Bull. Soc. Photogr. Imag. Japan. (2025) Vol. 35 No. 2: 19–21

Letter

Golden Metallic Luster from Poly (3,4-ethylenedioxythiophene) Single-layer Film

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Abstract: We successfully obtained a golden metallic luster from a reduced poly (3,4-ethylenedioxythiophene) (PEDOT) film by performing multi-step potentiostatic (MS-PS) polymerization, which involves alternating the oxidation of the monomer for polymerization and the reduction of the resulting polymer. This metallic luster turned purple in the oxidized state, thereby achieving electrochromism of the reflected color.

Key words: Golden metallic luster, Poly (3,4-ethylenedioxythiophene) single-layer film, Multi-step potentiostatic polymerization

Researches into metallic luster from materials that do not contain metallic elements has become active in recent years. [1-7] In this field, studies into conductive polymers that exhibit a golden metallic luster has been attracting particular attention. [8-12]

One research group reported that a golden metallic luster can be obtained from a thiophene derivative polymer.[8] In their works, polymer films with a metallic luster were obtained by chemical and electrochemical polymerization. In the electrochemical method, they reported that the formation of polymer lamellae is necessary to form highly reflective polymer films, and that a slow cyclic potential scan of 10 mV/s is required. [9] To shorten the preparation time and obtain polymer films with higher reflectivity, we have proposed a new electrochemical method, the multi-step potentiostatic (MS-PS) polymerization method, in which a constant potential for the oxidation of the monomer and a constant potential for the reduction of the resulting polymer are applied alternately.[13] This method allows for the continuous application of a constant potential, resulting in the formation of uniform polymers in a short time. Furthermore, this method allows for the film thickness, reflectivity, and color to be selected arbitrarily by changing the applied potential, the application time, and number of cycle repetitions.

It has also been reported that a golden metallic luster can be obtained from polymers of another thiophene derivative, 3,4-ethylenedioxythiophene.[10] However, this metallic luster is not obtained from a poly (3,4-ethylenedioxythiophene) [PEDOT] film alone, but from a bilayer film with polyaniline present as an underlayer. Furthermore, the mechanism behind this golden metallic luster is believed to be structural interference color. Here, we report on the appearance of a golden luster from a PEDOT single-layer film obtained by MS-PS polymerization.

The electrolyte solution was prepared by dissolving 5.6 mM 3,4-ethylenedioxythiophene (EDOT) and 0.1 M tetra-n-butylammonium perchlorate in acetonitrile. A cleaned ITO glass plate (Geomatec) was used as the electrode substrate, an Ag-AgCl electrode as the reference electrode, and a platinum wire as the counter electrode. Polymerization was performed using the multi-step potentiostatic (MS-PS) polymerization method. In the first step, a constant potential A of +1.3 V was applied for 15 seconds to oxidize the monomer, and in the second step, a constant potential B of -1.0 V was applied for 25 seconds to reduce the resulting polymer. The reflectance of the resulting polymer thin film was measured using a Konica Minolta CM-26dG spectrophotometer. Diffuse reflectance was measured by this colorimeter equipped with a d/8 type integrating sphere. The transmittance spectrum was measured using an Ocean Optics OP-TR/RF-GONIO-MN (spectral transmittance/reflectance measurement system).

Fig. 1 shows the reaction current during MS-PS polymerization. A constant potential of +1.3 V was applied for 15 seconds to oxidize the monomer, followed by a constant potential of -1.0 V for 25 sec-

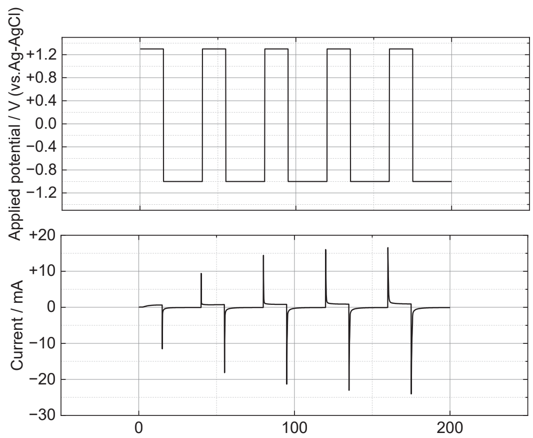

Fig. 1 Time dependence of applied potential and reaction current during MS-PS polymerization of EDOT.

