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Ultralight Floating Electrochromic Devices with Metallo-Supramolecular Polymer

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ABSTRACT

Ru(II)-based metallo-supramolecular polymer (polyRu) was synthesized by the complexation of Ru(II) ion and bis(terpyridyl)benzene. An electrochromic device (ECD) with polyRu worked as supercapattery by the suitable combination with the counter material. Based on the supercapattery property, ultralight floating ECDs were fabricated with polyRu coated on a flexible ITO PET film.

1 Introduction

Metallo-supramolecular polymers (MSPs) are a new category of electrochromic (EC) materials [1,2]. MSPs are composed of metal ions and organic ligands (Fig. 1) and exhibit appearance/disappearance of the metal-to-ligand charge transfer (MLCT) absorption, triggered by the electrochemical redox of the metal ions. High solubility of MSPs in methanol or water enables the spray or spin coating process on an ITO substrate to prepare a uniform thin polymer layer. Unlike inorganic EC materials such as Tungsten oxide, which need vapor deposition or spattering to make a layer, therefore, MSPs can be coated even on a flexible PET substrate, which is not so stable to heat. Herein we present ultralight floating EC devices (ECDs) with MSPs.

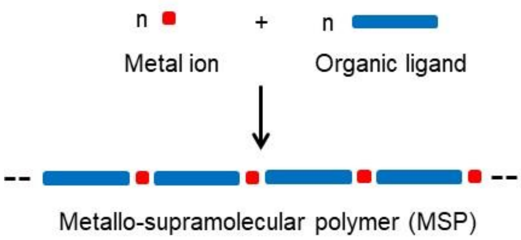

Fig. 1. A general structure of MSP.

2 Experiment

Ru(II)-based MSP (polyRu) was synthesized by 1:1 complexation of $RuCl_2(DMSO)_4$ and bis(terpyridyl)benzene by utilizing a microwave heating method (Fig. 2). The complexation was confirmed by the color change of the solution to orange.

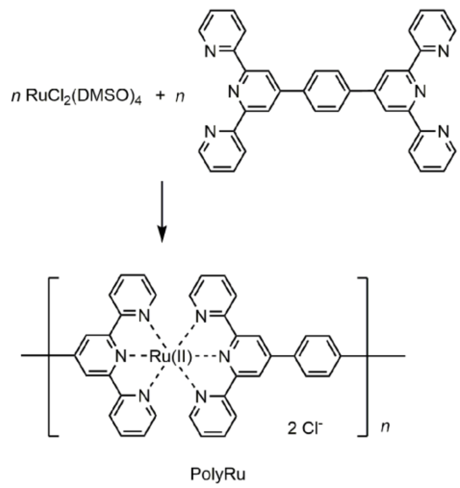

Fig. 2. Synthesis of polyRu.

3 Results and Discussion

3.1 EC Properties of polyRu

In the UV-vis. spectrum of a methanol solution of polyRu, the MLCT absorption of the complex moieties was observed at 508 nm. The orange color is the complementary color of the MLCT absorption.

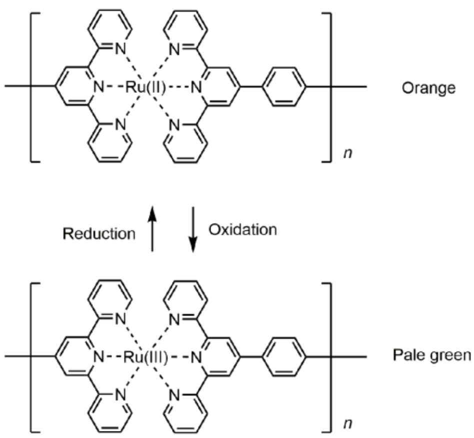

Fig. 3. EC changes in polyRu.

A polyRu film on an ITO glass showed reversible EC changes by applying 1.8 V and 0 V vs. Ag/Ag^{+}, according to the electrochemical redox between Ru(II) and Ru(III) (Fig. 3). It was confirmed by the UV-vis spectrum that the MLCT absorption disappeared at the Ru(III) state.

3.2 Supercapattery Properties

The EC changes are regarded as the charge/discharge process in battery. A study of the energy storage performances of a polyRu films in a nonaqueous electrolyte system revealed volumetric capacitances of 98.5 ± 7 F/cm^3 for polyRu at a current density of 2 A/cm^3. An ECD was fabricated by the combination with Prussian blue as the counter material. Interestingly, it was revealed that the ECD worked as supercapattery bearing both high energy density and high power density [3-5].

3.3 Fabrication of Floating ECDs

The supercapattery property of the ECD means that the charged state of the device can be converted to the discharged state by the simple short circuit operation between the two electrodes. Since the charged and discharged states have different colors, the short circuit phenomenon can be observed as the color change. In other word, the EC change does not need an external battery.

In addition, the use of polyRu as an EC material enabled to fabricate an ECD with PET substrates (Fig. 4).

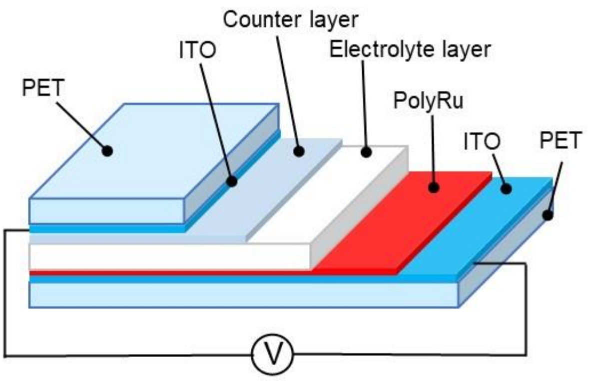

Fig. 4. An ECD with polyRu and ITO-PET.

By learning aerodynamics of leaves or seeds in nature, an ECD rotatable by updraft was designed (Fig. 5). Straight updraft was generated with a circulator. The fabricated ECD was extremely light, because heavy glasses were not used, and could be constantly rotated under the updraft. The time to change from the charged state (pale green) to the discharged state (orange) was successfully controlled by adjusting the resistance in the short circuit.

Finally, the color change from pale green to orange in the ECD was observed while the device was floating and rotating.

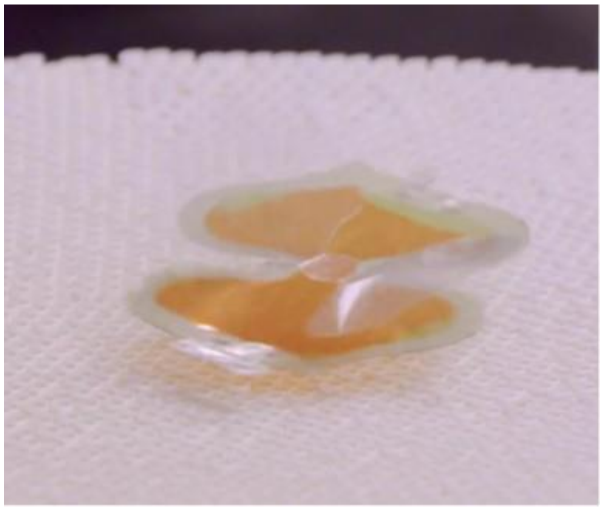

Fig. 5. An ultralight floating ECD with polyRu.

4 Conclusions

Ultralight floating ECDs without an external battery were successfully fabricated by utilizing the supercapattery property of ECDs with polyRu.

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