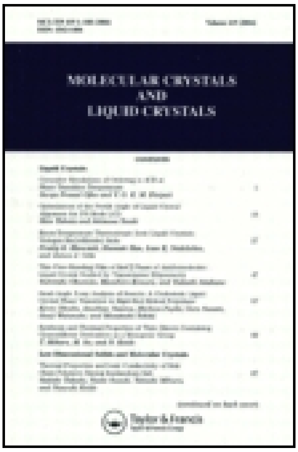

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Synthesis of Water-Dispersible Copper Hexacyanoferrate Nanoparticles and Electrochromism of the Thin Films

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Synthesis of Water-Dispersible Copper Hexacyanoferrate Nanoparticles and Electrochromism of the Thin Films

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A Prussian blue analog (PBA), copper hexacyanoferrate (Cu-PBA) has been synthesized as an insoluble aggregated solid of nanoparticles (NPs). The Cu-PBA NPs bore negative surface-charge via their surface modification using $[Fe^{II}(CN)_6]^{4-}$ *and were stably dispersed into water from the insoluble solid. Spin-coated thin films consisting of the Cu-PBA NPs on ITO glass substrates showed reversible electrochromism of red (reduced form) and yellow (oxidized form). The spectroscopic investigation revealed that the reduced form of Cu-PBA was a mixed valence form included Cu(I).*

Keywords Copper hexacyanoferrate; dispersion solution; electrochromism; nanoparticle; Prussian blue

Introduction

Prussian blue (PB) and its analogs (PBAs) have been fascinating coordination polymers having multi-functionalities and historically insoluble materials [1]. As the importance of printed electronics using ink-jet printers has globally increased, fabrication of dispersion solutions of such insoluble materials has been the current hot subject. NPs are one of the most promising candidates to prepare the dispersion solutions. We have proposed a new synthetic strategy directly to transform the insoluble PB, Ni- and Co-PBA NPs into various solvents via convenient and simple processes suitable for industrial application [2–5]. Copper hexacyanoferrates (Cu-PBA) have been investigated on electrochromism and electrochemical sensors functioning in a wide range from acid up to neutral pH; [6,7] nevertheless, such electrochemistry has been limited in physical or chemical deposited films in many cases. In this study, we successfully transformed insoluble Cu-PBA into water-dispersible

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15 nm NPs, which bore negative zeta-potentials via surface modification using $[Fe^{II}(CN)_6]^{4-}$. Electrochromism of spin-coated thin films consisting of the Cu-PBA NPs was investigated and the specific valence state of their reduced form was revealed through the X-ray photoelectron spectroscopy.

Experiment

1. *Apparatus*

The powder X-ray diffraction (XRD) and wavelength-dispersive X-ray (WDX) analyses were performed using a Rigaku MiniFlex II (Cu $K\alpha_1$ radiation) and a Rigaku Primini, respectively. The dynamic light-scattering (DLS) particle sizes and zeta-potentials were measured on an Otsuka ELS-Z2 M. The atomic force microscopy (AFM) images were observed on a Shimadzu SPM-9600 scanning probe microscope. Electrochemical analyses were carried out using Model-263A PAR. The UV-Vis absorption spectral change was recorded on an Ocean Optics Inc UV-USB4000. Time course change of transmittance in the electrochromic cycles was measured on a Shimadzu MultiSpec-1500 equipped with an ALS electrochemical analyzer model 1100P. The X-ray photoelectron spectroscopy was employed using a Quantum-2000 (Ulvac-PHI Inc.) to analyze electronic states of Cu-PBA.

2. *Synthetic Procedure*

Insoluble red colloidal particles of Cu-PBA were immediately precipitated from an aqueous mixture (30 mL) of $CuCl_2$ (1.36 g, 8.00 mmol) and $K_4[Fe(CN)_6]\cdot 3H_2O$ (1.69 g, 4.00 mmol). The centrifuged insoluble Cu-PBA solid was washed with water and stirred with an aqueous solution (20 mL) of $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.51 g, 1.2 mmol) for 3 days. Through the reaction period of each colloidal particle with $[Fe^{II}(CN)_6]^{4-}$, insoluble Cu-PBA solid was transformed into a transparent red aqueous dispersion solution.