Received 15th November, 2025; Accepted 23rd November, 2025; Published 5th December, 2025
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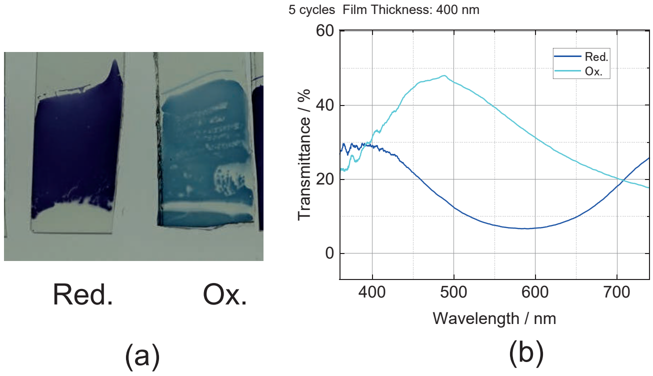

Fig. 2 Photographs of the obtained PEDOT single-layer films in the reductive state (Red.) and the oxidative state (Ox.). (a) Transmittance spectra of the PEDOT single-layer films in the reductive state (Red.) and the oxidative state (Ox.). (b)

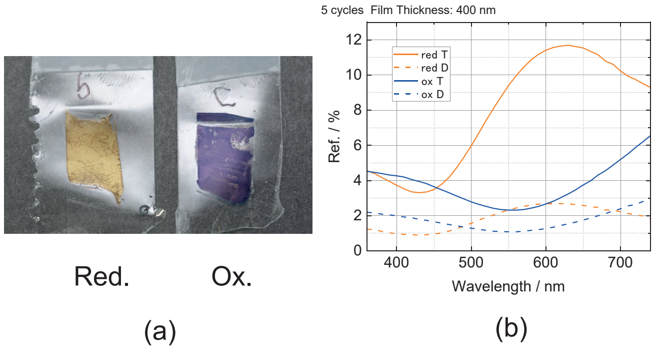

Fig. 3 Photographs of the obtained PEDOT single-layer films in the reductive state (Red.) and the oxidative state (Ox.). (a) Total reflectance (T) and diffuse reflectance (D) spectra of the PEDOT single-layer films. (b)

onds to reduce the PEDOT obtained on the electrode. This cycle was repeated five times. The reaction current gradually increases with increasing number of MS-PS polymerization cycles, indicating a continuous increase in the amount of PEDOT obtained on the electrode.

Fig. 2a shows a photograph taken from the back of the electrode illuminated with white light to confirm the transmission color of the PEDOT film obtained after five cycles of MS-PS polymerization. A deep blue color was observed in the reduced state, and a light blue color in the oxidized state. This color change is due to the well-known transmission color electrochromism of PEDOT. Fig. 2b shows the transmission spectrum of the PEDOT film obtained after five cycles of MS-PS polymerization. In the reduced state, a strong, broad absorption band centered at 600 nm was observed. In the oxidized state, ClO_4^- doping progressed, resulting in higher transmittance across the entire visible light band compared to the reduced state, with absorption observed in wavelengths below 450 nm and above 500 nm.

When a white light was illuminated against a black background, the PEDOT film surface formed on the ITO electrode appeared dark blue with slightly golden in the reduced state and light blue in the oxidized state. No metallic luster was apparent in either electronic state. The polymer film was then peeled off using adhesive tape, exposing the film surface on the electrode side. Fig. 3a is a photograph of the PEDOT film on the tape illuminated with white light. Under a white light source, a golden metallic luster was clearly observed in the reduced state. A purple luster was observed in the oxidized state. Fig. 3b shows the total reflectance and diffuse reflectance spectra of the PEDOT film immobilized on the tape (after five cycles of MS-PS polymerization). The reflectance maximum in the reduced state was observed at a wavelength of 620 nm, with a total reflectance value of 11.7%. Total reflectance is the sum of specular and diffuse reflectance components. The diffuse reflectance value in the reduced state was 2.7% at 620 nm, and approximately 77% of the total reflectance was the specular component, which is likely responsible for the observed metallic luster. The relatively smooth surface of the ITO electrode, the substrate for PEDOT deposition, likely contributed to the high specular reflectance. In contrast, in the oxidized state, the overall reflectance was low, with increased reflectance in wavelength regions on both sides of the 560 nm minimum reflectance. This is explained that the purple color is due to the blending of blue and red light.

Comparison of the transmission and reflection spectra revealed that the wavelength bands absorbed by the film in both electronic states were included in the wavelength bands reflected from the film. This relationship is similar to the green metallic luster of safflower pigments studied in our previous work.[5,6] This reflected light is expected to be due to the re-emission of secondary light associated with resonance between electronic vibrations in the PEDOT color-forming structures and incident electromagnetic waves. After MS-PS polymerization (5 cycles), the reflectance spectrum of the PEDOT film immobilized on the electrode was measured against a black background. The upper surface of the film exhibited a reflection around 400 nm (total reflectance 3%), as well as a reflection component around 600 nm (total reflectance 2%). While the overall reflectance was significantly lower than that of the lower surface (backside), it was clear that the upper surface also possessed a golden reflection component. (as mention above) The difference in reflectance is expected to be primarily due to the rougher surface condition of the upper surface compared to the lower surface. Our important concern is whether the MS-PS polymerization resulted in PEDOT lamella formation, resulting in a metallic luster. This remains to be clarified in future studies.

In this study, we demonstrated that a golden luster and high reflectivity can be obtained from a PEDOT single-layer film in a reduced state.

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