Effects of dye adsorption on the electron transport properties
in ZnO-nanowire dye-sensitized solar cells

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Mercurochrome and N3 dyes are employed to be the sensitzers in the ZnO-nanowire (NW) dye-sensitized solar cells (DSSCs). A lower fill factor is obtained in the N3-sensitized cell which results in comparable efficiencies in both ZnO-NW DSSCs although the N3 molecules possess a wider absorptive range for light harvesting. Electrochemical impedance spectroscopy and open-circuit photovoltage decay measurements are employed to investigate the electron transport properties in both ZnO-NW DSSCs. The results indicate that more abundant electron interfacial recombination occurs in the N3-sensitized ZnO-NW DSSC due to the higher surface trap density in the ZnO-NW photoanode after N3 dye adsorption. © 2007 American Institute of Physics.

Dye-sensitized solar cell (DSSC) is one of the most promising low-cost solar cells.1−3 A TiO2 nanoparticle (NP) film with a thickness of ~10 μm on a transparent conducting oxide (TCO) electrode is typically employed to be the anode of the DSSCs. A recorded solar light-to-current conversion efficiency of the DSSCs more than 10% is achieved using this high surface-area photoanode.1 Diffusion is recognized to be the major mechanism for electron transport through the NP film.2 It is essential for an efficient DSSC that the electron diffusion through the NP film should be significantly faster than the electron recombination with oxidized species adsorbed on the TiO2 surface or in the electrolyte. How to enhance the electron transport rate in the photoanode has attracted much attention for improving the efficiency of the DSSCs.2 Recently, the improvement of the electron transit in the anode of the DSSCs has been reported by using the single crystal and vertical ZnO nanowire (NW) arrays on TCOs.4,5 However, the efficiencies of the (Bu4N)2Ru(dcbpy)2(NCS)2 (N719 dye)-sensitized ZnO-NW cells with a NW length as long as 18–24 μm are still inferior to those of TiO2-NP DSSCs. It is suggested to be ascribed to insufficient surface area of the NW array for dye adsorption which results in the low photocurrents in the ZnO-NW DSSCs.4 The best performance of the ZnO-NW DSSCs to date is characterized by short-circuit current density ($I_{sc}$) of 5.8 mA cm$^{-2}$, open-circuit voltage ($V_{oc}$) of 0.71 V, fill factor (FF) of 0.37, and overall efficiency ($\eta$) of 1.5%.5 Apart from the low photocurrent, the low FF in the ZnO-NW DSSC, which implies the large series resistance existence and/or severe electron interfacial recombination occurring, is also a restriction for its efficiency. The dye and electrolyte employed in the reported ZnO-NW DSSCs, which are directly adopted from the TiO2-based DSSCs, may be not proper for ZnO material. It has been demonstrated that the performance of the ZnO-NP DSSCs decreases with increasing concentration of Ru(dcbpy)$_2$(NCS)$_2$ (N3) dye on the surface of the photoanodes since the formation of the aggregates (N3−Zn$^{2+}$) of N3 dyes with Zn$^{2+}$ ions results in inefficient electron injection from N3−Zn$^{2+}$ to ZnO-NP photoanodes.6 On the other hand, mercurochrome (C_{2}H_{2}Br_{2}HgNa_{2}O) is one of the best photosensitizer for ZnO photoanode7 to date and is much cheaper than the Ru-complex dyes. In the present work, mercurochrome- and N3-sensitized ZnO-NW DSSCs were fabricated to study the effect of the dye adsorption on the performances of the ZnO-NW DSSCs. Electrochemical impedance spectroscopy (EIS) and open-circuit photovoltage decay (OCVD) measurements are employed to investigate the electron transport properties in both ZnO-NW DSSCs.

