Investigation of Interfacial Charge Transfer Processes in Energy Conversion Devices

DISSERTATION

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Abstract

The past few decades have witnessed great technological advances in the energy conversion devices impacting our lifestyle. Knowledge of the interfacial charge transfer processes in those electrochemical energy conversion devices (e.g. solar cells, water splitting cells, etc.) is crucial to both the fundamental science development and the practical device optimization. The focus of this dissertation is to elucidate interfacial charge transfer processes related to dye-sensitized photocathodes and heterogeneous hydrogen evolution catalysis electrodes.

A fundamental and systematic investigation of NiO based p-type dye-sensitized solar cells (p-DSCs) using electrochemical impedance spectroscopy (EIS) is presented for the first time. Based on this, the low fill factors ($FF$s) of NiO p-DSCs are probed by investigating the charge transfer resistances of the key interfaces of the cells under various bias and illumination conditions. The quantitative analysis demonstrates that the $FF$ value is largely attenuated by the recombination of holes of NiO with the reduced dyes.

The effects of searching alternative and more efficient photocathodes are explored. The dye-controlled interfacial charge transfer is studied at ITO/dye and tin oxide/dye interfaces. The generation of high cathodic photocurrents via sensitizing n-type semiconductors is demonstrated. The study reveals a new perspective toward the selection of electrode materials for sensitized photocathodes.
The photoelectrode and electrocatalyst can be integrated into solar fuel production devices. We also study the heterogeneous hydrogen evolution reaction (HER) electrocatalysis using molecular clusters mimicking the active MoS\(_2\) edge sites. A dimeric molecular analog [Mo\(_2\)S\(_{12}\)]\(^{2-}\) is conceptually designed as the smallest unit possessing both the terminal and bridging disulfide ligands. The electrochemical investigations show that [Mo\(_2\)S\(_{12}\)]\(^{2-}\) is a superior heterogeneous HER catalyst under acidic conditions. Computations suggest that the bridging disulfide ligand of [Mo\(_2\)S\(_{12}\)]\(^{2-}\) exhibits a hydrogen adsorption free energy near zero (-0.05 eV). We use this catalyst as a model case to study the charge transfer process in the catalytic cycle. The work helps shed light on the rational design of HER catalysts and biomimetics of hydrogen evolving enzymes.
Dedication

This document is dedicated to my beloved family.
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I would like to sincerely thank my advisor, Dr. Yiyiing Wu, for his excellent guidance, patience, caring and providing me with a very positive research atmosphere throughout the five years during my Ph.D. studies. He not only teaches me how to do the scientific research efficiently, but also helps me improve my expression and presentation skills. It is my great honor to be Dr. Wu’s student. I have been enjoying spending five years in this lab.

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Chapter 1 Introduction

1.1 Dye-sensitized solar cell

There has been increased global awareness concerning the potential energy crisis in our society. Solar energy is believed to be one of the most promising clean energy options to meet our energy demand in the future, as the sun provides 10000 times more energy than the global energy consumption. People have been interested for a long time in the idea of harnessing the sunlight. Photovoltaic (PV) solar cell is the most common approach to generate an electrical power from the solar radiation.

Since invented by Grätzel et al. in 1991, dye-sensitized solar cells (DSCs) have remained the focus of intense investigations on the international level (The initial 1991 Nature paper has already been cited over 21250 times so far.), because of their low fabrication cost and competitive energy conversion efficiencies. This photovoltaic converter vividly mimics the photosynthesis process in nature, separating the light harvesting and charge-carrier transport function to two components: sensitizer and semiconductor, which is fundamentally different from those inorganic semiconductor solar cells or organic bulk heterojunction (BHJ) solar cells.

The research of DSC benefits from, and in turn promotes the developments of a lot of research fields, including electrochemistry, photochemistry, organic and organometallic synthesis, semiconductor, nano technology, etc. The DSCs with porphyrin sensitizers have
reached an energy conversion efficiency of 13%. The perovskite solar cell, which can be viewed as a special type of DSC with the CH₃NH₃PbI₃ family perovskites as the sensitizer, has reached an efficiency of ~20%. All these progresses in fundamental research and industrial developments show that DSC is a very promising technique for real-life application in near future. In this section we present a broad overview of the DSC, including the basic operation principles and the various key components.

