Nature-Inspired Flexible Electrochromic Devices

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ABSTRACT

Nature-inspired flexible electrochromic devices have been fabricated using electrochromic metallo-supramolecular polymer for the first time in the world. The use of Ru(II)-based polymer, which changes the color between red and green, and the multi-layer coating method have enabled to reproduce the nature of a real fallen leaf by the devices.

1 INTRODUCTION

Electrochromic (EC) display devices have received attention to an application of sunlight-adjusting window in office and vehicles. Actually, EC devices have been already installed on the windows of Boeing 787. Basic requirements for EC windows are flatness and squareness of the device and homogeneous color change during electrochromic switching. A vapor deposition of inorganic EC materials such as Tungsten oxide on a flat ITO glass substrate will be one of the promising ways to satisfy the requirements.

In 2004 we found electrochromism of Fe(II)-based metallo-supramolecular polymer (polyFe) by chance (Fig. 1) [1-4] then have investigated the EC properties of metallo-supramolecular polymers and their EC devices [5-17]. More recently, we have developed two-dimensional (2D) EC nanosheets of metallo-supramolecular polymers [18]. The color change in the polymers is triggered by electrochemical redox of the metal ions, because the metal-to-ligand charge transfer (MLCT) absorption of the polymer disappears/reappears by the redox.

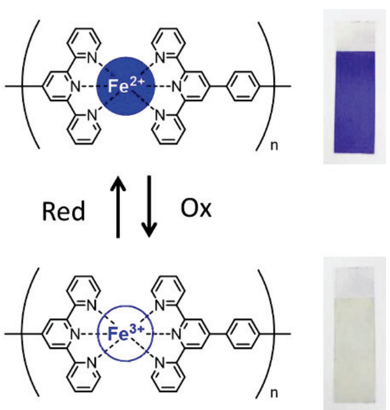

Fig. 1 Electrochromic behavior of polyFe

The "novel" electrochromic materials have unique properties such as wide color variation and high durability for the repeated color changes. In addition, representative features for the device applications are amorphous nature of the polymer and instant preparation of the polymer film by spray-coating of a methanol solution of the polymers. These properties will enable fabrication of a new-type EC devices, that is, non-flat and free-shaped EC devices with heterogeneous color changes.

We focus on "an artistic aspect" of EC display devices and report nature-inspired flexible EC devices using metallo-supramolecular polymers in this presentation.

2 EXPERIMENT

Fig. 2 shows a structure of the nature-inspired flexible EC devices. We tried to reproduce a fallen leaf by an EC system for the first time in the world. In nature, color of leaves is not uniform and the color change in fall is not also even. In order to realize the natural color change in a fallen leaf, we modified the device fabrication process.

We chose a plastic ITO sheet as flexible substrate of the EC device and processed the sheet to a leaf shape by laser beam machining. We selected Ru(II)-based metallo-supramolecular polymer (polyRu) as the electrochromic material, because the red and pale green colors in the reduced and oxidized states of the polymer could be suitable to reproduce the colors of fallen leaves in the device. The polymer was synthesized by the 1:1 complexation of $RuCl_2$ and bisterpyridine according to the literature [4].

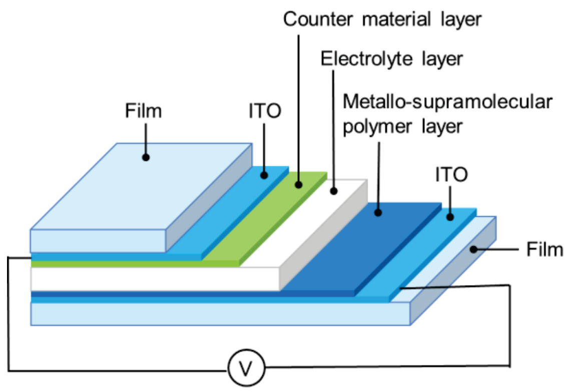

Fig. 2 A nature-inspired flexible EC device structure

PolyRu was multi-layer-coated on a plastic ITO sheet by spray-coating of a methanol solution of the polymer, using an automated spray coater of Apeiros API Corporation. Counter material was also coated on another plastic ITO sheet. The fallen leaf EC device was fabricated by sandwiching an electrolyte composed of $LiClO_4$ and PMMA with the two ITO sheets. Then, we equipped electric wiring and modified the device surface to mimic real leaf surface.