Figure 1 shows the ZnO NWs grown on the seeded fluoro-doped tin oxide (FTO) substrates using chemical bath deposition method in the aqueous solution of zinc acetate and hexamethylenetetramine at 95 °C. Well-aligned ZnO NWs with an average diameter of 50 nm were formed on the FTO, as illustrated in Fig. 1(a). Figure 1(b) shows the high-resolution transmission electron microscopy HRTEM image of an individual ZnO nanowire, revealing that the nanowire possesses the single-crystal structure and the lattice spacing of around 0.52 nm along the longitudinal axis direction corresponds to the d spacing of ZnO (001) crystal planes. The corresponding selection area electron diffraction (SAED) is shown in the inset of Fig. 1(b). Two dyes, N3 and mercurochrome, were used for sensitizing the ZnO-NW electrodes. Liquid electrolyte solutions composed of 0.1M LiI, 50 mM I$_2$, 0.5M 4-tertbutylpyridine, and 0.6M 1-propyl-2,3-dimethyldiazolium in 3-methoxypropionitrile as well as

![FIG. 1. (a) Cross-section scanning electron microscopy image of ZnO nanowire arrays on FTO. (b) HRTEM image of an individual ZnO NW and its corresponding SAED pattern (inset).](image-url)
0.3\textit{M} Pr$_3$Ni and 30 mM I$_2$ in a 3:2 volume ratio of ethylene carbonate and acetonitrile were employed for N3- and mercurochrome-sensitized DSSCs, respectively.\textsuperscript{7,8} Figure 2 shows the photocurrent density (\(J\))-voltage (\(V\)) characteristics of the N3- and mercurochrome-sensitized ZnO-NW DSSCs (N3/ZnO NW and mercurochrome/ZnO-NW DSSCs) under the AM1.5 illumination at 100 mW/cm$^2$. With a nanowire length of 4.6 \(\mu\)m, the performances of both ZnO-NW DSSCs are summarized in Table I. \(J_{sc}\) of the N3/ZnO-NW DSSC is only slightly larger than that of the mercurochrome-sensitized one although the N3 molecules possess wider absorbptive wavelengths of 400–800 nm in comparison with mercurochrome (400–600 nm).\textsuperscript{7} On the other hand, the fill factor of the N3/ZnO-NW DSSC is significantly lower than that of the mercurochrome-sensitized one, which results in a comparable efficiency of the N3/ZnO-NW DSSC to that of the mercurochrome-sensitized cell.

Since the ZnO-NW arrays on FTO substrates employed in both cells are fabricated using the same procedure, the series resistances in both photoanodes are suggested to be the same. The lower FF in the N3/Zn-NW DSSC implies that the photoelectrons in the N3-sensitized electrode are easier to back react with I$_3^-$ in the electrolyte in comparison with the mercurochrome-sensitized one. Electron transport properties in both ZnO-NW DSSCs were investigated using EIS. EIS measurements were carried out under the illumination of AM1.5 100 mW/cm$^2$ by applying a 10 mV ac signal over the frequency range of $10^{-2}$–$10^5$ Hz on the top of voltage using a potentiostat with a frequency response analyzer. Figure 3 shows the Nyquist plots of the impedance data of both Zn-NW DSSCs under illumination at the applied bias of \(V_{oc}\). According to the diffusion-recombination model,\textsuperscript{9} a suggested equivalent circuit representing the nanowire DSSCs shown in the inset of Fig. 3 is employed to fit the impedance spectra for extracting the impedance of the nanowire portions. The results are the solid lines shown in Fig. 3. Estimation of the electron transport parameters in the nanowire portions of the DSSCs was conducted from the Nyquist plots of the nanowire portions according to the procedure demonstrated by Adachi et al.\textsuperscript{10} The electron transport resistance in ZnO NWs \((R_{w}=r_wL,\text{ as shown in the equivalent circuit, and } L\text{ is the thickness of the anode})\), charge-transfer resistance related to recombination of an electron \((R_k=r_k/L)\), first-order reaction rate constant for electrons being lost \((k_{eff})\), lifetime of an electron in ZnO NWs \((\tau)\), and the effective diffusion coefficient \((D_{eff})\) of an electron in ZnO NWs of the mercurochrome and N3/ZnO-NW DSSCs estimated from the impedance analyses are listed in Table I. The \(D_{eff}\) is calculated using the relation of\textsuperscript{10}

\[
D_{eff} = (R_\text{C}/R_w)(L^2/\tau).
\]

As revealed in Table I, the electron transport resistances in ZnO NWs \(R_w\) are quite similar in both cells whereas the electron recombination resistance \(R_k\) in the mercurochrome/ZnO-NW DSSC is larger than that in N3-sensitized cell. The smaller \(R_k\) in the N3/ZnO-NW DSSC, which indicates the more abundant electron interfacial recombination occurring, is consistent with the observation of the lower FF in the cell in comparison with the mercurochrome-sensitized one. Moreover, the smaller \(R_k\) results in the lower effective diffusion coefficient in the N3-sensitized ZnO NWs, which influences the \(J_{sc}\) of the ZnO-NW DSSC as well.