![Diagram of a TiO₂ based DSC](image)

**Figure 1.1** Structure of a TiO₂ based DSC: liquid-based DSCs are comprised of a transparent conducting oxide (such as FTO) on glass, a nanoparticle photoanode (such as TiO₂) covered in a monolayer of sensitizing dye, a hole-conducting electrolyte (such as I₃⁻/I⁻) and a platinum-coated FTO glass back-contact.
Figure 1.1 shows the structure of a conventional DSC. A normal DSC consists of a transparent conducting oxide (TCO) substrate, a nanoporous TiO$_2$ film coated with a monolayer of sensitizer, an electrolyte with redox mediator, and a platinized counter electrode. The TCO substrate is usually degenerate semiconductor indium tin oxide (ITO) or F-doped tin oxide (FTO). The nanoporous TiO$_2$ film is usually several micrometer thick, consisting of TiO$_2$ nanoparticles with tens of nm size, which leads to transparent film and high surface area (surface roughness factor up to 1000). Light absorber is the key component of the solar cell. Various types of sensitizers, including Ru-based complexes, organic molecules, conjugated polymers, quantum dots, and emerging inorganic-organic hybrid perovskite materials, have been developed for the photosensitization of semiconductors. The most commonly used redox couple is I$^-$/I$_3^-$. The asymmetric redox chemistry of this redox couple ensures fast sensitizer regeneration with slow recombination at the semiconductor/electrolyte interface, which is the key of the success of DSC. Recently people also investigated cobalt-based complexes to replace I$^-$/I$_3^-$, in order to enhance the photovoltage and reduce the overpotential lost in the dye regeneration process. Detailed progress of redox mediators in DSC can be found in review articles. The counter electrode is used to electrocatalytically reduce triiodide to iodide. Pt is found to be a very good catalyst for I$^-$/I$_3^-$ redox couple. Carbon-based materials (e.g. graphene) are also applied for the purpose of reducing the fabrication cost.

Figure 1.2 shows the operation mechanism of traditional TiO$_2$ based DSC. The photoexcitation of a dye molecule is followed by the electron injection from the lowest unoccupied molecular orbital (LUMO) of the sensitizer into conduction band (CB) of the
n-type semiconductor (n-SC). The oxidized dye is then regenerated by oxidizing the redox couple in the electrolyte solution.

The crucial parameters of the solar cell performance characterization include open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), fill factor ($FF$) and the overall sunlight-to-electric-power energy conversion efficiency ($\eta$). The efficiency is given by the following expression:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}}$$

(Equation 1.1)

**Figure 1.2** Operation mechanism of the traditional DSC: the sensitizing dye absorbs a photon (energy $h\nu$), the electron is injected into the CB of the metal oxide (TiO$_2$) and collected. The oxidized dye is reduced by the electrolyte, which is regenerated at the counter-electrode to complete the circuit.
1.2 P-type DSC and sensitized photocathode

One tempting direction to further improve the energy conversion efficiency is to construct a tandem DSC (Figure 1.3), which is a combination of a sensitized photoanode from an n-type DSC (n-DSC) and a sensitized photocathode from a p-type DSC (p-DSC) in a simple sandwich configuration. In a tandem DSC, the overall photovoltage is additive, which can be maximized to be $> 1$ V. Another advantage of a tandem DSC over a single-absorber n-DSC is the capability of more efficient light absorption, since both the anode and the cathode in a tandem DSC are photoactive, while only the anode is photoactive in a n-DSC.

![Figure 1.3](image)

**Figure 1.3** Working principle of a tandem DSC, which consists of an n-type (left part) and p-type (right part) DSC. The red arrow shows the electron flow direction.
However, in a tandem DSC, the photocurrent is limited by the electrode with a lower photocurrent. Unlike the extensively studied n-DSCs, p-DSCs still suffer from low efficiencies and thus limit the overall efficiency of the resulting tandem DSCs. Therefore, improving the efficiency of the p-DSC is of significant importance. As shown in the right part of Figure 1.3, the p-DSC operates in the reverse mode of the conventional n-DSC in that the photo-excitation of a dye molecule is followed by the electron injection from the valance band (VB) of the p-type semiconductor (p-SC) to the dye (also known as the hole injection from the excited dye to the VB of p-SC). The reduced dye is then regenerated by reducing the redox couple in the electrolyte solution. Recently, several groups (including our group) have made considerable progress in enhancing the photovoltaic performance of p-DSCs, making it promising to construct highly efficient tandem DSCs in the future.

