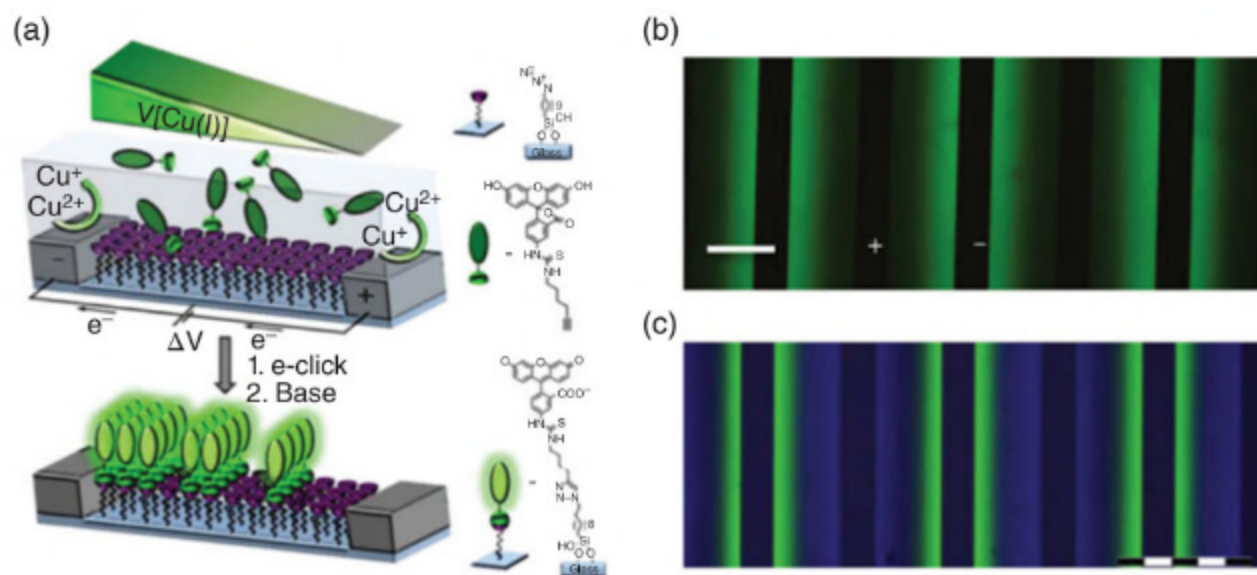


Figure 4.4 Micrometer-scale surface "clicked" gradient formation via a $[Cu(I)]$ solution gradient. (a) Schematic representation of the electrochemical generation of a $[Cu(I)]$ gradient in solution between the electrodes of an interdigitated electrode array via the reduction of $Cu(II)$ to $Cu(I)$ and oxidation of $Cu(I)$ to $Cu(II)$ at the cathode and anode, respectively. (b) Fluorescence microscopy image of the resulting surface gradient. Scale bar, 100 nm. *Source:* Krabbenborg et al. 2013.²³ Reproduced with permission of Nature Publishing Group.

$\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ complexes, which could find potential applications in biochemistry.²² Huskens and co-workers reported an electrochemically induced Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition, Cu(I) catalyst was generated through the electro-reduction of Cu(II) at the cathode, a stable concentration of $[\text{Cu}(\text{II})/\text{Cu}(\text{I})]$ was maintained and a gradient concentration of $[\text{Cu}(\text{I})]$ formed by the application of a potential difference on the electrode (Figure 4.4). Subsequently, a surface-bound fluorescein dye gradient was prepared by means of the “e-click” reaction of a fluorescein-labeled alkyne to an azide-terminated monolayer due to the catalyst concentration gradient. Gradient features such as steepness and surface density could be easily controlled through the electroparameters in a high sensitive and controlled manner.²³ Moreover, bicomponent gradients have been fabricated via a two-step procedure of the “e-click” reaction of two different alkyne-modified dyes and followed by switching of the polarity of the electrodes after the first step. Meanwhile, by means of the transfer patterned “e-click” method, bi-directional surface gradients can be obtained.²⁴

Multiple “Click” Reaction in One Pot. Polymer-based thin films bearing reactive groups offer significant advantages for the intricate design of surface functionalities. Schaaf et al. reported a one-pot strategy to prepare polymer films at the substrate through the Cu^{I} -catalyzed “click” reaction between two polymers bearing either azide or alkyne groups (Figure 4.5). All the reactants present simultaneously in the reaction solution, Cu^{I} was generated electrochemically from Cu^{II} ions present in the solution by the application of a multiple potential cycled between -350 and $+600$ mV (vs. Ag/AgCl) on the polymer surface.

