Multicolor Rewritable Paper Coated with Metallosupramolecular Polymers for Electrochromic Printing and Natural Erasing by Humidity

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ABSTRACT

In this work, a Fe(II)/Ru(II)-based MSP (polyFe/polyRu) for electrochromic printing and erasing is demonstrated using a flexible ITO/PET substrate. By adjusting the voltage between the electrochromic (EC) layer and the printing and/or erasing counterpart, writing and erasing on the flexible substrate was accomplished. At high relative humidity, the printed paper could be erased. The EC layer exhibited good EC properties. A multicolor printed paper was finally demonstrated.

1 Introduction

The scientific community has recently been very interested in a stimuli-responsive rewritable paper since it might replace conventional paper while being more environmentally friendly and sustainable. Because of this, it has been demonstrated that chromogenic materials are an alternative to rewritable paper. Extreme conditions for carrying out the changes and poor performances make the recent developments challenging and must be addressed. Numerous stimuli-responsive materials have been investigated recently, including organic molecules, organic polymers, photonic crystals, inorganic oxides, and many others. However, rewritable paper made of electrochemically color-switchable (electrochromic) materials has not received as much attention.

Among several EC materials, recently, it was demonstrated that metallosupramolecular polymers (MSPs) exhibit excellent EC characteristics.¹ But obtaining self-standing printed EC films is important by removing the printed paper from the device without endangering the film to use it as a rewritable paper. Like this, the fabrication of the EC device has temperature restrictions because of the flexible EC substrate. Due to the possibility of coating the MSPs below 100 °C and the expectation that the polymer networking nature will prevent the film from splitting throughout the printing process, the MSPs may be an acceptable EC material. By considering the above facts, in this work, we used the Fe(II)/Ru(II)-based MSPs for electrochromic printing and erasing on a flexible ITO/PET substrate and studied their EC behavior.

2 Experiment

2.1 Synthesis of polyFe and polyRu MSPs

PolyFe and PolyRu were synthesized as per the literature.²,³

2.2 Preparation of EC films

A 1:1 volume ratio of methanol and 2-propanol was used to make the polyFe and polyRu solutions. On ITO, homogeneous polymer films were generated by spin coating. Like how the process mentioned above was solely employed, only polyFe film was obtained by making the solution in methanol.

2.3 Preparation of solid-state electrolyte films

Acetonitrile (30 mL) and PMMA (14.0 g) were combined and stirred overnight until a translucent gel formed. To create a highly viscous liquid electrolyte, propylene carbonate (PC) (40 mL) and a solution of LiClO₄ in acetonitrile (40 mL) containing 6.0 g were added to the gel and stirred for 2 hours. To create an electrolyte film (thickness: 1-2 mm), the liquid electrolyte was put over a petri dish and left for 48 hours in an ambient environment to obtain a self-standing film.

2.4 Printing and erasing procedure using MSP films

The electrolyte film was applied to an ITO-coated glass (ITO/glass) to create the erasing unit. The erasing unit was covered with an insulating sheet that included hollowed-out symbols, letters, or other designs to prepare the printing unit. Glass substrates were printed with ITO-coated PET substrates for printing under bending conditions. The printing unit was mounted on the MSP film, and a +3 V potential bias was established between the substrates with the EC layer and the printing unit to achieve a colorless printing state. The colored erased circumstance was achieved by removing the printing unit after printing, placing the erasing unit on the printed EC film, and applying a -3 V potential bias.

3 Results

We used a 1:1 complexation approach to produce polyFe and polyRu, respectively (Fig. 1A).²,³ The resultant polymers were soluble in polar solvents like...
methanol and water. We developed a thin layer of polyFe on an ITO-coated PET substrate through spin coating. The thickness of the films was ~200 nm, confirmed through AFM images. The film characteristics were characterized by the SEM images and XPS spectra. The gel electrolyte film plays a crucial role in printing and erasing units. The gel electrolytes were obtained using PMMA, PC, and LiClO₄ as described in the experimental section. The erasing unit was prepared by covering the ITO/glass substrate with the gel film. Similarly, the printing unit was prepared by covering the erasing unit with a designed insulating PVC layer. By bringing the printing unit into contact with the EC film and applying +3 V between the layers, electrochemical printing was completed because only the portion of the polyFe film that came into touch with the electrolyte was electrochemically oxidized to alter the color from blue to colorless, the printed blue sheet was displayed in fig. 1B. Placing the erasing unit on the printed EC paper and applying the opposite potential between the layers allowed the printed characters to be erased.

4 Discussion

From the SEM image, it was observed that the film exhibited amorphous properties. The absorbance of the sandwiched device by attaching the respective printing and erasing units was 583 nm due to MLCT transition. The device exhibited cathodic potential at +2.24 V, termed a printing-colorless state, and a reduction potential of −1.01 V, termed an erasing-colored state. The printing was confirmed from XPS by monitoring the change in the binding energy of Fe2p3/2 state from 708.3 eV to 710.0 eV due to the change in oxidation state from Fe(II) to Fe(III). MLCT transition was restricted in this high-valent state, and a colorless state appeared. By applying +3.5 V, the transmittance change from color to colorless state was 62%, and the time taken for this conversion was 0.9 s. The device took 0.6 s by applying the respective negative potential to return to its original state. In the bending state, the bleaching and coloring intervals with a 65% change in transmittance were 2.2 and 1.5 seconds, respectively. The device switching stability was checked up to 2500 cycles, and no change in the performance was observed. Further, we studied the effect of relative humidity (RH) on the printed paper. At 30% RH, after printing, the printed paper could hold the oxidized state up to 160 h with minimal change in the transmittance. Still, as the RH increased, the memory time decreased due to the interference of the humid air, which could provide the electrons to reduce the printed film from colorless to color state.

Finally, we demonstrated multicolored EC printing by using polyFe and polyRu. The film was prepared as demonstrated in the experimental section. The difference in holding time of the cathodic potential and the anodic potential created different colors due to the preferential oxidation/reduction of Fe(II/III) and Ru(II/III) (Fig. 1C). The original color of the film was red-purple. At +3 V, by keeping the potential for 3 s in the presence of the printing unit, it became colorless, and in the presence of the erasing unit, by keeping the potential of -3 V for 1 s, only Ru(III) ion get reduced and a yellow red color appeared. Thus, three different colors were obtained.

5 Conclusions

Herein, we developed a new approach to obtain a rewritable EC film. The EC film exhibited a sub-second switching time (< 1 s), long memory time (> 7 days), high transmittance change (62%) and long switching cycles (2500 cycles). The synthetic simplicity, structural robustness, easy writing and erasing technique, long memory time, high switching cycles, and natural erasing of the material might attract future intense investigation in this area.

Fig. 1 (A) Structure of the MSPs. (B) Printing and erasing of the EC paper. (C) Transmittance change during the redox process at different holding time, monitored at 580 nm and 503nm.

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