Application of mononuclear metal complexes with a hexamethylene–dithiocarbamate ligand as photosensitizers for dye–sensitized solar cells

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Abstract

We present a new approach using mononuclear metal complexes with a hexamethylene-dithiocarbamate ligand, $[M(Hm–dtc)_n]$ ($M = Cu^{2+}$, n = 2 (1); $M = Ni^{2+}$, n = 2 (2); $M = Co^{3+}$, n = 3 (3); $M = Fe^{3+}$, n = 3 (4); $Hm–dtc^- =$ hexamethylene-dithiocarbamate), as dye materials for dye–sensitized solar cells (DSSCs). DSSCs based on a $[Cu(Hm–dtc)_2]$ dye exhibited relatively high power conversion efficiency due to their high short–circuit photocurrent density and long electron lifetime.

Keywords: mononuclear metal complexes, hexamethylene-dithiocarbamate ligand, dye, dye-sensitized solar cells, power conversion efficiency

1. Introduction

Interest in scientific research on dye–sensitized solar cells (DSSCs) and their practical applications has increased substantially [1-4]. The sensitizing dyes in DSSCs must harvest solar light ranging from the UV–visible and near–IR regions. Although ruthenium polypyridyl complexes are generally used as the effective sensitizers due to their intense charge transfer absorption in whole visible range, it is important to study new materials for sensitizing dyes to develop the field of materials science. We have attempted to investigate the performance of DSSCs containing a series of mononuclear metal complexes with a dithiocarbamate ligand as new sensitizing dyes. Copper dithiocarbamate complexes [5,6] exhibit an intense ligand-to-metal charge transfer (LMCT) band at ~430 nm, as well as a large absorption around 640 nm based on the d–d transition due to delocalized d–orbitals in the sulfur atoms of the dithiocarbamate ligands. In addition, dithiocarbamate derivatives are versatile ligands with the ability to stabilize transition metals in a wide range of oxidation states, and useful as

bridging ligands for coordination polymers and metal clusters. In this paper we report the fabrication, performance and conducting properties of DSSCs containing mononuclear metal complexes with a hexamethylene–dithiocarbamate ligand, [M(Hm–dtc)$_n$] (M = Cu^{2+}, n = 2 (1); M = Ni^{2+}, n = 2 (2); M = Co^{3+}, n = 3 (3); M = Fe^{3+}, n = 3 (4); Hm–dtc$^-$ = hexamethylene-dithiocarbamate).

2. Experimental details

To prepare the DSSCs, the mononuclear metal complex (0.3 mol), [M(Hm–dtc)$_n$] 1–4, was mixed with TiO$_2$ paste (0.1 mL) for the electrode, and painted on an Indium Tin Oxide (ITO, sheet resistance 10 Ω/sq.) glass [7]. It was annealed at 50 °C for 0.5 hr. For the counter electrode, an aqueous solution of poly(3,4–ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) was mixed with deionized water (D. I.) at a volume ratio of 1:1. The mixed solution was spin–coated (2000 rpm for 10s) on ITO glass and annealed at 160 °C for 10 min. This process was repeated three times. The two prepared electrodes were assembled to fabricate a sandwich–type cell with a 50 μm spacer, and the electrolyte, which was a solution of lithium iodide (LiI, 0.5 M) and iodine (I$_2$, 0.005M) in polyethylene Glycol, was injected between the electrodes. The performance of the solar cell was measured under irradiation with an AM 1.5G (100 mW/cm^2) solar simulator (Bunkoukeiki Co., KP–3201). The cell device area was 0.30 cm^2.

3. Results and Discussion

Figure 1 exhibits the photocurrent density–voltage (J–V) curves for DSSCs 1, 2, 3, and 4. The short–circuit photocurrent density (J$_{sc}$) increases in the order 1 > 4 > 3 > 2. The open–circuit voltage (V$_{oc}$) is unaffected by changing the dye materials and the average value is 0.55 V. This could be because the V$_{oc}$ of DSSCs is determined by the energy difference between the conduction band energy (E$_{CB}$) of the semiconductor and the redox energy level [8]. The obtained power conversion efficiency (PCE, η) of DSSCs

based on dye 1 is 0.067 % (J$_{sc}$ = 0.25 mA/cm^2, V$_{oc}$ = 0.55 V, and FF = 0.49). The detailed parameters of the DSSCs (J$_{sc}$, V$_{oc}$, fill factor (FF), and η) are summarized in Table 1. In DSSCs with different [M(Hm–dtc)$_n$] complex dyes, the increase in the photocurrent density rather than V$_{oc}$ or FF contributes to improved efficiency.