Sensitized photoanode and photocathode (Figure 1.4) also have crucial application in dye-sensitized photoelectrosynthesis cells (DSPECs) for solar water splitting and fuel production. For example, sensitized photocathode is important for proton and CO₂ reduction reaction. Considerable advances in this emerging direction have been made in the past few years.

Sensitized photocathode is indispensable to tandem DSCs and DSPECs. However, NiO suffers from parasitic absorption and slow hole diffusion, leading to unsatisfactory performances in p-DSCs. In addition, NiO is known to suffer from large pseudocapacitance, complex Ni(III)/Ni(II) surface states, electrochromic properties and easy dissolution in acids, which greatly limits its application for both fundamental mechanism investigation and practical DSPEC device optimization. Therefore,
understanding the limiting factor of current sensitized photocathode and searching for novel cathode material alternative to NiO are needed to cross the hurdle.

**Figure 1.4** Scheme of dye-sensitized photoelectrodes for DSCs and DSPECs: (a) photoanode, (b) photocathode. Arrows show the electron flow direction. Electron donor/acceptor represents the redox mediator or fuel production catalyst.

### 1.3 Chapter outlines

The introduction in Chapter 1 is followed by Chapter 2, which contains systematic investigation of NiO based p-DSC by electrochemical impedance spectroscopy (EIS). Semicircles observed in the impedance Nyquist plots are unambiguously assigned to the specific interfaces. A comprehensive equivalent circuit based on the transmission line model is generated for p-DSCs for the first time. Key recombination parameters, including the hole transport resistance, recombination resistance, chemical capacitance, and the hole
transport time and the hole lifetime, are extracted from impedance spectra and thoroughly discussed.

In Chapter 3, I focus on probing the low $FF$s and unsatisfactory efficiencies of NiO p-DSCs based on the discoveries in Chapter 2. The systematic impedimetric probing of NiO p-DSCs under full voltage regions and different illumination conditions is reported. An in-depth understanding of the hole recombination charge transfer processes in the NiO photocathode is provided, and the and critical reasons responsible for low $FF$ is discussed in detail. Under constant 1 sun illumination, the recombination resistance of the cell deviates from exponential relationship with the potential and saturates at around $130 \, \Omega \, \text{cm}^2$ at short circuit (SC) condition, which is ascribed to the overwhelming recombination with the reduced dye anion. The small dc resistance, mainly due to small recombination resistance ($R_{\text{rec}}$), correlates well with the slope of the steady state $J-V$ curve. The analysis demonstrates that the $FF$ value is largely attenuated by recombination with dye.

Chapter 4 comprises the exploration of n-SCs for alternative sensitized photocathodes. Our dye-sensitized mesoporous ITO and tin oxide electrodes are able to deliver high cathodic photocurrents close to the highest record for p-DSCs. Ultrafast transient absorption spectroscopy studies help to indicate that the cathodic photocurrent originates from reduction of the photoexcited sensitizer by electrons in the n-SCs. Furthermore, different sensitizers have been examined to study the charge transfer at the dye/semiconductor interface. It is found that the match of the energy level ($E(D^*/D^-)$) of the dye and the CB of n-SC is crucial for efficient and effective hole injection. Our results
reveal a new perspective toward the selection of electrode materials for sensitized photocathodes.

Chapter 5 presents the heterogeneous hydrogen evolution electrocatalysis study using MoS$_2$ molecular mimics. MoS$_2$ edges have been identified as the active sites for hydrogen evolution reaction (HER) electrocatalysis. A dimeric molecular analog [Mo$_2$S$_{12}$]$^{2-}$ is conceptually designed as the smallest unit possessing both the terminal and bridging disulfide ligands. The electrochemical investigations show that [Mo$_2$S$_{12}$]$^{2-}$ is a superior heterogeneous HER catalyst under acidic conditions. Computations suggest that the bridging disulfide ligand of [Mo$_2$S$_{12}$]$^{2-}$ exhibits a hydrogen adsorption free energy near zero (-0.05 eV). The work helps shed light on the rational design of HER catalysts and biomimetics of hydrogen evolving enzymes.