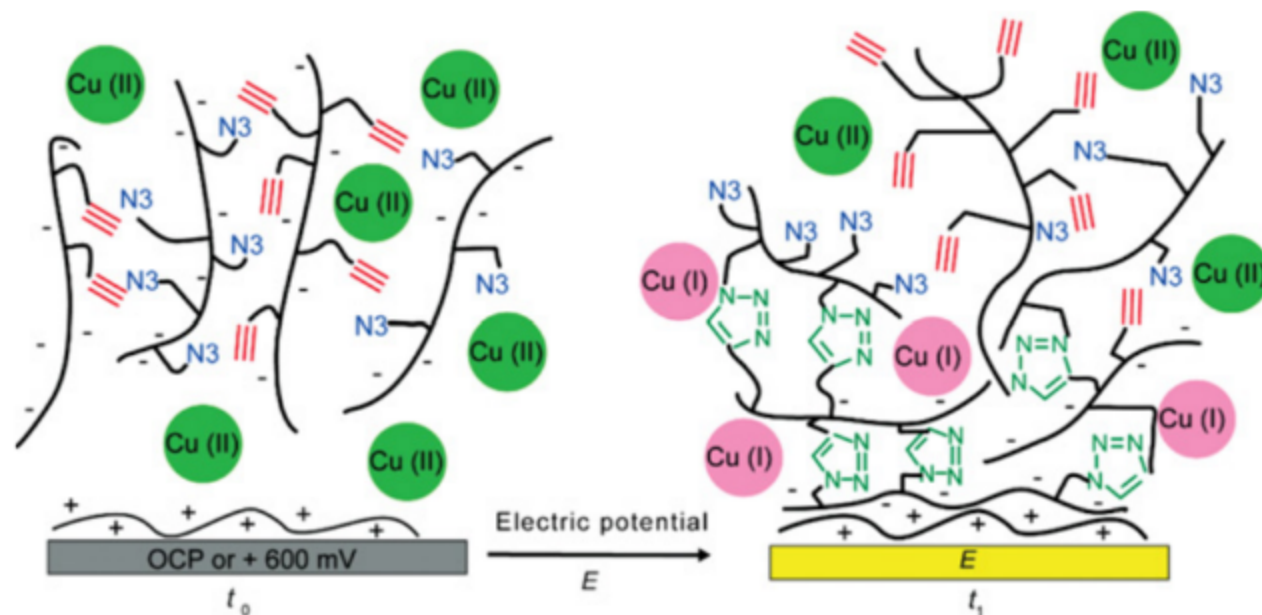


Figure 4.5 One-pot Cu^{I} -driven formation of films using electrochemically controlled “click” reaction. *Source:* Rydzek et al. 2011.²⁵ Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The Cu^{I} catalyst then diffused from the surface toward the solution and started the click reaction. Resulted in the continuous buildup of a film through the formation of triazole molecules between the azide- and alkyne-bearing units at the film/solution interface. Meanwhile, this concept was extended to other systems of the film formation, for example, supramolecular coordination-driven assembly.²⁵

This “electro-click” method makes it possible to impart a variety of functionalities such as hydrophobicity/hydrophilicity or “smart” units onto surface very easily. Multicomponent surfaces can also be generated either through sequential “click” reactions or in a self-sorting manner, and multiple modifications are

available in one pot. Moreover, efficient “click” reactions conducted in aqueous conditions are crucial to the end-functionalization of bioconjugated polymers.

