

## Dye-sensitized Solar Cells with Halide-bridged Mixed-valence Cu(I)–Cu(II) Coordination Polymers with Hexamethylenedithiocarbamate Ligand

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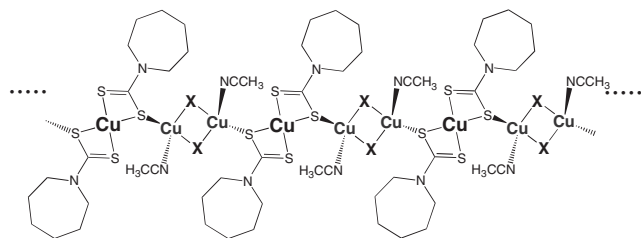
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The application of halide-bridged mixed-valence Cu(I)–Cu(II) coordination polymers with hexamethylenedithiocarbamate (Hm-dtc) ligand as sensitizing materials for dye-sensitized solar cells (DSSCs) with poly(3,4-ethylenedioxythiophene) tetramethacrylate (PEDOT-TMA) counter electrode is novel. DSSCs having coordination polymers in comparison with a mononuclear Cu(Hm-dtc)<sub>2</sub> complex exhibited better power conversion efficiency because of the high photocurrent density.

The design and construction of coordination polymers has attracted considerable interest because of their potential applications in material science and in functional devices.<sup>1</sup> However, the applications of coordination polymers in photovoltaic devices are less developed than those of conventional mononuclear complexes such as copper phthalocyanines<sup>2</sup> and ruthenium complexes,<sup>3</sup> even though the coordination polymers have regular networks for the conductive pathways of the photo-generated electrons.

In this paper, we discuss the photovoltaic properties of DSSCs with coordination polymers, [Cu<sup>I</sup><sub>2</sub>Cu<sup>II</sup>X<sub>2</sub>(Hm-dtc)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>n</sub> (Hm-dtc<sup>−</sup> = hexamethylenedithiocarbamate; X = Br<sup>−</sup> (1) and I<sup>−</sup> (2)) (Scheme 1), in comparison with a mononuclear [Cu(Hm-dtc)<sub>2</sub>] complex (3) as sensitizing dyes. Halide-bridged mixed-valence Cu(I)–Cu(II) coordination polymers, which consist of a mononuclear copper(II) unit Cu(Hm-dtc)<sub>2</sub> connected by dinuclear copper(II) units Cu<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>X<sub>2</sub>, had a one-dimensional (1D) infinite chain structure.<sup>4,9</sup> These polymers exhibit electroconductive properties because of the approaching energy levels of the magnetic orbital of the copper(II) ion and the highest occupied molecular orbitals (HOMOs) of the dithiocarbamate ligand, the copper(I) ion, and the bridging Br or I anions.<sup>4</sup> The carrier transport properties of electroconductive Cu(I)–Cu(II) coordination polymers facilitate the application of these polymers to optoelectronic devices.

The DSSCs were fabricated using the following process: The metal complexes (0.3 mol), [Cu<sup>I</sup><sub>2</sub>Cu<sup>II</sup>X<sub>2</sub>(Hm-dtc)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>n</sub> (X = Br<sup>−</sup> (1) and I<sup>−</sup> (2)), [Cu(Hm-dtc)<sub>2</sub>] (3), were mixed with

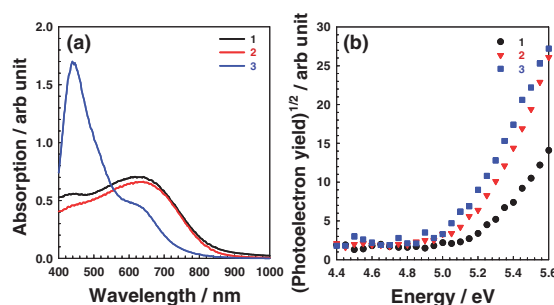


**Scheme 1.** Structure of mixed-valence Cu(I)–Cu(II) coordination polymer (X = Br<sup>−</sup> (1) and I<sup>−</sup> (2)).