Results and Discussion

The XRD pattern of the insoluble Cu-PBA solid was consistent with that of the insoluble PB solid [2–5]. It suggests that the crystal lattice of the Cu-PBA is a similar face-centered cubic (fcc) structure surrounded by 3-D cyano-bridged Fe-CN-Cu networks. From significant line broadening of the XRD signals of the insoluble Cu-PBA solid, Scherrer's single-crystalline size was calculated as 15.6 nm. Based on the metal composition ratio, Cu/Fe, estimated to be 2.03 (mole/mole) from the WDX analysis, the insoluble Cu-PBA solid is a simple charge-compensated complex salt of $2Cu^{2+}$ and $[Fe^{II}(CN)_6]^{4-}$, $Cu^{II}_2[Fe^{II}(CN)_6]$ with five water molecules. If the insoluble Cu-PBA solid is a physical agglomerate of colloidal NPs, the NPs will be dispersed into various solvents freely from each other via their surface modification. According to the previous procedures [2,3,5], the Cu-PBA NPs were surface-capped with $[Fe^{II}(CN)_6]^{4-}$ after the successive reaction of their insoluble solid with $K_4[Fe(CN)_6]$ (Figure 1). Thus, the surface-capped Cu-PBA NPs were dispersed in water through electrostatic repulsion of their surface negative charges (zeta-potentials) of −46 mV. The number-averaged DLS particle size was 30 ± 8 nm in a dilute solution (4 μmol/ml as $Cu_2[Fe(CN)_6]$). The dispersion solution of the Cu-PBA

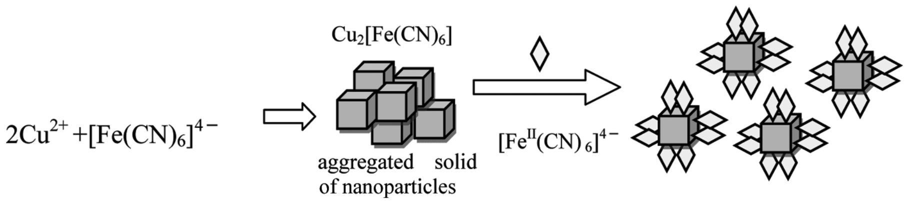

Figure 1. Synthetic scheme of the water-dispersible Cu-PBA nanoparticles bearing negative surface-charges.

NPs exhibited high transparency and remarkable red color due to an absorption band at $\lambda_{max} = 472$ nm. The transparency is one of the specific optical properties of NPs in not only their dispersion solutions but their thin films, because the nanoparticle sizes much smaller than visible light wavelengths effectively suppress the incident-light scattering like small molecules and ions [2–5].

The Cu-PBA NPs were spin-coated on ITO glass substrates using their high-concentration dispersion solution (200 μmol/mL) to obtain transparent red thin films of 220-nm thickness. In a similar spin-coated thin film on a mica substrate, the Cu-PBA NPs were observed as averaged diameter of 14.8 nm from the AFM images. The as-prepared thin films on ITO showed the electrochromic change between red and yellow (Figure 2(a)) under controlled potentials at 0 and 1.5 V *vs.* SCE, respectively. In the cyclic voltammetry of a similar spin-coated thin film on a gold substrate, the reversible wave at 0.75 V is ascribable to a formal redox couple between $Cu^{II}_2[Fe^{II}(CN)_6]$ (reduced red form) and $Cu^{II}_2[Fe^{III}(CN)_6]$ (oxidized yellow form) (Figure 2(b)). The electrochromic reversibility of the spin-coated thin film on ITO was confirmed based on time course change in electronic spectral transmittance under applied two alternate potentials between 0.1 and 1.4 V *vs.* SCE (Figure 3) along with no serious degradation of its redox currents of more than 300 electrochromic cycles.

So far, the reduced form of Cu-PBA has been discussed as a formula, $Cu^{II}_2[Fe^{II}(CN)_6]$ [8]. In order to elucidate the origin of the intense red color of the reduced form, the electronic states of Cu were further investigated. According to the X-ray photoelectron spectra (XPS), the electronic states were different between