4.3 Electrochemically Induced Surface-Initiated Atom Transfer Radical Polymerization

Polymer brushes, a forest of polymer chains attached on the surface, with the polymer chains stretching away from the surface because of the high grafting density of polymer chains, which can be easily obtained with the advent of controlled/“living” radical polymerization techniques, for example, atom transfer radical polymerization (ATRP),²⁶ reversible addition-fragmentation transfer,²⁷ and nitroxide-mediated polymerization.²⁸ The controlled/“living” characteristics of radical polymerizations allow polymers to be synthesized with predetermined molecular weight, low dispersity, and well-defined architectures, which

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have largely contributed to the development and implementation of polymer synthesis, biotechnology, materials science, and surface science.^{7,29}

ATRP in aqueous media is of particular interest for the preparation of water-soluble polymers in biorelevant research fields, for example, polymer–protein conjugates and other biohybrids, have excellent potential for biomedical appli-

cations. However, ATRP in water provides several intriguing challenges, such as rigorous experimental conditions and a limited control over polymer growth and unavoidable radical termination reactions. Several hypotheses have been advanced to explain the difficulty of gaining a fine-controlled ATRP in aqueous conditions, for example, a high ATRP equilibrium (K_{ATRP}), defined as the ratio of activation (k_{act}) and deactivation (k_{deact}) rate coefficients, will lead to high radical concentration and high probability of termination reactions. Moreover, the halidophilicity of $\text{Cu}^{\text{II}}\text{L}^{2+}$, the disproportionation of $\text{Cu}^{\text{I}}\text{L}^+$, may also contribute to the outcome of the polymerization under aqueous conditions.^{30,31}

Electrochemically Mediated Atom Transfer Radical Polymerization (eATRP). The use of electrochemistry as an external stimulus for surface-initiated polymerization has gained great interest recently, because it is easy to control the polymerization process by adjusting electrochemical parameters such as the applied potential, current, and the total charge passed, furthermore, these various system parameters can be used to modulate and optimize the polymerization process *in situ* as well as the quality of the resultant polymers. Matyjaszewski et al. were the first to report an electrochemically mediated atom transfer radical polymerization (eATRP) in 2011.^{31,32} The applied electrochemical potentials were used to reversibly activate the copper catalyst through the one-electron reduction of an initially added air-stable $\text{Cu}^{\text{II}}/\text{L}$ (Figure 4.6). Polymerization kinetics was modulated in a real-time manner by varying the magnitude of applied potentials, which substantially enhanced the level of control of an ATRP process.

eATRP on Conducting Substrate. A conventional SI-ATRP process always suffers from drawbacks in terms of rigorous synthetic protocols, limited controllability, heavy consumption and waste of unreacted monomers. With the aim of expanding the scope of the SI-ATRP and attaining a good control in

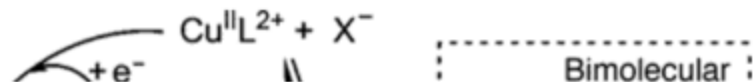
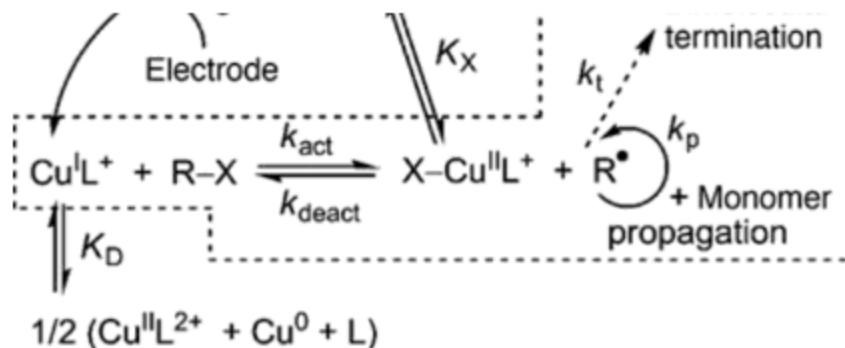