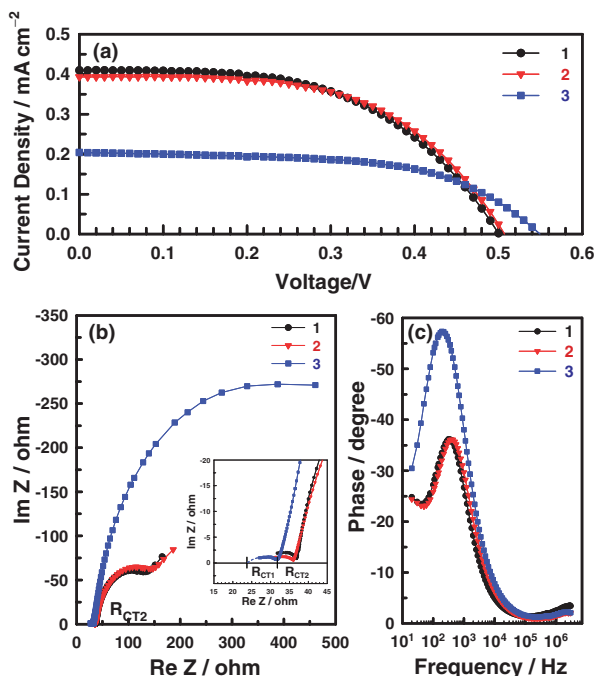
a TiO<sub>2</sub> paste (0.1 mL) for the work electrode and screen-printed on an indium tin oxide (ITO, sheet resistance: 10 Ω/square) glass substrate. The substrate was then annealed at 50 °C for 0.5 h. For the counter electrode, an aqueous solution of poly(3,4-ethylenedioxythiophene) tetramethacrylate (PEDOT-TMA) mixed with ethanol at a volume ratio of 1:1 was used. The mixed solution was spin-coated (2000 rpm for 10 s) on an ITO glass substrate and dried at 50 °C for 10 min. The fabrication temperature for both the TiO<sub>2</sub> electrode and the counter electrode was 50 °C, which was sufficiently low for the application of DSSCs based on coordination polymers to flexible devices. The two prepared electrodes were assembled to fabricate a sandwich cell with a 50 μm spacer. The electrolyte, which was a solution of 0.5 M lithium iodide (LiI) and 0.005 M iodine (I<sub>2</sub>) in poly(ethylene glycol), was injected between the electrodes.<sup>5</sup>

Figure 1a shows the absorption spectra obtained by diffuse reflectance of the coordination polymers 1 and 2 and the mononuclear complex 3 (0.01 mmol) doped in MgO (80 mg). The absorption of the coordination polymers occurs mainly in the visible regions and extends into the near-IR region. From this, these polymers could be considered to be sufficient sensitizing dye materials for DSSCs. At wavelengths above 550 nm, the absorption of the Cu(I)–Cu(II) coordination polymers, with slightly higher absorption of complex 1 than that of complex 2, is clearly higher than that of the mononuclear metal complex 3.

The photoemission yield curves of metal complexes are shown in Figure 1b. The highest occupied molecular orbital (HOMO) energy levels of complexes 1, 2, and 3 are 5.20, 5.10, and 4.95 eV, respectively. These values are sufficiently low to accept electrons from the redox electrolyte (4.8 eV). From HOMO values, the lowest unoccupied molecular orbital (LUMO) energy levels obtained by the band edges of the absorption spectra are determined to be 3.72, 3.62, and 3.50 eV, respectively. The energy levels of LUMO are effectively well-



**Figure 1.** (a) Vis–NIR absorption spectra and (b) photoemission yield curves of metal complexes under an atmospheric condition: [Cu<sup>I</sup><sub>2</sub>Cu<sup>II</sup>X<sub>2</sub>(Hm-dtc)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>n</sub> (X = Br<sup>−</sup> (1) and I<sup>−</sup> (2)), [Cu(Hm-dtc)<sub>2</sub>] (3).



**Figure 2.** (a) Photocurrent density–voltage ( $J$ – $V$ ) curves under AM 1.5 illumination. Impedance spectra of DSSCs with different dye materials at open-circuit voltage. (b) Nyquist plots and (c) Bode plots. The  $\text{TiO}_2$  electrode area is  $0.3 \text{ cm}^2$ :  $[\text{Cu}^{\text{I}}_2\text{Cu}^{\text{II}}\text{X}_2(\text{Hm-dtc})_2(\text{CH}_3\text{CN})_2]_n$  ( $\text{X} = \text{Br}^-$  (1) and  $\text{I}^-$  (2)),  $[\text{Cu}(\text{Hm-dtc})_2]$  (3).

