Electrochromic and electrochemical properties of copper Prussian blue analog nanoparticles prepared by micro flow mixing method

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Prussian blue ($Fe_4[Fe(CN)_6]_3$, PB) and its analogues (PBAs) have been fascinating for electrochromic application because of their excellent properties of cycling stability, fast response, and low cost. The PBAs have been reported much for electrochromic applications. However, among PBAs, study on copper Prussian blue analog (Cu-PBA) is scarcely. Cu-PBA presents reddish brown to yellow electrochromism. These brown or yellow colors can represent a color of wood for a building or furniture. In this study, we prepared Cu-PBA nanoparticles by different concentration of Cu (II) ion using micro flow mixing method, and examined their electrochromic and electrochemical properties.

Aqueous solutions of 0.3-0.7 mol/l of $CuSO_4$ and a solution of 0.4 mol/l of $K_3[Fe(CN)_6]$ were mixed by a micro flow mixer. The flow rates of both the solutions were 50 ml/min. The resulting precipitate was washed 5 times with Milli-Q water, and aqueous solution of $K_3[Fe(CN)_6]$ was added to increase their dispersibility in water via surface modification. The Cu-PBA dispersed liquid was stirred at room temperature over 10 days. Cu-PBA films were coated on indium tin oxide (ITO)/glass substrates by spin-coating method using the Cu-PBA dispersed liquid with the concentration of 0.1 g/ml. Their electrochemical properties were characterized in 0.1 M potassium bis (trifluoromethanesulfonyl) imide / propylene carbonate electrolyte. Saturated calomel electrode (SCE), Pt wire, and Cu-PBA films were used for reference, counter, and working electrodes respectively. The working electrode area was set to 1.0 cm^2.

Fig. 1 shows XRD patterns of the Cu-PBA nanoparticles prepared with Cu/Fe ratios from 0.75 to 1.75. The diffraction peaks of all the films agree with cubic $Cu_3[Fe(CN)_6]_2$. Fig. 2 shows the FESEM image of the Cu/Fe=1.50 sample (particle size = 25-47 nm). The transmittance spectra of as-deposited, oxidized at 1.6 V (reddish brown), and reduced at -0.4 V (yellow) are shown in Fig. 3. The Cu-PBA film shows a transmittance change of about 20% at 500 nm. Cyclic voltammogram (CV) of the Cu/Fe=1.50 sample shows a pair of main redox peaks between -0.4 V and 1.6V as shown in Fig. 4. The transferred charge density of the Cu/Fe=1.50 sample was about 15 mC/cm^2. In conclusion, Cu-PBA nanoparticles prepared by micro flow mixing method indicate good electrochromic and electrochemical properties. The brown and yellow Cu-PBA films can imitate colors of wood.

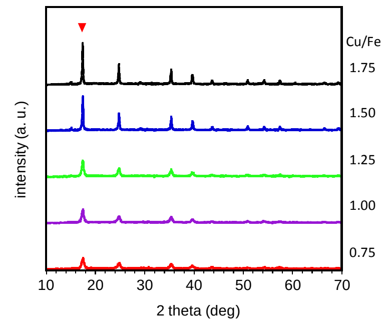

Fig. 1. XRD patterns of Cu-PBA films prepared by different Cu/Fe ratios of reactants.

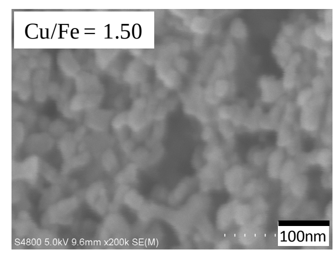

Fig.2. FESEM image of Cu-PBA nanoparticles (Cu/Fe = 1.50).

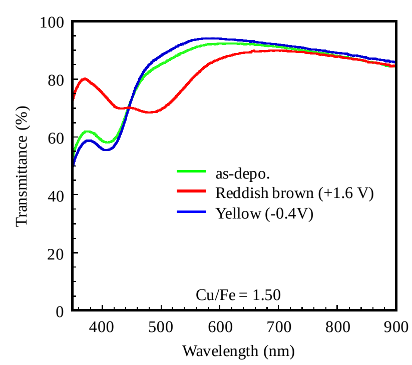

Fig. 3. Transmittance spectra of Cu-PBA nanoparticle film (Cu/Fe = 1.50).

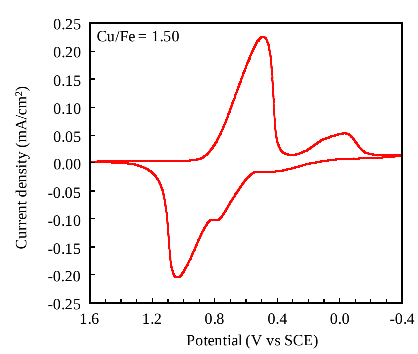

Fig. 4. Cyclic voltammogram of Cu-PBA nanoparticle film between -0.4 V and 1.6V at a scan rate of 5mV/s.

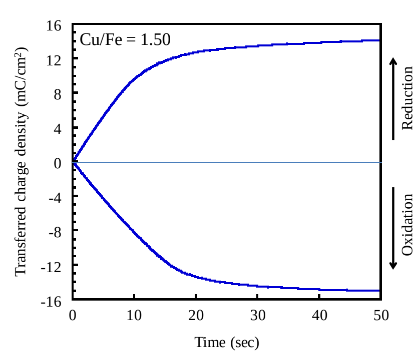

Fig. 5. Transferred charge density of Cu-PBA films applied voltage at reduction (-0.4 V) and oxidation state (1.6 V).