Figure 4.6 Mechanism of conventional (delimited by



the dashed line) and aqueous eATRP. Source: Bortolamei et al. 2011.³¹ Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

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copolymerization of the two different monomers of HEMA and SPMA indicated the controlled/“living” nature of eATRP and the preserved end chain functionality, which would offer the possibility of postmodification of polymer brushes via further orthogonal electro-induced chemical reactions, for example, “e-click” chemistries. The very small amount of oxygen in the polymerization solution was scavenged by the lower oxidation state of $\text{Cu}^{\text{I}}/\text{L}$ catalyst, whereas the $\text{Cu}^{\text{I}}/\text{L}$ could be (re)generated electrochemically after each reduction/oxidation cycle and hence deoxygenation of the polymerization solution seems to be no longer needed, which is very attractive in practical applications.

Since electrochemistry permits a dynamic equilibrium between the two oxidation states of $\text{Cu}^{\text{I}}/\text{L}$ and $\text{Cu}^{\text{II}}/\text{L}$, the monomer/catalyst solution can be reused many times (Figure 4.7d).

Surface Patterning through eATRP. Surface patterning is always the method of choice for precise functionalization of surfaces at the micro- or nanoscale with strict arrangement and control of surface functionalities. The so-called “top-down” methods, for example, microcontact printing (μCP), scanning probes, UV, and e-beam lithographies, are commonly employed to generate patterns on surfaces.^{4,34} μCP has been widely used as a simple and flexible method to replicate patterns from a microstructured poly(dimethylsiloxane) (PDMS) stamp, reactive molecules of the “ink” (e.g., thiols) on the PDMS patterns is then transferred to the surface of the substrate (e.g., gold) by conformal contact. Different features of patterned surfaces can be achieved by simply varying the pattern profiles on the PDMS stamp, and more complex patterns could be obtained by multistep printing.³⁵ For example, by a two-step printing of a thiol initiator on gold and followed by SI-ATRP, binary polymer brushes (i.e., surfaces containing two different polymers) were prepared (Figure 4.7c).

eATRP on Other Substrates. This electrochemical method for SI-ATRP is highly versatile and compatible with both conducting and nonconducting substrates. As shown in Figure 4.7a, Cu^{I} was generated *in situ* from the initiator layer and thus the working electrode should have sufficient conductivity.³³ However, a relative high concentration of $[\text{Cu}^{\text{I}}/\text{L}]/[\text{Cu}^{\text{II}}/\text{L}]$ around the initiator layer accelerated the polymerization rate with heavy termination reactions, and further linear growth of the polymer brush was quite limited. In particular, this effect will be exacerbated by the fact that when the activation rate coefficient (k_{act}) in aqueous media is very high.^{30,33,36}

In order to explore the limits of control of aqueous ATRP and define a set of guidelines for conducting a successful ATRP in water, we reported eATRP to control the polymerization in a confined microscale gap through catalyst diffusion, Cu^{I} activators generated at the platinum working electrode and diffused to the ATRP initiator modified substrate, which was positioned close to the working electrode (Figure 4.8). The concentration ratio of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ was

adjusted and maintained throughout the polymerization by simply adjusting applied potentials and arrangements of the initiator-covered substrate, and the

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under a cathodic current and initiated the polymerization, and the oxidation of the $\text{Cu}^{\text{I}}/\text{L}$ was achieved via an anodic current yielding inactive $\text{Cu}^{\text{II}}/\text{L}$ species for the cessation of polymerization; the SI-ATRP can be started, stopped, and restarted in a highly responsive manner by the application of multistep intermittent potentials (Figure 4.9b). The controllability over the polymer growth was dramatically enhanced.

