

# Electro-Click Modification of Conducting Polymer Surface Using Cu(I) Species Generated on a Bipolar Electrode in a Gradient Manner

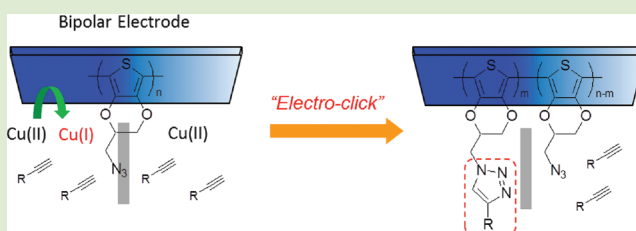
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## S Supporting Information

**ABSTRACT:** The electro-click reaction of azide-functionalized poly(3,4-ethylenedioxythiophene) (PEDOT-N<sub>3</sub>) and a terminal alkyne was investigated using electrogenerated Cu(I) species on a bipolar electrode in a gradient manner. The introduction of a perfluoroalkyl group derived from the alkyne moiety onto the PEDOT surface only at the cathodic part of the bipolar electrode was successfully characterized by X-ray analyses and the surface properties of the modified film were studied. The spectroscopic analysis of the rhodamine-functionalized PEDOT prepared similarly in a gradient manner was also performed with a UV-vis spectrophotometer.



Recent progress in surface modification of inorganic and organic substrates is quite remarkable for facile and versatile control of functionalities of the surfaces. Among them, an electrochemical approach for surface modification has been developed, in particular, for modification of the surface of electrode itself.<sup>1,2</sup> The electrochemical generation of active and short-lived species at or near the electrode surface can be utilized immediately for the surface modification. For example, the electrogenerated phenyl radical by one-electron reduction of the corresponding diazonium salt undergoes covalent bond formation to electrode materials such as graphite and metals.<sup>3–5</sup> On the other hand, the “electro-click” reaction, namely, the azide–alkyne cycloaddition mediated by electrogenerated Cu(I) (Scheme S1, Supporting Information), has been reported recently as a facile and efficient method to create a functional surface.<sup>6–10</sup> Larsen and his co-workers successfully demonstrated that the Cu(I) species was generated by the reduction of Cu(II) species derived from electrolytes (CuSO<sub>4</sub>) only at the cathode surface and could be used for electro-click reaction of the azide-functionalized polymer film and dissolved alkynes on the cathode, whereas a spatially apart polymer film on the anode remained intact.<sup>11</sup>

Among the issues on surface modification, the fabrication of a functional gradient surface has become an important challenge.<sup>12,13</sup> However, the formation of surface gradient is not straightforward. Björefors and co-workers reported pioneering research on the molecular gradient on the electrode surface. A stable and distinct potential slope on a bipolar electrode,<sup>14–20</sup> that is, an electrode that simultaneously acts as both an anode and a cathode, was powerful means for the gradual cathodic desorption of alkanethiols of self-assembled monolayers on gold substrate.<sup>21,22</sup> Recently, we reported electrochemical doping followed by the chemical reaction of conducting

polymer films on a bipolar electrode.<sup>23–25</sup> Both approaches involved the introduction of dopants (counteranions compensating for cationic charges of the polymers) and chlorine atom attached through covalent bonds, respectively, at the anodic surface of the bipolar electrode and resulted in the formation of the composition gradient across the polymer films. It is worth noting that these electrode-surface modifications driven by the electrochemical doping and reaction can reflect directly on the potential distribution of the bipolar electrode.

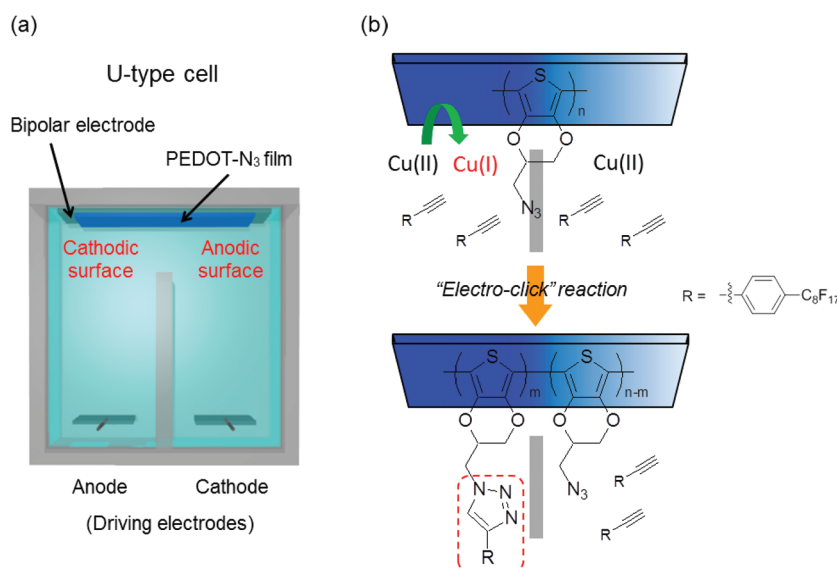
In this Letter, we investigated the gradient modification of an azide-functionalized conducting polymer film via an electro-click reaction in the presence of a terminal alkyne using electrogenerated Cu(I) species on a bipolar electrode. The catalyst Cu(I) should be generated at the cathodic side of the bipolar electrode with a concentration gradient, which would affect the density of the modifier introduced.