The conclusions and the outlook of this thesis are summarized in Chapter 6.

References


3. Deng, Y.; Peng, E.; Shao, Y.; Xiao, Z.; Dong, Q.; Huang, J. Scalable fabrication of efficient organolead trihalide perovskite solar cells with doctor-bladed active layers.


Chapter 2  Investigation of interfacial charge transfer and charge transport in NiO p-DSCs

2.1 Introduction

In nano-size semiconductors, no significant space charge layer can be established with particles whose dimensions are inferior to the Debye length. The light-induced charge separation relies on the kinetic competition at interface, instead of an electric field. DSC is a kinetically determined cell. A good understanding of the electrochemistry and kinetics at these interfaces is of paramount importance to both fundamental research and practical device optimization.

EIS is a frequency-domain approach which measures the current response to the application of an AC voltage as a function of the frequency.\textsuperscript{1} In the past decade, EIS has been widely used to study the kinetics of electrochemical and photoelectrochemical processes in n-DSCs.\textsuperscript{2-11} The Nyquist diagram under illumination typically features three semicircles, assigned to the charge transfer process at the platinized counter electrode (in the range of kHz), the diffusion and recombination of the photoinjected electrons in the porous TiO\textsubscript{2} film (in the range of 1-100 Hz) and Nernst diffusion within the electrolyte (in the range of mHz), respectively.\textsuperscript{4, 7} The transmission line model developed by J. Bisquert and his coworkers has achieved great success in describing the electronic processes in the porous metal oxide.\textsuperscript{2, 5} This model is widely employed to fit and analyze the impedance
data, and to investigate the properties of DSCs with different photoanode electrodes, electrolyte composition, and dye molecules. As such a convenient and powerful tool for the analysis of complex electrochemical systems, EIS has the potential to play an important part in the characterization and analysis of the p-DSCs and thus facilitates a better understanding of the ionic and electronic processes in the p-DSCs. However, to the best of our knowledge, there is no reported systematic study on the EIS application in the p-DSCs. Thus, we report a systematic and fundamental study of the impedance spectra of NiO p-DSCs. Experiments were designed to provide unambiguous evidences to assign the semicircle features observed in the Nyquist plots. By applying the equivalent circuit developed in the paper, kinetic processes are separated and key parameters can be extracted from the impedance spectra. Crucial information on the hole transport and recombination process, including recombination resistance, hole transport resistance, chemical capacitance and hole transport time and lifetime, is derived and discussed.

Intensity modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) is a powerful set of techniques for the characterization of DSCs, based on perturbing the system by sinusoidally modulated photo flux. It is similar to EIS in that (i) in general, a small amplitude modulation is superimposed on a larger dc component in order to ensure the linear response and (ii) the modulation frequency varies over several magnitude (mHz to MHz), and the phase and magnitude response is recorded and put into the corresponding transfer function. The summary of the three methods (EIS, IMPS, IMVS) is shown in Table 2.1. We also used IMPS/IMVS to probe the p-DSC and compare the information obtained from these different techniques.
Table 2.1 Experiment methods involving frequency response analysis

<table>
<thead>
<tr>
<th>Method</th>
<th>Input</th>
<th>Output</th>
<th>Transfer function</th>
</tr>
</thead>
<tbody>
<tr>
<td>EIS</td>
<td>Voltage ($V$)</td>
<td>Current ($j$)</td>
<td>$Z = \frac{dV}{dj}$</td>
</tr>
<tr>
<td>IMPS</td>
<td>Photon flux ($I$)</td>
<td>Current ($j$)</td>
<td>“$Y$” = $\frac{dj}{dI}$</td>
</tr>
<tr>
<td>IMVS</td>
<td>Photon flux ($I$)</td>
<td>Voltage ($V$)</td>
<td>“$Z$” = $\frac{dV}{dI}$</td>
</tr>
</tbody>
</table>

2.2 Experimental section

2.2.1 NiCl$_2$ paste preparation

The NiO paste was prepared using a modified method based on a triblock copolymer F-108 template.$^{29-30}$ Briefly, 1.0 g of anhydrous NiCl$_2$ and 1.0 g F-108 powder were ground to a fine powder and dissolved in 3.0 g deionized (DI) water and 6.0 g ethanol. The solution was kept undisturbed in a capped vial for three days at 30 °C. The resulting slurry was centrifuged to remove excess polymer. The concentration of Ni in the paste can be tuned by slightly reducing the solvent amount. For example, the paste containing 1.0 g of anhydrous NiCl$_2$, 0.9 g of F-108, 2.5 g DI water and 5.0 g ethanol can produce thicker film while still maintain decent transparency.