Gradients Created by Cu(I) Catalyst Diffusion. Gradient polymer brushes, with gradual variation of physicochemical properties along the surface, are in great demand for biochemical applications, the exploration of new classes of polymer brushes is of importance both in the fields of surface science and materials chemistry. They are especially promising in controlling of dynamic phenomena, for example, directional motion of molecules, droplets, and cells. A higher concentration ratio of $[\text{Cu}^{\text{I}}/\text{L}]/[\text{Cu}^{\text{II}}/\text{L}]$ generated at the initiator layer resulted in a fast polymerization rate, whereas a lower concentration ratio of $[\text{Cu}^{\text{I}}/\text{L}]/[\text{Cu}^{\text{II}}/\text{L}]$ led to a slow polymerization rate. If an ATRP initiator coated

substrate was placed at a tilt angle with respect to the working electrode (Figure 4.8), the $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ concentration ratio would vary along the initiator surface; this concentration difference would result in different polymerization rates along the surface and lead to a three-dimensional (3D) gradient polymer brush with a gradual in-plane variation in height. The shape, steepness of the gradient could be easily controlled by the topology feature of the initiator, the arrangement of the working electrode in combination with the variation of the applied potentials (Figure 4.10). This approach using the catalyst concentration variation at a surface for gradient buildup is quite promising to create novel functional surfaces.

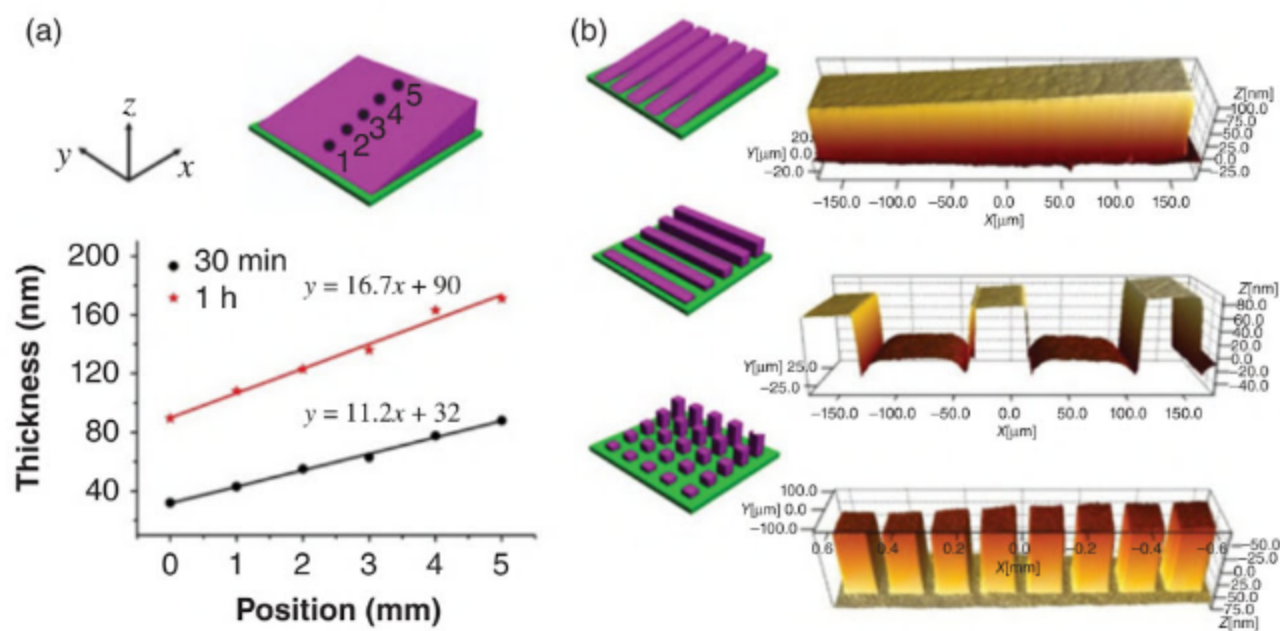


Figure 4.10 Gradient polymer brushes formation on homogeneous (a) and patterned (b) surfaces through Cu(I) catalyst diffusion. *Source:* Li et al. 2013.³⁷ Reproduced with permission of American Chemical Society.

