

## Bipolar Electrochemistry for Material Synthesis in Synergy with Electrophoresis

(<sup>1</sup>*School of Materials and Chemical Technology, Tokyo Institute of Technology*, <sup>2</sup>*JST PRESTO*) ○Shinsuke Inagi<sup>1,2</sup>

**Keywords:** Bipolar Electrochemistry; Electropolymerization; Electrophoresis; Templated Electrolysis; Conducting Polymer

Bipolar electrochemistry, which refers to an electrochemical system at a wireless electrode (bipolar electrode, BPE) driven under an applied electric field, has been recognized as not only a simple subset of conventional electrosynthetic systems but a reaction system with a highly unique nature.<sup>1-3</sup> One notable feature is the presence of the electrophoretic effect due to the low electrolyte concentration. The electrophoresis enhances the mass transfer of ionic species in a specific direction, thus enabling the efficient construction of anisotropic materials.<sup>4</sup> For example, in the AC-bipolar electropolymerization of 3,4-ethylenedioxythiophene monomer, the corresponding conducting polymer microfibers were obtained at the terminals of BPEs, where the generated cationic oligomers/polymers migrated in the direction of the electric field, as demonstrated in our previous studies.<sup>5-7</sup> In this presentation, highly efficient templated electropolymerization of ionic monomers to give one-dimensional (1D) nanostructures is described.

We recently reported that electrophoresis is a promising tool for effective migration of ionic monomers into a porous template fixed on an electrode in the bipolar electrochemical setup.<sup>8</sup> Low concentration of supporting electrolytes is a key condition to generate an electric field, that drives BPEs and induces electrophoretic effect as well. In the electrochemical setup shown in Figure 1a,b, an anodic aluminum oxide (AAO) membrane-modified ITO was used as a BPE anode and a bare ITO was used as a BPE cathode, both of which are connected through an ammeter. This split-BPE was immersed into an electrolytic solution composed of boron trifluoride diethyl ether complex (BF<sub>3</sub>-OEt) and potassium 3-thiophenetrifluoroborate as a monomer. Application of a certain voltage between feeder electrodes generated an electric field in the solution to drive the split-BPE for electropolymerization of the thiophene monomer on the AAO-modified BPE anode. At the same time, the negatively charged monomer migrated efficiently into the pores of the AAO by the electrophoretic effect. Consequently, highly dense and robust nanowires of the polythiophene derivative was obtained (Figure 1c) compared to those prepared by the conventional electrode system. In a similar way, we also conducted the cathodic electropolymerization of a ruthenium complex bearing vinyl groups as a positively charged monomer in the electrochemical setup with the opposite polarity (Figure 1d). Efficient electroplating of cobalt and platinum was demonstrated in the similar electrochemical cell to fabricate the corresponding robust metal nanorods.<sup>9</sup>

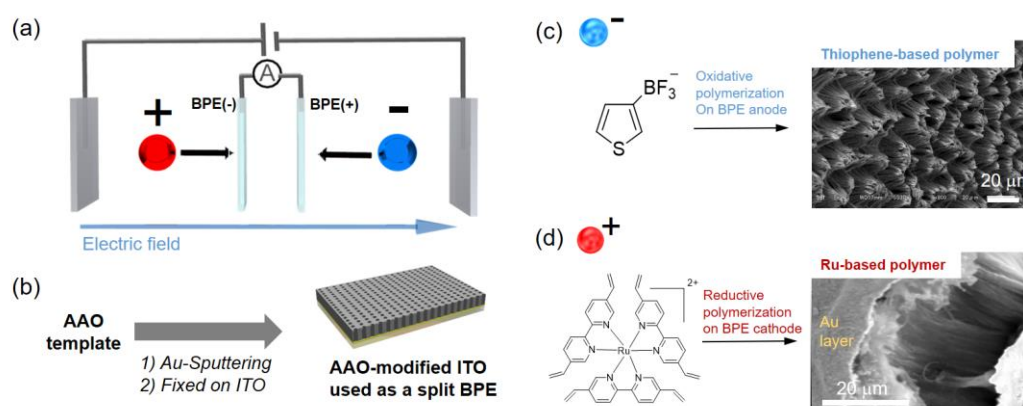


Figure 1. Electrophoresis-assisted formation of 1D materials by DC-bipolar electrolysis using AAO templates: (a) conceptual illustration; (b) preparation of an AAO-modified ITO electrode, which was used as a BPE in the split-BPE configuration; (c) oxidative polymerization of a thiophene monomer; (d) reductive polymerization of a Ru-containing vinyl monomer.

- 1) S. E. Fosdick, K. N. Knust, K. Scida, R. M. Crooks, *Angew. Chem. Int. Ed.* **2013**, 52, 10438.
- 2) G. Loget, D. Zigah, L. Bouffier, N. Sojic, A. Kuhn, *Acc. Chem. Res.* **2013**, 46, 2513.
- 3) N. Shida, Y. Zhou and S. Inagi, *Acc. Chem. Res.* **2019**, 52, 2598.
- 4) N. Shida, S. Inagi, *Chem. Commun.* **2020**, 56, 14327.
- 5) Y. Koizumi, N. Shida, M. Ohira, H. Nishiyama, I. Tomita, S. Inagi, *Nat. Commun.* **2016**, 7, 10404.
- 6) T. Watanabe, M. Ohira, Y. Koizumi, H. Nishiyama, I. Tomita, S. Inagi, *ACS Macro Lett.* **2018**, 7, 551.
- 7) Y. Zhou, N. Shida, Y. Koizumi, T. Watanabe, H. Nishiyama, I. Tomita, S. Inagi, *J. Mater. Chem. C* **2019**, 7, 14745.
- 8) Y. Zhou, N. Shida, Y. Koizumi, K. Endo, I. Tomita, S. Inagi, *Macromolecules* **2020**, 53, 8123.
- 9) Y. Koizumi, H. Nishiyama, I. Tomita, S. Inagi, *Chem. Commun.* **2018**, 54, 10475.