The atomic layer deposition (ALD) of aluminum oxide (Al$_2$O$_3$) is a standard process in semiconductor technology. The detailed experimental condition can be found in literature.$^{31}$
2.2.2 Solar cell fabrication

Glass pieces (2.5×2.5×0.3 cm$^3$) coated with FTO (Hartford Glass Co.) were pre-cleaned before each use, by sonication in soap water, DI water, ethanol and acetone solution, respectively. The sol-gel paste was deposited on top of the FTO substrates by doctor blade method, and the film area (0.25 cm$^2$) was confined by the scotch tape. The film was calcinated at ambient atmosphere in an oven at 450 °C for 0.5 hr, with the ramping rate of 2 °C min$^{-1}$.

The thickness of the film was controlled by the Ni paste concentration and layers of doctor blade. The films were prepared with two thickness: 0.6 μm and 1.5μm. The thin film (0.6 μm) was immersed in a P1 dye solution (0.3 mM in acetonitrile) for overnight, and the thick film (1.5μm) was immersed in a O2 dye solution (0.3 mM in acetonitrile) for overnight. The counter electrodes were platinized by thermal decomposition of H$_2$PtCl$_6$ (Aldrich) from isopropanol on a FTO at 385 ºC for 20 min. A 60 μm thick Surlyn 60 hotmelt foil (Solaronix) was used as the primary sealing material. Then, an electrolyte composed of 1.0 M LiI and 0.1 M I$_2$ in 3- methoxypropionitrile (MPN) was then injected through the hole predrilled on the counter electrode. The hole was sealed afterward with a glass cover slide. The cell made from thin and thick film was labeled as Cell N1 and Cell N2, respectively.

The TiO$_2$ n-DSC was made using N719 dye. A transparent TiO$_2$ nanoparticle layer was prepared by spreading a paste of TiO$_2$ nanoparticles (Solaronix) to the thickness of one layer of the scotch tape and the electrode was annealed at 450 °C for 30 min. The film area is 1 cm×1 cm. The film thickness is about 2 μm. The electrolyte is 1.0 M LiI, 0.1 M
I₂, 0.6 M 1,2 DMPII and 0.5 M TBP. The other steps and parameters are the same with those of the NiO DSC.

2.2.3 Electrochemical measurement

Photovoltaic measurements were performed using a solar simulator (Small-Area Class B, Solar Simulator, PV Measurements) providing 1000 Wm⁻² AM1.5G (1 sun) equivalent light intensity. The illumination intensity was tuned by inserting neutral density filters (Newport) with different transmission values. The $j-V$ curve was recorded using the Reference 600 potentiostat (Gamry Instruments, Warminster, PA). The scan rate of linear sweep voltammetry (LSV) is 1 mV s⁻¹.

EIS was tested with the same potentiostat in the frequency range of $2 \times 10^5$–$1 \times 10^{-2}$ Hz. The working electrode was connected to the metal oxide electrode, and the counter and reference electrode were connected to the platinized counter electrode. The AC amplitude was 10 mV. The cells were measured under certain illumination condition at $V_{OC}$ or in the dark under different bias. The EIS data were analyzed using Gamry Echem Analyst software.

IMVS/IMPS was tested under white light, using a CompactStat electrochemical analyzer and programmable modulight (Ivium Technologies, Fernandina Beach, FL). The amplitude was 10% of the bias light. IMVS and IMPS were tested under OC and SC, respectively. The time constant was obtained based on the peak frequency in the corresponding “Bode” plot:\(^{32-33}\)

\[
\tau_h = 1/(2\pi f_{\text{min, IMVS}}); \tag{Equation 2.1}
\]

\[
\tau_tr = 1/(2\pi f_{\text{min, IMPS}}). \tag{Equation 2.2}
\]
2.3 Results and discussions

2.3.1 Typical $J$-$V$ curve

The $J$-$V$ characteristic curve in Figure 2.1 reveals the photovoltaic performance of a typical NiO p-DSC N1 under 1 sun illumination. A $V_{OC}$ of 131 mV and a $J_{SC}$ of 1.24 mA cm$^{-2}$ were observed. The $FF$ is 0.34, and the energy conversion efficiency is 0.055%. The low $V_{oc}$ can be ascribed to the small difference between the VB edge of NiO and the redox potential of iodide/triiodide.