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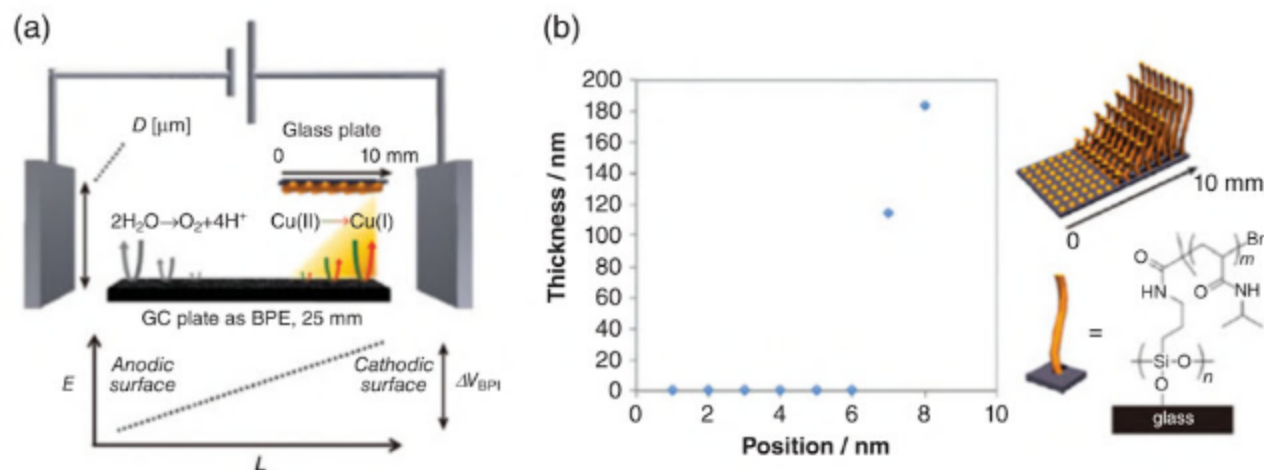


Figure 4.11 (a) Schematic view of fabrication of gradient and patterned polymer brushes by bipolar electrolysis assisted eATRP. (b) Film thickness profile at various positions along the poly(NIPAM)-tethered substrate. *Source:* Shida et al. 2015.³⁸ Reproduced with permission of John Wiley and Sons.

Patterning and Gradient Formation by Bipolar Electrolysis Assisted eATRP. Inagi et al. reported a bipolar electrochemical method for the fabrication of both gradient and patterned polymer brushes via eATRP (Figure 4.11). A potential gradient generated on a BPE allowed the formation of a concentration gradient of a $[\text{Cu}^{\text{I}}]$ catalyst at the BPE and produced a reaction field over which the concentration ratio of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ varied gradually and hence offered a means

to control the polymerization rate during the eATRP process on an initiator-modified surface, resulting in 3D gradient growth of polymer brushes. *N*-Isopropylacrylamide (NIPAM) was successfully polymerized from an initiator-modified substrate surface set close to the BPE.³⁸ The chain end functionality was preserved during the eATRP process and could be reinitiated after the first step of polymerization; the height of the polymer brush increased in a linear manner with increasing the polymerization time. This new method can be used to polymerize a wide range of monomers to fabricate complex gradient with controlled thickness, steepness, and modified area by varying the electrolytic conditions.

Moreover, patterned polymer brushes were prepared by using an electrolytic system with an insulating cylinder and BPE that was mounted below the cylinder, generating a circular potential distribution and a circular cathodic surface under the cylinder, the Cu^I catalyst generated electrochemically around the cathodic area of the BPE mesh (Pt) and diffused to the initiator surface and initiated the polymerization, resulted in the site-selective formation of a circular pattern of polymer brush on the initiator surface.