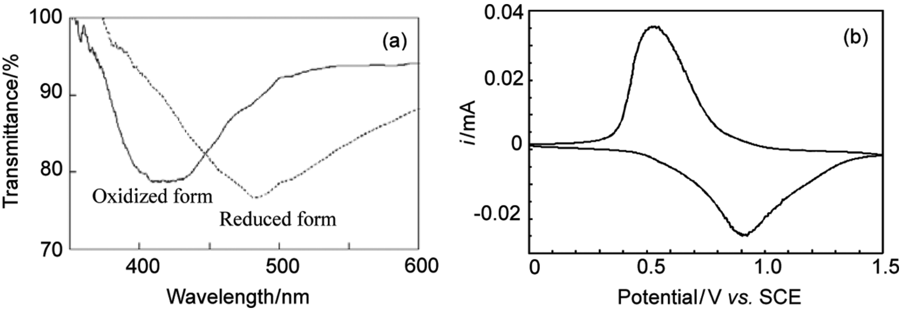

Figure 2. (a) Electronic spectra of the spin-coated thin film of the Cu-PBA nanoparticles in the oxidized form at 1.5 V and the reduced form at 0 V *vs.* SCE. (b) Cyclic voltammogram of the spin-coated thin film on a gold substrate in a KPF_6 propylene carbonate solution at a scan speed of 0.01 V/s.

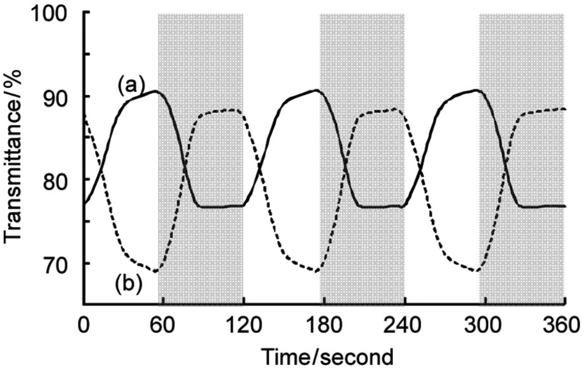

Figure 3. Time course change in transmittance at 480 nm (a) and 410 nm (b) of the spin-coated thin film of the Cu-PBA nanoparticles under applied two alternate potentials at 0.1 (gray) and 1.4 V (white) *vs.* SCE in KPF_6 propylene carbonate solution.

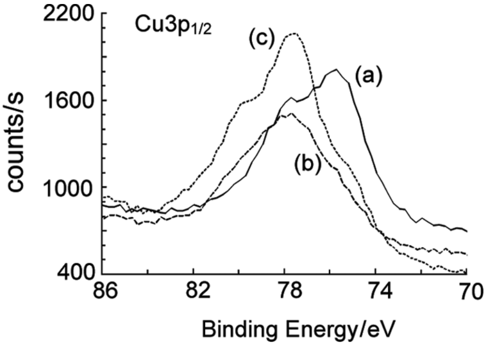

Figure 4. X-ray photoelectron spectra of the reduce form (a) and the oxidized form (b) of the Cu-PBA nanoparticles and $CuCl_2$ (c) as a referential sample of Cu(II).

the reduced and oxidized forms (Figure 4). Cu(II) species appeared at 77–78 eV according to a reference sample of $Cu^{II}Cl_2$. The main peak energy of the oxidized form was 77.8 eV, while that of the reduced form was significantly shifted to a lower energy (75.7 eV), suggesting that the reduced form included Cu(I) in the valence states. The charge transfer between mixed valence Cu and Fe via the cyano-bridged d-π bonding network is related to the intense red color. In the fcc structures of PB and PBA, transition metals are surrounded by the octahedral configuration. The homogeneous distribution of Cu(I) and/or the positional exchange between Cu(I) and Cu(II) through the d-π electronic network probably maintain the fcc crystal structure against local Jahn-Teller distortion due to Cu(II) from a regular octahedron.

Conclusion

We have developed a simple procedure to obtain water-dispersion solutions of the Cu-PBA NPs via surface modification using $[Fe^{II}(CN)_6]^{4-}$, which exhibit high transparency and an intense red color. Spin-coated thin films of the Cu-PBA NPs on ITO show a reversible electrochromic change between red and yellow. The mixed valence state, $(\mathrm{Cu}^{\mathrm{I}}_x\mathrm{Cu}^{\mathrm{II}}_{2-x})[\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_6]_{1-x}[\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_6]_x$ is caused by the stable fcc crystal structure and the red color. The valence states of the reduced form may be altered via valence tautomerization, which is sensitive to surroundings. The valence state of Fe is under further investigation by using Mössbauer spectroscopy.

Acknowledgment

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