<table>
<thead>
<tr>
<th>DSSC</th>
<th>(\eta) (%)</th>
<th>(J_{sc}) (mA/cm$^2$)</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>(k_{eff}) (s$^{-1}$)</th>
<th>(\tau) (s)</th>
<th>(R_w) (\ohm)</th>
<th>(R_k) (\ohm)</th>
<th>(L) (\mum)</th>
<th>(D_{eff}) (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercurochrome/ZnO NW</td>
<td>0.83</td>
<td>3.30</td>
<td>0.516</td>
<td>0.489</td>
<td>5.13</td>
<td>0.1951</td>
<td>312.5</td>
<td>0.376</td>
<td>4.6</td>
<td>$9.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>N3/ZnO NW</td>
<td>0.73</td>
<td>3.86</td>
<td>0.565</td>
<td>0.333</td>
<td>5.84</td>
<td>0.1711</td>
<td>223.2</td>
<td>0.393</td>
<td>4.6</td>
<td>$7.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
the low trap density in the photoanode, i.e., a higher response time in response time in the low voltage region depends on the surface function of Wu et al. subsequent decay of the $V_{oc}$ after turning off the illumination, the response time is obtained by the reciprocal of the derivative of the decay curve normalized by the thermal voltage.\(^{11}\)

$$\tau_n = \frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}. \quad (2)$$

By assuming that the electron recombination is a first-order dependence on the electron concentration, the electron lifetime from high to low $V_{oc}$ is dominated by the factors of free electrons in the conduction band, electrons in the bulk traps after thermal detrapping to the conduction band, and electrons in traps after thermal detrapping to the conduction band then capture by the surface traps, respectively.\(^{11}\) The response time in the low voltage region depends on the surface trap density in the photoanode, i.e., a higher response time in the low $V_{oc}$ region represents the photoanode possessing a lower surface trap density.\(^ {11}\) Figure 4 shows the response time in the mercurochrome/and N3/ZnO-NW DSSCs as a function of $V_{oc}$. It reveals that the response times in the mercurochrome/ZnO-NW DSSC are higher than those in the N3-sensitized one in the low $V_{oc}$ region, indicating that the N3-sensitized ZnO NWs possess a higher surface trap density in comparison with mercurochrome-sensitized one. It has been demonstrated that the structure of the ZnO crystals is destroyed after loading the Ru-complex dyes. Protons releasing from the dye molecules in the ethanolic solution will dissolve ZnO to generate (N3–Zn\(^{2+}\)) aggregates.\(^{5}\) The observation of a higher surface trap density in the N3-sensitized ZnO NWs confirms that the N3 dye is harmful to the surface of the ZnO NWs. In addition to inefficient electron injection,\(^{5}\) increase of the surface trap density of the ZnO anode after dye adsorption is also a drawback of the Ru-complex dyes employed as the sensitizer in ZnO DSSCs although they perform very well in the TiO\(_2\)-based solar cells. On the other hand, the lower surface trap density of mercurochrome-sensitized ZnO NWs is consistent with the higher FF in the mercurochrome/ZnO-NW DSSC, indicating that the mercurochrome dye is more appropriate for the ZnO-based DSSC in comparison with the Ru-complex dyes.

In summary, the mercurochrome- and N3-sensitized ZnO-NW DSSCs were fabricated to investigate the effect of the dye adsorption on the performances of the ZnO-NW DSSCs. Although the N3 molecules possess wider absorptive wavelengths for light harvesting, similar efficiencies are obtained in both cells due to a considerably lower FF in the N3/ZnO-NW DSSC. EIS measurements reveal that the electron recombination resistance in the mercurochrome/ZnO-NW DSSC is larger than that in N3-sensitized cell. OCVD analyses further show that the N3-sensitized ZnO-NW anode possesses a higher surface trap density in comparison with the mercurochrome-sensitized one. It indicates that more electron interfacial recombination occurs in the N3-sensitized ZnO-NW DSSC due to the higher surface trap density in the ZnO-NW photoanode after N3 dye adsorption.

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