**Table 1.** Photovoltaic performance and electron lifetime of DSSCs with different dyes under AM 1.5 illumination condition

Dye <sup>a</sup>	$J_{\text{sc}}$ / $\text{mA cm}^{-2}$	$V_{\text{oc}}$ / $\text{V}$	$FF$ /—	$\eta$ / $\%$	$\tau$ / $\text{ms}$
1	0.41	0.50	0.53	0.11	0.51
2	0.39	0.50	0.56	0.11	0.41
3	0.20	0.55	0.58	0.06	0.84

<sup>a</sup> $[\text{Cu}^{\text{I}}_2\text{Cu}^{\text{II}}\text{X}_2(\text{Hm-dtc})_2(\text{CH}_3\text{CN})_2]_n$  ( $\text{X} = \text{Br}^-$  (1) and  $\text{I}^-$  (2)),  $[\text{Cu}(\text{Hm-dtc})_2]$  (3).

matched with the  $E_{\text{CB}}$  of the  $\text{TiO}_2$  semiconductor (3.8 eV) in order to inject the electrons from the dyes.<sup>6</sup>

Figure 2a shows the photocurrent density–voltage ( $J$ – $V$ ) curves of DSSCs 1, 2, and 3. There are clear differences in the short-circuit current density ( $J_{\text{sc}}$ ) and open-circuit voltage ( $V_{\text{oc}}$ ) of DSSCs between the Cu(I)–Cu(II) coordination polymers and the mononuclear complex. The details of the parameters,  $J_{\text{sc}}$ ,  $V_{\text{oc}}$ , fill factor ( $FF$ ), and power conversion efficiency (PCE,  $\eta$ ), of cells with different dye materials are summarized in Table 1. The  $J_{\text{sc}}$  value of DSSC 1 is slightly higher than that of DSSC 2. This observation is well supported by the absorption spectra shown in Figure 1a. In the DSSCs using polymers 1 and 2 as compared to complex 3, it would lead to an increase in the photocurrent density as a result of the fact that the LUMO levels of polymers 1 and 2 are closer to the  $E_{\text{CB}}$  of  $\text{TiO}_2$ . The  $V_{\text{oc}}$  value of DSSCs with polymers 1 and 2 is 0.50 V, which is smaller than that of complex 3. This difference may be attributed to the more strongly positive shift of the  $E_{\text{CB}}$  of  $\text{TiO}_2$  in the case of polymers 1 and 2.

Figure 2b shows the Nyquist plots from the electrochemical impedance spectra (EIS) measured between 20 Hz and 3 MHz at the open-circuit voltage under illumination. The inset exhibits the magnification of the high-frequency region.  $R_{\text{CT1}}$  and  $R_{\text{CT2}}$  correspond to the resistance of the charge transport at the surface of the counter electrode and resistance between the  $\text{TiO}_2$ /dye and the electrolyte, respectively.<sup>7</sup> In DSSCs with different dyes, the variation in  $R_{\text{CT1}}$  is extremely small.  $R_{\text{CT2}}$  values of DSSCs 1 and 2 are smaller than that of DSSC 3. This supports the relatively high photocurrent density of DSSCs 1 and 2 compared to that of DSSC 3.

Figure 2c shows the Bode phase angle of DSSCs with different dye complexes. The carrier lifetimes between the  $\text{TiO}_2$ /dye and the electrolyte of DSSCs 1, 2, and 3 as calculated using the characteristic frequency<sup>8</sup> are 0.51, 0.41, and 0.84 ms, respectively. The carrier transfer between the  $\text{TiO}_2$ /dye and the electrolyte in DSSCs using complex 3 is more effective than that in DSSCs using polymers 1 and 2. This may be attributed to the fact that the HOMO energy level of complex 3 is closer to the energy level of the redox electrolyte than that of polymers 1 and 2. The difference in the carrier lifetime of DSSCs 1 and 2 is considerably small.

DSSCs with a Cu(I)–Cu(II) coordination polymer instead of a mononuclear complex exhibit a relatively high efficiency compared to DSSCs with a mononuclear complex. This is because of the lower resistance between the  $\text{TiO}_2$ /dye and the electrolyte.

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