At first, the polymerization of 3,4-(1-azidomethylethylenedioxy)thiophene (EDOT-N<sub>3</sub>) was carried out by a potential sweep method to provide its polymeric film (PEDOT-N<sub>3</sub>) on an indium tin oxide (ITO) electrode (5 mm × 20 mm). After dedoping, the neutral polymer was obtained as a blue-colored film. The polymer film fixed on the ITO substrate was subjected into the U-type electrolytic cell as a bipolar electrode (Figure 1a). The U-type cell was equipped with a pair of driving anodes and cathodes (10 mm × 10 mm) and was filled with a mixed solution of water/*t*-BuOH (*v/v* = 2:1) containing copper sulfate (10 mM) and alkyne with a perfluoroalkyl group (10 mM). The copper sulfate plays a role as the supporting electrolyte and source of Cu(I) ion catalyzing

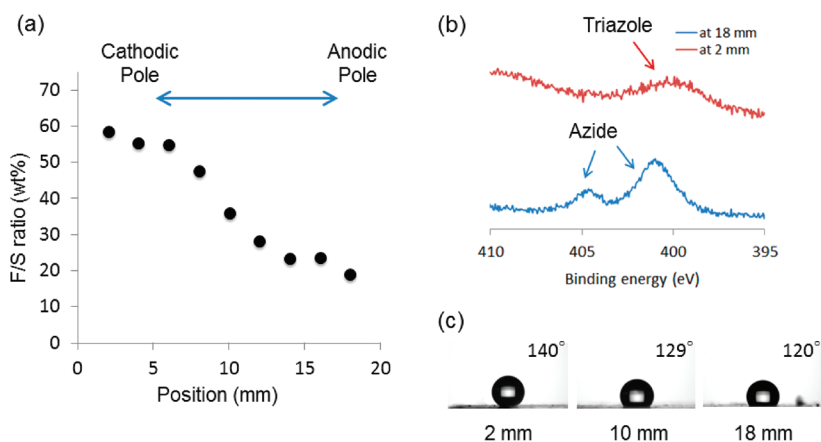
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**Figure 1.** Schematic illustrations of (a) the U-type cell used for bipolar electrolysis and (b) the electro-click reaction of PEDOT-N<sub>3</sub> film and terminal alkyne using cathodically generated Cu(I) species.



**Figure 2.** (a) Weight ratio ( $F/S$ ) of the modified film at each position of the bipolar electrode determined by EDX analysis. (b) XPS analysis on N1s of the modified polymer film, measured at 2 and 18 mm from cathodic edge. (c) Contact angle of water droplet (1  $\mu\text{L}$ ) at different positions.

azide–alkyne cycloaddition (Figure 1b). On the bipolar electrode in this U-type cell, one side facing the cathode acts as an anodic surface and the other side as a cathodic surface. In addition, there appears a potential gradient across the surface of the bipolar electrode.

When a constant current (0.50 mA) was passed between the driving anode and cathode, the color change of PEDOT-N<sub>3</sub> from deep blue to transparent blue at around the anodic surface was observed due to the anodic doping of the polymer. On the bipolar electrode, the electrons released to the anodic surface from PEDOT-N<sub>3</sub> must be consumed at the cathodic surface; in other words, anodic and cathodic reactions should take place simultaneously. The most likely cathodic reaction in this system is the reduction of the Cu(II) ion to generate the Cu(I) ion. After 30 mC of charge was passed between the driving electrodes, the polymer film was further dedoped at  $-0.8$  V (vs SCE) in a solution without copper species and alkynes to recover the whole film to its neutral state.

To survey the introduction of a perfluoroalkyl group, energy dispersive X-ray (EDX) analysis was employed. The line analysis of fluorine and sulfur at the different positions was performed for the modified polymer film. Figure 2a shows the