![Figure 2.1](image)

**Figure 2.1** $J$-$V$ characteristic curve of a typical NiO p-DSC N1 under 1 sun. The inset shows the chemical structure of the P1 dye.
2.3.2 Effect of AC amplitude

Figure 2.2 Nyquist plots of the NiO p-DSC using different AC amplitudes: (a) at $V_{OC}$ under 1 sun, (b) in the dark at 0.12 V bias.

In EIS measurements, the impedance spectra should be independent of the amplitude of the AC perturbation. Therefore, we first examined the choice of the AC amplitude to ensure a linear response. A NiO p-DSC was tested using different AC amplitudes (1 mV, 2 mV, 5 mV and 10 mV) at OC condition under 1 sun or at 120 mV bias in the dark. As shown in Figure 2.2, the Nyquist plots almost remain the same when different amplitudes are applied. Also, all the data can be perfectly fitted with Kramers-
Kronig transforms. Therefore, we conclude that our p-DSCs are in the linear response region with a 10 mV AC perturbation.

2.3.3 Impedance spectra of the cell with thin film

![Figure 2.3](image)

Figure 2.3 (a) Nyquist plot of the cell N1 under 1 sun at open circuit voltage; (b) the equivalent circuit used to fit the impedance data.

Figure 2.3 shows the Nyquist plot of the cell N1 under 1 sun at $V_{OC}$ (131 mV). Two semicircles, a smaller one in high frequency region (around 1k Hz) and a larger one in low frequency region (several Hz), were clearly detected. The equivalent circuit model in Figure 2.3b was used to fit the Nyquist plot. Each semicircle implying a charge transfer process, is represented by a resistance-capacitance (R-C) parallel circuit. For the sake of precise fitting, the capacitance element is replaced by a constant phase element (CPE) whose impedance can be expressed as: $^{34}$
\[
Z_{CPE} = \frac{1}{(j\omega)^\alpha Y_0}
\]

(Equation 2.3)

in which \(Y_0\) is a constant with the dimension of Siemens·sec\(^\alpha\), or Ss\(^\alpha\), and \(\alpha\) is an empirical constant. When CPE is in parallel with a resistance, the capacitance can be calculated by the following equation:\(^{35}\)

\[
C = \frac{(Y_0R)^{\nu\alpha}}{R}
\]

(Equation 2.4)

The fitting curve is shown as the red solid line in Figure 2.3a. The fitting parameters are summarized in Table 2.2.

Some control experiments were designed to determine the assignment of the two semicircles in the Nyquist plot. First, three counter electrodes with different amount of platinum loading (C1: 10 \(\mu\)g cm\(^{-2}\); C2: 2 \(\mu\)g cm\(^{-2}\); C3: 1 \(\mu\)g cm\(^{-2}\)) were prepared by thermal decomposition of \(\text{H}_2\text{PtCl}_6\) isopropanol solution. The counter electrode area was fixed strictly to be the same for the three cells. The dramatically changed semicircle at high frequency region in the Nyquist plots shown in Figure 2.4 asserts that it can be attributed to the charge transfer reaction at electrolyte/counter electrode interface. The low resistance of C1 is due to its high platinum loading which facilitates electrocatalytic activity of the oxidation reaction of the iodide at the anode.
Figure 2.4 (a) Nyquist plots of NiO p-DSCs (C1-C3) using different counter electrodes under 1 sun at open circuit voltage. Solid lines show the fitting curves. (b) Bode plots of the cell C3 under different illumination intensities (1 sun, 0.5 sun, and 0.2 sun). Solid lines show the fitting curves.