3 RESULTS

Fig. 3 shows the fabricated fallen leaf EC device. The color change from red to pale green occurred upon applying 1.5 V between the two ITO electrodes. The opposite color change from pale green to red happened by changing the current direction. The divalent state (Ru^{2+}) of polyRu shows reddish color due to the MLCT absorption around 500 nm. When the polymer is oxidized electrochemically, Ru ions become the trivalent state (Ru^{3+}) and the MLCT absorption disappears (Fig. 4).

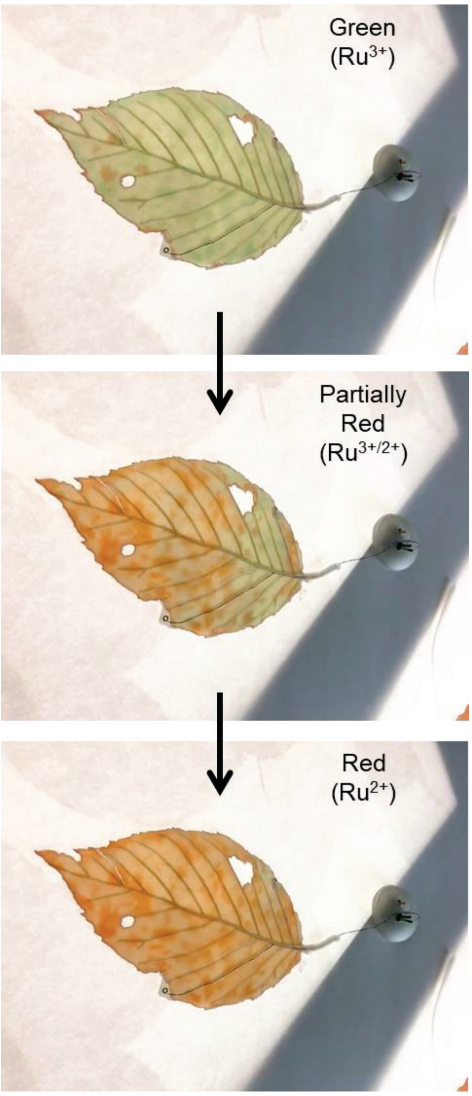

Fig. 3 A fallen leaf EC device with polyRu

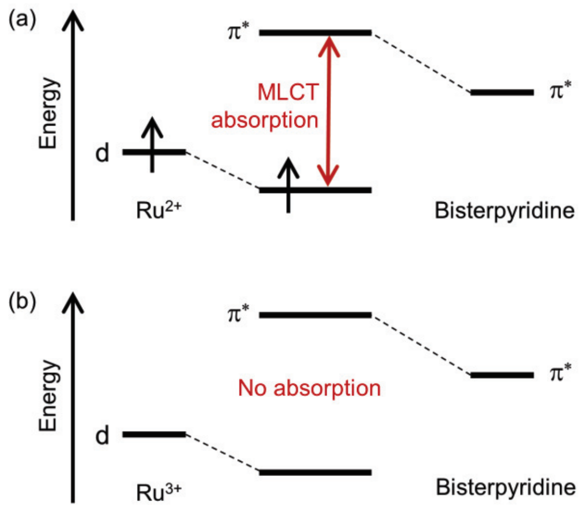

Fig. 4 A proposed mechanism of electrochromism between (a) the colored (red) and (b) the colorless (pale green) states of polyRu

We prepared un-uniformed EC polymer layer in the device by multi-layer coating and found that the thinner polymer layer part in the device changed the color faster upon applying the voltage. As the result, the leaf device well-reproduced the nature of a real fallen leaf. In addition, we could also stop the color of the device in the intermediate between the red and pale green states by quitting the power supply, because the device has memory properties.

4 CONCLUSIONS

We fabricated nature-inspired flexible EC devices using metallo-supramolecular polymer for the first time in the world. The use of Ru(II)-based polymer, which changes the color between red and pale green, and the multi-layer coating method have enabled to reproduce the nature of a real fallen leaf in the EC devices.

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