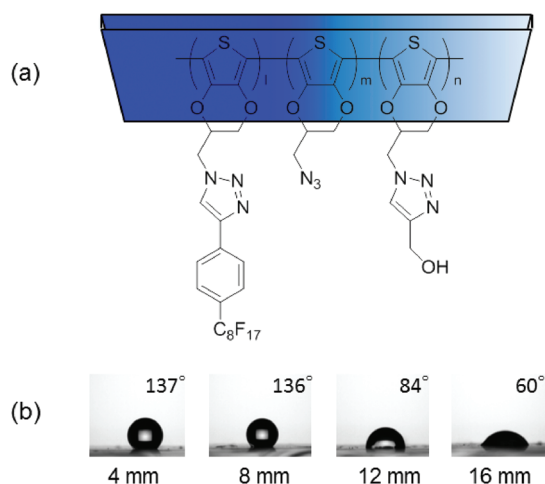
plot of weight ratio ( $F/S$ ) measured at each position. The higher fluorine content was detected at the cathodic part (0–10 mm from the cathodic edge) compared to the other pole, indicating the effective introduction of the perfluoroalkyl group via an electro-click reaction on the bipolar electrode. Thus the electrogenerated Cu(I)-mediated click reaction reflected well the potential profile on the bipolar electrode. The blank test of the PEDOT-N<sub>3</sub> film by EDX did not exhibit a little  $F/S$  ratio (15–25%) derived from the contaminating PF<sub>6</sub> anion even though the dedoping treatment was conducted (Figure S1, Supporting Information). The  $F/S$  ratio observed at the anodic part in Figure 2a was not derived from the perfluoroalkyl group but from the PF<sub>6</sub> anion still contained in the film. In this cell system, the Cu(I) species once generated can diffuse to the anodic pole but would be reoxidized to Cu(II), an inactive form for the click reaction.

To investigate the surface state of the modified PEDOT film, X-ray photoelectron spectroscopy (XPS) analysis was performed at different positions. Figure 2b shows the XPS profiles measured at the cathodic side and anodic side, respectively. At the anodic area (18 mm from the cathodic edge) characteristic N1s peaks were observed at 401 and 405 eV, which were

assignable to the nitrogen of azide group.<sup>26</sup> On the opposite side (2 mm from cathodic edge), only a single peak appeared at 400 eV derived from the nitrogen of triazole ring.<sup>26</sup> The formation of triazole ring is the direct evidence of the proceeding of the electro-click reaction selectively at the cathodic side of the bipolar electrode.

Surface modification with perfluoroalkyl groups is well-known to provide a highly hydrophobic surface due to its low surface free energy.<sup>27,28</sup> Such a postmodification of material surface is of great importance. Then the surface property of the gradually perfluoroalkylated PEDOT was investigated by static contact angle measurement of the water droplet on the film. Figure 2c shows the photograph of the water droplet (1  $\mu\text{L}$ ) mounted on each position of the modified film. The contact angle at the fluorinated surface was 140°, while that at the pristine surface was 120°. The gradual decrease of the contact angle from the cathodic surface to anodic surface corresponded well to the modification level by an electro-click reaction on the bipolar electrode.

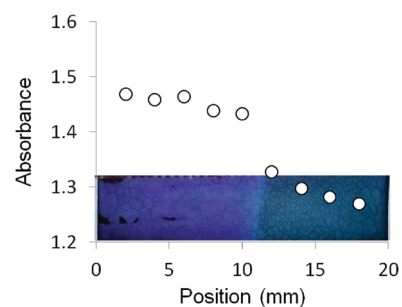
Next, the sequential surface modification of PEDOT-N<sub>3</sub> was investigated. The hydrophobic gradient surface prepared above was further electro-clicked in the presence of propargyl alcohol in the U-type cell with the inversed polarity of the feeder electrodes. The measurement of contact angle on the polymer film indicated that the alcohol-introduced surface turned to be hydrophilic (Figure 3). This sequential electro-click method makes it possible to impart a variety of functionalities onto a polymer surface very easily.



**Figure 3.** (a) Schematic illustration of sequentially modified PEDOT film. (b) The results of contact angle measurement using a water droplet (0.1  $\mu\text{L}$ ) on the film. The positions shown under the photographs represent the distance from the cathodic edge.

Finally we demonstrated another example of electro-click reaction on the bipolar electrode. A rhodamine-based alkyne was used as a visible-indicator. After the electro-click reaction on the bipolar electrode, the polymer film was uniformly oxidized to the doped state to reduce background absorption of PEDOT in the visible range. Accordingly, the cathodic part turned purple, detectable to the naked eye. To better understand this color change, the spectroscopic study was carried out for the film. The UV-vis absorptions of the film were measured at different positions from the cathodic edge using a slit (Figure S2, Supporting Information). Figure 4 shows the plot of absorbance at 550 nm in the course of

position from the cathodic edge. The profile was in good agreement with the foregoing results of the X-ray analyses.



**Figure 4.** Photograph of PEDOT-N<sub>3</sub> film gradually modified with rhodamine and the absorption profile (550 nm) across the film.

In conclusion, we have demonstrated the electrochemical surface modification of a PEDOT-based conducting polymer in a gradient manner using an electro-click reaction on a bipolar electrode. A variety of gradient functionalities such as gradient hydrophobicity/hydrophilicity and a visible marker could be introduced onto the PEDOT film. The electrogenerated catalyst with its concentration distribution near the surface of bipolar electrode involved the click reaction with reflecting the density profile. This approach using the concentration gradient of reagents for surface modifications is quite promising to create versatile functionality-gradient surfaces. A further investigation to expand the scope of this methodology is now under way.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and additional supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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