Table 2.2 Fitting results of the Nyquist plot of the cell N1 at $V_{OC}$ under 1 sun

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (± error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_s$ ($\Omega$)</td>
<td>22.5±0.3</td>
</tr>
<tr>
<td>$R_1$ ($\Omega$)</td>
<td>43.8±1.6</td>
</tr>
<tr>
<td>$Y_0$ 1($S \cdot s^a$)</td>
<td>(4.9±0.9)×10^{-5}</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>0.78±0.02</td>
</tr>
<tr>
<td>$R_2$ ($\Omega$)</td>
<td>144.4±3.8</td>
</tr>
<tr>
<td>$Y_0$ 2($S \cdot s^a$)</td>
<td>(7.1±0.4)×10^{-4}</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.88±0.02</td>
</tr>
</tbody>
</table>
In order to decide the kinetic process related to the second semicircle in Nyquist plot, the illumination intensity condition was varied from 0.2 to 1.0 sun by using neutral density filters. Figure 2.4b shows the selective comparison of Bode plots of the cell C1 under different light intensity at $V_{OC}$. The low frequency peak shifts obviously to the lower frequency region as the light intensity decreases, implying a trend of longer time constant. As we know, the recombination process is expected to be slow under low light intensities due to a low hole concentration in the NiO film. As the light intensity increases, the concentration of the photo-injected holes will also increase, speeding up the recombination charge transfer process. Therefore, the results in Figure 2.4b provide strong evidence to assign the second semicircle in the Nyquist plots to the recombination charge transfer process at the NiO/dye/electrolyte interface. The detailed comparison of the Nyquist plots and the summary of charge transfer resistance and time constant under different light intensities can be found in Figure 2.5-2.6. $\log(R_{rec})$ and $\log(\tau)$ are in linear relation with $\log(I)$. 

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Figure 2.5 Nyquist plots of the cell C1 at $V_{OC}$ under different illumination intensities (1 sun, 0.8 sun, 0.6 sun and 0.4 sun). Solid lines show the fitting curves.

Figure 2.6 Recombination charge transfer resistance and hole lifetime of the cell C1 under different illumination intensities (from 0.2 sun to 1 sun).

The physical meaning of each element in the equivalent circuit shown in Figure 2.3b has been clarified so far. $R_s$ is the ohmic series resistance of the cell, which is contributed by the sheet resistance of the substrates, resistivity of the electrolyte, and electrical contacts of the cell. $R_1$ and CPE1 represent the charge transfer resistance and double layer capacitance at the electrolyte/counter electrode interface, while $R_2$ and CPE2
stand for the recombination charge transfer resistance \( R_{\text{rec}} \) and capacitance \( C \) at the NiO/dye/electrolyte interface.

2.3.3 Impedance spectra of the cell with thick film

A simplified transmission line model\(^2\) \(^5\) (Figure 2.7a) was used to fit the impedance data of Cell N2. A representative Nyquist plot at \( V_{\text{OC}} \) under 1 sun illumination can be seen in Figure 2.7b. Based on the conclusion of Chapter 2.2.2, the higher-frequency semicircle in the Nyquist plots corresponds to the charge transfer at the counter electrode, while the lower-frequency one corresponds to the hole recombination process at the NiO/dye/electrolyte interface. The thick NiO film here allows for the study of the hole transport property. The hole transport resistance \( (R_t) \) merges with the high-frequency semicircle at the junction of the two arcs. Linear \( R_t \) can only be seen clearly when the first semicircle is very small (see Figure 2.8). Caution was taken to make the fitting decouple them well, and the crucial parameters, such as \( R_t \), the hole recombination resistance \( (R_{\text{rec}}) \) and the chemical capacitance \( (C_{\mu}) \) of NiO were obtained. Comprehensive fitting results of this Nyquist plot are shown in Table 2.3.
Figure 2.7 (a) Equivalent circuit of NiO p-DSCs. (b) Nyquist plots of Cell N2 at $V_{OC}$ under 1 sun illumination. The red solid line shows the fitting curve.