In this study, the annealing temperature of TiO$_2$ was 50 °C, which is sufficiently low to apply on flexible devices. It has been reported that DSSCs performance improves with increasing annealing temperature of the TiO$_2$ electrode due to a decrease in the internal resistance and an enhancement of electron injection efficiency [9].

The Vis-IR absorption spectra of 1, 2, 3, and 4 in CHCl$_3$ are shown in Fig. 2. In dye 1, the absorptions occur mainly in the visible regions, extending into the near IR. This supports the observation that DSSCs based on dye 1 exhibit a higher J$_{sc}$ compared to that of DSSCs with others dyes. In dyes 2 and 3, there is pretty small absorption in the visible range with peaks at 640 nm and 620 nm, respectively.

The energy levels for [M(Hm–dtc)$_n$] complex dyes are also listed in Table 1.
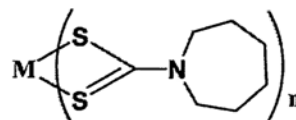
Scheme 1. Structure of [M(Hm–dtc)$_n$] (M = Cu^{2+}, n = 2 (1); M = Ni^{2+}, n = 2 (2); M = Co^{3+}, n = 3 (3); M = Fe^{3+}, n = 3 (4)).
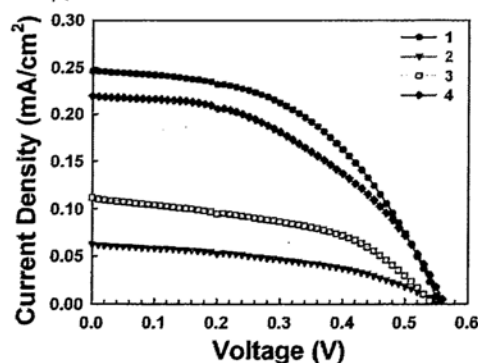
Fig. 1. Photocurrent density–voltage (J–V) curves for DSSCs: [Cu(Hm–dtc)$_2$] (1), [Ni(Hm–dtc)$_2$] (2), [Co(Hm–dtc)$_3$] (3), [Fe(Hm–dtc)$_3$] (4).

Table 1. Energy levels and photovoltaic performances of DSSCs with different dyes under AM 1.5.

Dye[*]	J_{sc} /mAcm^{-2}	V_{oc} /V	FF -	η /%	HOMO /eV	LUMO /eV
1	0.25	0.55	0.49	0.067	−4.92	−3.41
2	0.06	0.56	0.43	0.015	−5.13	−3.46
3	0.11	0.54	0.47	0.029	−5.08	−3.50
4	0.22	0.56	0.45	0.056	−4.78	−3.15

[*][Cu(Hm–dtc)$_2$] (1), [Ni(Hm–dtc)$_2$] (2), [Co(Hm–dtc)$_3$] (3), [Fe(Hm–dtc)$_3$] (4).

These highest occupied molecular orbital (HOMO) energy levels, obtained from cyclic voltammetry (CV), are sufficiently low to accept electrons from the I_3^-/I^- redox electrolyte (-4.8 eV). This means that the oxidized dyes could effectively be reduced and regenerated by electrolytes in DSSCs based on the mononuclear metal complex dyes. From the HOMO values, the energy levels for the lowest unoccupied molecular orbital (LUMO) were achieved according to the band edges of the absorption spectra as shown in Fig. 2. The energy levels for the LUMOs of the metal complexes are effectively well–matched with the E_{CB} of the semiconductor as sensitizing dyes to inject electrons into the TiO$_2$ electrode [10,11]. In DSSCs based on dyes 2 and 3, this would lead to increases in the photocurrent density, which is expected from the absorbance abilities in the visible range as a result of the negative shifting of LUMO levels closer to the E_{CB} of TiO$_2$ (−3.8 eV).
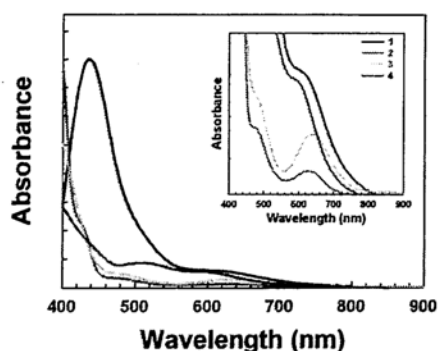

