The research of employing polyoxometalates as pure-inorganic electron-transfer mediators on dye-sensitized solar cells

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ABSTRACT

Two Keggin-type polyoxometalates [$K_6Co^{II}W_{12}O_{40}$ (denoted as {$Co^{II}W_{12}$}) and $K_5Co^{III}W_{12}O_{40}$ (denoted as {$Co^{III}W_{12}$})] were firstly employed as the redox couple in dye-sensitized solar cells. Photocurrent density–photovoltage curves, cyclic voltammetry curves, photocurrent action spectra and UV–vis spectra demonstrated that {$Co^{II}W_{12}$} and {$Co^{III}W_{12}$} displayed weak absorption in the visible light region, potential matching with dye and TiO_2 conducting band, and significant conversion efficiency.

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Nowadays, the shortage of energy urges human being to explore renewable energy resources, especially to take full advantage of solar energy. Dye-sensitized solar cells (DSSCs) pioneered by O'Regan and Grätzel have attracted extensive attentions since their fabrication in 1991 [1]. Typically, a DSSC is mainly fabricated by a semiconductor dye-sensitized photoanode, an electrolyte and a counter electrode. The operational principle of electron transfer processes in the interior of DSSCs involves the injection of electrons of photo-excitation dye into the conduction band of TiO_2, and regeneration of the dye molecules by electron transfer from reduced species in an electrolyte. The electrolyte, as a hinge between two conductive transparent electrodes, provides internal electric conductivity, thus it plays one of crucial roles in determining the cell performance. The iodide/triiodide redox shuttle is a widely used electron-transfer mediator working in electrolytes of DSSCs which have reached 11.1% under irradiation of AM 1.5 [2a]. However, the development of semiconductors, photo-sensitizers, and counter electrodes [3] is hindered by the disadvantages of the I^-/I_3^- system, such as the absorption of visible light at high concentration, the corrosiveness towards the Pt cathode and sealing materials, the leakage from the cell due to the high vapor pressure of I_2, and the relatively high overpotential for dye regeneration [2j]. In order to avoid the problems associated with the iodide/triiodide system, more and more redox mediators have so far been exploited as alternative redox couples [2], such as the halogens, interhalogen, and pseudohalogens [2b], including Br^-/Br_3^- [2c,d], IBr_2/I_2Br, $SCN^-/(SCN)_3^-$ and $SeCN^-/(SeCN)_3^-$ [2e], but their chemical instability restricts their practical use. Another type of an alternative redox couple is transition-metal-complexes based systems, such as iron-complexes, copper-complexes [2g,h], Nickel-complexes [2i] and cobalt-complexes [2f]. Cobalt model complexes have favorable properties [3] in contrast to the I^-/I_3^- system, such as low absorption in the visible range, noncorrosiveness towards the Pt cathode, and facile tuning of their redox potential by varying the ligands, which make them extremely attractive as promising substitutions for triiodide species. In order to modify the electrochemical and physical properties of Co-complexes, the substituted bipyridine, tripyridine and phenanthroline units have been introduced as the ligands to develop a series of Co redox couples [4]. Grätzel et al. introduced a $Co^{II/III}$tris(bipyridyl)-based redox couple in conjunction with zinc porphyrin co-sensitized with Y123 dye and obtained a conversion efficiency of 12.3% [5]. In addition to changing ligands, another strategy in optimizing the efficiency of Co-complexes is to develop a co-mediator mixture that is employing two or more than two redox couples in electrolytes to accomplish the multistep electron transfer processes, thus decreasing the electron recombination to improve the conversion efficiency of DSSCs [4a,6]. Moreover, a number of researches have been concentrated on changing other components of DSSCs, such as counter electrodes [4b] and dye [7]. As far as we know, the majority of investigations of Co redox mediators are focused on a unitary form, which is metal–organic complexes; nevertheless, previous works presented that the efficiency of Co-complexes in DSSCs was limited by the rapid electron–hole recombination at the TiO_2 photoelectrode/electrolyte interface, slow dye regenerations and slow mass transport problems in

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the TiO_2 photoelectrode [7,8]. Hence, finding a new kind of Co redox mediator is always an urgent and necessary struggling direction to improve the efficiency of Co redox mediator fundamentally.