Overall, electrochemically induced ATRP for surface modifications with polymers has a number of attractive features, including improved livingness and controllability over the whole polymerization process, less catalyst loading,

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tion either in potentiostatic or galvanostatic mode.^{37,39,40} It would be applied to any copper-catalyzed reactions and provided a robust and effective way for accurately determining, for example, redox behavior of catalyst and reaction kinetics.^{41,42}

4.4 Possible Combination of eATRP and “e-Click” Chemistry on Surface

This new concept of electro-induced surface-initiated film buildup and the generality of the electro-induced surface reactions make it applicable to any substrate presenting reactive moieties. The Cu^I-catalyzed azide–alkyne cycloaddition is utilized particularly compatible with ATRP, due to the ease of incorporating clickable functionality into polymers either through the use of functional monomers or postpolymerization reactions; the halogen groups of polymer chain end can be substituted by azido moieties for the “click” reaction. Moreover, ATRP and azide-alkyne cycloaddition use the same catalyst in each process and allow for the one-pot synthesis, and the choice of SI-ATRP together with “click” chemistry has allowed various functional surfaces for novel applications. For example, a wide range of azide-containing biomolecules such as biotin, carbohydrates, and proteins can be immobilized at polymeric surfaces without losing their biological functionalities.^{43,44}

The “click” chemistry can be employed as a potential candidate of coupling reactions between polymeric surfaces and incoming functional molecules of interest. Vermonden and co-workers reported the synthesis of polymers through ATRP and the subsequent azide substitution and ‘click’ chemistry, three reactions using only one catalyst in one pot.⁴⁵ The reaction was catalyzed by the ATRP catalyst (Cu) in aqueous solution at ambient condition and followed by a “click” reaction using the same catalyst after the substitution of the living chain end of the polymer chains. This electrochemical means for surface modifications is highly versatile, compatible with many functional groups, solvents, and substrates. The application of “click” chemistry together with ATRP

will contribute to rapid development in the available range of polymeric architectures, functional materials, and bioconjugates.⁴⁶

4.5 Surface Functionality

Control over the surface functionality and interaction with the local environment are key to the performance of materials used in practical applications. The recently developed electrochemically mediated reactions, in particular

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4.6 Summary | 137

“e-click” and eATRP reactions, have contributed greatly to the control over surface profiles in terms of length-scale, structure, and functionality. SI-ATRP has been successfully used to synthesize polymers with various functionalities that respond to external stimuli such as temperature, light, pH, or ionic strength, which could find application in sensor and “smart surface.” A polymeric thin film bearing reactive groups offers the possibility to modify such film via further chemical reactions. ATRP is tolerant to many functional groups, and these functional groups might be capable of robust orthogonal “click” chemistry, which are highly efficient and selective, and can be incorporated into hybrids with novel properties.

Multiple functional groups can be incorporated into polymers by using

either direct polymerization of functional monomers or postmodification reactions. A few nanometers of polymers grown from nanoparticles or flat surfaces, dramatically change surface properties such as dispersibility and stabilization,⁴⁷ wettability,⁴⁸ lubricity,⁴⁹ antifouling and antimicrobial properties,^{50,51} membrane science,⁵² actuation,⁵³ and biorelated applications.^{11,54} Novel organic/inorganic hybrids which combine the best of each constituent synergistically, indicating many new applications. Biomaterials and bioconjugates composing hydrophilic segments and especially stimuli-responsive polymers have largely contributed to the development in the fields of biotechnology, drug and gene delivery, and tissue engineering.^{44,55}

Nowadays, chemists and engineers have abilities to design and fabricate functional surfaces in terms of both structure and morphology by taking advantages of functional materials, and the chemical complexity on 2D and 3D surfaces with well-defined spatial control has significantly increased. However, the complexity of these surfaces is typically limited to one or two different functionalities, and the challenge of controlling over the spatial distribution of the physical and chemical properties still remains and hence new methodologies should be developed to fabricate more complex structures and surfaces with high fidelity and functionalities.

4.6 Summary

In this chapter, a number of recent advances in the field of electrochemically induced copper-catalyzed surface reactions have been described. With the ability to polymerize these materials by means of either “e-click,” electrochemically mediated surface-initiated polymerization (eSIP) process, or the possible combination of the two techniques, polymers are formed with controlled size, composition, and architecture. Such exciting and varied possibilities are set to find applications in many research fields, such as organic electronics, biotechnology, and tissue engineering. Nevertheless, detailed mechanistic understand-

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