Fig. 2. Absorption spectra of dyes in CHCl$_3$: [Cu(Hm–dtc)$_2$] (1), [Ni(Hm–dtc)$_2$] (2), [Co(Hm–dtc)$_3$] (3), [Fe(Hm–dtc)$_3$] (4).

Electrochemical impedance spectra (EIS) were used to investigate the series resistances and interfacial charge transfer processes in DSSCs based on the different dyes [12-15].

Figure 3 (a) shows the Nyquist plots from impedance spectra measured with a frequency range of 20 Hz to 3 MHz at the open-circuit voltage with AM 1.5. The inset shows a magnification of the high frequency region. The ohmic serial resistance (R$_s$) corresponds to the electrolyte and the ITO resistance is 32 (DSSC 1), 30 (DSSC 2), 26 (DSSC 3), and 38 ohm (DSSC 4), respectively. Although the reason remains unclear, the difference in resistance is very small. There is no significant variation in the carrier transport resistance (R$_{CT}$), indicated by the arc at the high frequency range [16] as shown in the magnification figure, at the surface of the PEDOT:PSS counter electrodes. It is similar in value compared to that of the Pt based counter electrode [17]. The lowest impedance is observed in the DSSCs based on dye 1.
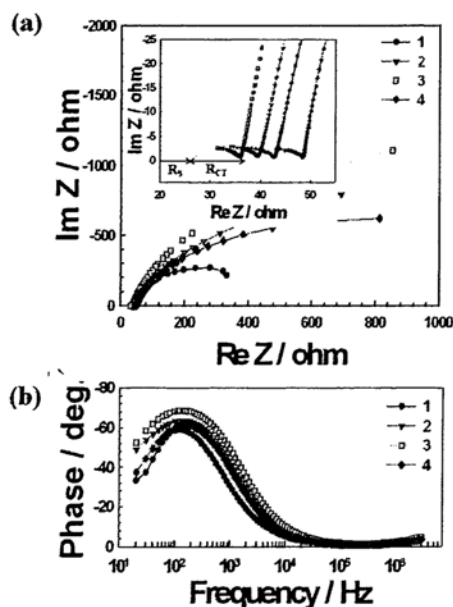

Fig. 3. Impedance spectra of DSSCs with different dye materials, [Cu(Hm–dtc)$_2$] (1), [Ni(Hm–dtc)$_2$] (2), [Co(Hm–dtc)$_3$] (3), [Fe(Hm–dtc)$_3$] (4), under V_{oc} and irradiation conditions. (a) Nyquist and (b) Bode plots. The applied bias voltage and ac amplitude is open–circuit voltage and 10 mV, respectively. The device area is 0.3 cm^2.

Figure 3 (b) shows the Bode phase angle with different dyes. The electron lifetimes obtained from the characteristic frequency angles [18,19] are 1.33 ms for **1**, 1.14 ms for **2** and **3**, and 1.06 ms for **4** respectively. In DSSCs based on dye **1**, it is possible that long lifetime implies more effective electron transfer between TiO_2/dye and electrolyte [13,15], resulting in increased photocurrent density. The results are consistent with the photovoltaic performances of these devices and energy levels for various dyes.

Using mononuclear metal complexes, DSSCs can be fabricated with PEDOT:PSS counter electrode. DSSCs based on the [Cu(Hm–dtc)$_2$] dye exhibited high efficiency, a relatively high photocurrent density, and a long lifetime for electrons injected into TiO_2. Further improvement of photovoltaic performance is expected to optimize the conditions.

4. Conclusions

Using mononuclear metal complexes, DSSCs can be fabricated with PEDOT:PSS counter electrode. DSSCs based on the [Cu(Hm–dtc)$_2$] dye exhibited high efficiency, a relatively high photocurrent density, and a long lifetime for electrons injected into TiO_2. Further improvement of photovoltaic performance is expected to optimize the conditions.

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