Polyoxometalates (denoted as POMs) are a well-known class of transition metal oxide nanoclusters with well-defined structures [9], catalytic activity [10], reversible multielectron electrochemical reactions [11], and unique photoelectrochemical properties [12]. POMs are soluble and stable in various kinds of conventional organic solvents. Meanwhile, the signals of the transition metal redox reaction could be detected in the transition metal based POMs in organic solvents. The redox potential of the transition metal in POMs can be tuned by changing different connections and building blocks. The aforementioned properties are beneficial for employing the POMs into DSSCs. S. Anandan et al. impregnated a POM in polyvinylidene fluoride polymer as a solid polymer electrolyte to restrain the electron–hole recombination in DSSCs [13]. In our previous work, POMs have been successfully introduced into counter electrodes [14], electrolytes [15], and dye [16]. Above-mentioned excellent properties and pioneering studies indicate that POMs are competent for optimizing the efficiency of electrolytes; however, POMs have not been utilized as electron-transfer mediators in DSSCs fundamentally.

In this paper, we attempt to employ two Keggin-type POMs [$K_6Co^{II}W_{12}O_{40}$ (denoted as $\{Co^{II}W_{12}\}$) and $K_5Co^{III}W_{12}O_{40}$ (denoted as $\{Co^{III}W_{12}\}$)] into DSSC electrolytes as a redox couple and obtained relatively high open circuit voltage (V_{oc}) and fill factors (FF). To the best of our knowledge, this is the first report of pure-inorganic-cobalt-compound redox shuttle for DSSCs. The utilizing of POMs as effective electron-transfer mediators may open new perspectives for developing high-performance redox couples of DSSCs.

In order to test the absorption of the redox couple in the visible region of spectrum, we carried out UV–vis absorption measurement of $\{Co^{II/III}W_{12}\}$. The lower the absorbance of oxidized and reduced species, the more visible light could be harvested by dye on a photoelectrode [4c]. As seen in Fig. 1, both oxidized and reduced species had maximum absorptions in the UV region. For $\{Co^{II}W_{12}\}$, $\lambda_{max} = 260$ nm and $\varepsilon = 10{,}968$ $(mol^{-1} \cdot dm^3 \cdot cm^{-1})$; for $\{Co^{III}W_{12}\}$, $\lambda_{max} = 262$ nm and $\varepsilon = 4447$ $(mol^{-1} \cdot dm^3 \cdot cm^{-1})$. Meanwhile, in the visible region, only the weak absorption tails remained, with $\varepsilon_{620\ nm}$ ($\{Co^{II}W_{12}\}$) $= 63$ $(mol^{-1} \cdot dm^3 \cdot cm^{-1})$ and $\varepsilon_{440\ nm}$ ($\{Co^{III}W_{12}\}$) $= 68$ $(mol^{-1} \cdot dm^3 \cdot cm^{-1})$. The weak absorption of the redox couple in the visible light ensures enough visible light to be harvested by dye other than the electrolyte, even if the concentration of the redox couple is high in the electrolyte. The result of UV–vis spectra indicates that, $\{Co^{II/III}W_{12}\}$ species are suitable to be applied in DSSCs as a redox couple.

To estimate the effect of redox mediator concentration on the performance of an electrolyte, five solutions with different concentrations of $\{Co^{II}W_{12}\}$ (0.01 M, 0.02 M, 0.03 M, 0.04 M and 0.05 M) were prepared.
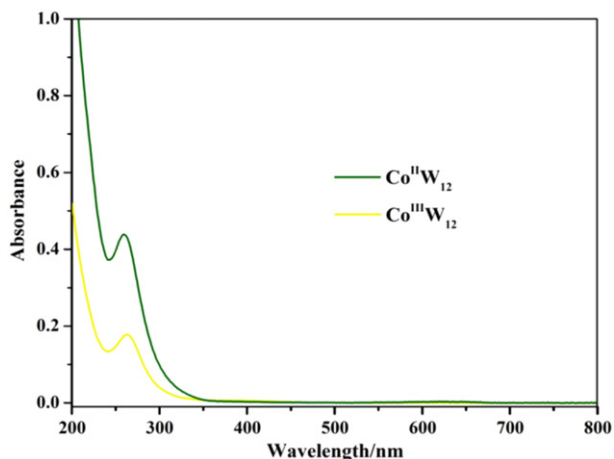
The Co^{III}/Co^{II} concentration ratio was maintained at 0.06 in each 3-methoxypropionitrile:DMF (v:v = 1:1) mix solvent (the photocurrent density–photovoltage (J–V) curves of DSSCs were shown in Fig. S1). Photovoltaic parameters of DSSCs based on electrolytes with different concentrations of $\{Co^{II}W_{12}\}$ were summarized in Table S1. As seen in Fig. 2, both V_{oc} and short current density (J_{sc}) are independent of the cobalt complex concentration above 0.01 M. According to a previous report [4c], the conductivity is enhanced along with the increasing of electron-transfer mediator concentration; meanwhile, the viscosity of an electrolyte is also raised, leading to the decrease of the diffusion of the redox mediator. As a result, the increase of conductivity is compensated by the decrease of viscosity.

The Co^{III}/Co^{II} concentration ratio is also an important factor on photovoltaic performance. To quantify this effect and find the optimal ratio of Co^{III}/Co^{II} concentration, six electrolytes with different ratios (0.05, 0.06, 0.07, 0.08, 0.09, 0.10) were prepared, each containing 0.02 M $\{Co^{II}W_{12}\}$ in 3-methoxypropionitrile:DMF (v:v = 1:1) mix solvent, and the Co^{III}/Co^{II} concentration ratio was controlled by changing the concentration of $\{Co^{II}W_{12}\}$. The optimal Co^{III}/Co^{II} ratio was found to be 0.07 (the photocurrent density–photovoltage (J–V) curves of DSSCs were shown in Fig. S2). Photovoltaic parameters of DSSCs based on electrolytes with different concentration ratios of Co^{III}/Co^{II} were summarized in Table S2. As seen in Fig. 3, there is an inverse relationship between the J_{sc} and the Co^{III}/Co^{II} ratio above 0.07, namely, the Co^{III} species made an adverse influence on J_{sc} when the Co^{III}/Co^{II} ratio was above 0.07. The J_{sc} of a DSSC is mainly influenced by dye loading and the electron–hole recombination [17]. Dye loading is not a variable quantity in our experiment condition. Therefore the electron–hole recombination should mainly affect the J_{sc} of a DSSC. This suggests that the electron–hole recombination reaction is advanced along with the increasing of the concentration of Co^{III} species [4c], thus resulting in the decrease of the J_{sc} values.

Appropriate additives are able to optimize the efficiency of an electrolyte thus improving the performance of a DSSC [18]. 4-Tert-butylpyridine (denoted as TBP) and $LiClO_4$ are known to be widely used as additives in electrolytes of DSSCs. TBP is able to increase V_{oc} but decrease J_{sc}. The first phenomenon is attributed to the following reasons: i) TBP is able to passivate the recombination centers to reduce back electron transfer at the dyed TiO_2 photoelectrode/electrolyte interface [18b,19,20a,b]; ii) the TBP also shifts the conduction band of TiO_2 negative in potential [20c]. The second phenomenon is explained by two concepts: ii) the negative shift in the potential of the conduction band of TiO_2 lowers the efficiency of electron injection from the photoexcited dye to the semiconductor [20d]; ii) as the concentration of TBP is increased, the viscosity of electrolytes increases and consequently
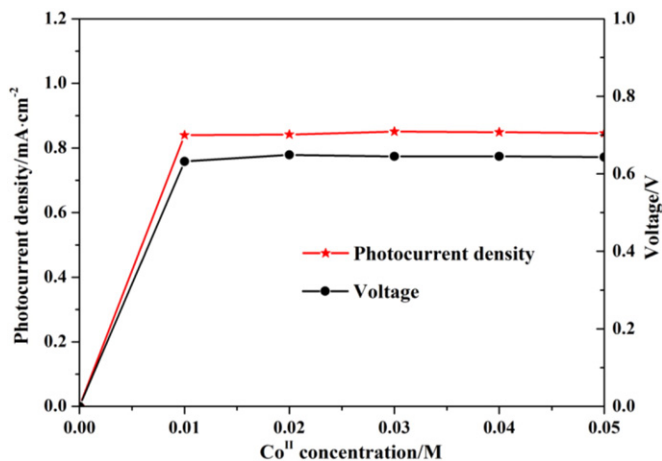

Fig. 1. UV–vis spectra of $\{Co^{II}W_{12}\}$ and $\{Co^{III}W_{12}\}$ in DMF (2×10^{-5} M).

Fig. 2. Influence of the redox mediator concentration on the current density and photovoltage measured under full AM 1.5 sunlight. The Co^{III}/Co^{II} concentration ratio was maintained at 0.06.