Figure 2.8 Nyquist plot of a p-DSC with small $R_{CE}$. 
Table 2.3 Fitting results of the Nyquist plot of the Cell N2 at $V_{OC}$ under 1 sun

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_s$ (Ω)</td>
<td>20.2</td>
</tr>
<tr>
<td>$R_{CE}$ (Ω)</td>
<td>13</td>
</tr>
<tr>
<td>$\alpha_{CE}$</td>
<td>0.83</td>
</tr>
<tr>
<td>$Y_{0\ CE}$ (S·s²)</td>
<td>$3.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>$R_t$ (Ω)</td>
<td>41</td>
</tr>
<tr>
<td>$R_{rec}$ (Ω)</td>
<td>116</td>
</tr>
<tr>
<td>$\alpha_{\mu}$</td>
<td>0.88</td>
</tr>
<tr>
<td>$Y_{0\ \mu}$ (S·s²)</td>
<td>$7.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

It is informative to discuss the trend of the key parameters of the transmission line model, $C_{\mu}$ and $R_t$, in NiO p-DSCs. As shown in Figure 2.9, $C_{\mu}$ features very slight variations over the range of measured potentials. The trend of $R_t$ is closely parallel to the variation of $C_{\mu}$. For TiO$_2$, according to the classical multiple trapping model,$^{36-37}$ only electrons in CB are mobile and hence the conductivity is directly proportional to the population of CB electrons.$^{17, 38}$ A slope close to 60 mV dec$^{-1}$ in log($R_t$)-$V$ plot was indeed observed in literature.$^9, 39-40$ However, the constant $R_t$ here unambiguously excludes the band-like transport scheme in NiO. The hole might hop from one localized states (i.e. Ni$^{3+}$) to another (see Figure 2.10).$^{41}$
Figure 2.9 (a) Hole recombination resistance $R_{\text{rec}}$, hole transport resistance $R_t$, and chemical capacitance $C_\mu$ as a function of $V_{\text{OC}}$. (b) Hole life time $\tau_h$ and hole transport time $\tau_{tr}$ (measured by EIS, IMVS and IMPS) as a function of $V_{\text{OC}}$. Note that IMPS was carried out under short circuit, and the $\tau_{tr}$ here is plotted vs. the $V_{\text{OC}}$ under the same light intensity.

The crucial physical parameters of the p-DSC were calculated using the following equations: 5, 10, 18, 42
\[ \tau_h = R_{rec} C_\mu \]  \hspace{1cm} \text{(Equation 2.5)}

\[ \tau_{tr} = R_t C_\mu \]  \hspace{1cm} \text{(Equation 2.6)}

\[ L = d \cdot \left( \frac{R_{rec}}{R_t} \right)^{1/2} \]  \hspace{1cm} \text{(Equation 2.7)}

\[ \eta_{cc} = 1 - \left( \frac{\tau_{tr}}{\tau_h} \right) \]  \hspace{1cm} \text{(Equation 2.8)}

\[ \sigma = \frac{d}{(A \cdot R_t)} \]  \hspace{1cm} \text{(Equation 2.9)}

\[ D = \frac{d^2}{\tau_{tr}} \]  \hspace{1cm} \text{(Equation 2.10)}

We further compare the hole transport time (\( \tau_{tr} \)) and lifetime (\( \tau_h \)) at different \( V_{oc} \) obtained from EIS with those from IMPS/IMVS. As shown in Figure 2.9b, the results are in close agreement. In addition, the hole transport property does not differ much at OC (measured by EIS) and SC (measured by IMPS). The advantages of using EIS are (i) it can separate the contributions of resistance and capacitance to the time constant (Here we found that both invariant \( C_\mu \) and \( R_t \) determine the constant \( \tau_{tr} \)); (ii) the hole transport and recombination resistances and time constants can easily be obtained under the exact same condition, so that the hole diffusion length (\( L \)) and charge collection efficiency (\( \eta_{cc} \)) at any particular operating condition can be calculated.

Under intense light and high \( V_{OC} \), both hole diffusion length (\( L \)) and charge collection efficiency (\( \eta_{cc} \)) (see Figure 2.11a) drop dramatically. Interestingly, opposite trend was observed for n-DSCs, in which \( L \) is longer at higher voltage. Here \( L \) is just slightly longer than the film thickness \( d \) at \( V_{OC} \) under 1 sun illumination, implying that only parts of the holes can be collected (\( \eta_{cc}=0.65 \)). This trend can be one of the reasons responsible for current loss at high voltage and the low \( FF \) of p-DSCs. The sharply
decreasing $L$ and $\eta_{cc}$ prevent the cell from achieving higher voltages, because injected holes cannot be well-collected in this instance.

**Figure 2.10** Scheme of two charge carrier transport models: (a) multiple trapping model; (b) hopping model.43

**Figure 2.11** Crucial parameters of Cell N2 as a function of $V_{OC}$: (a) hole diffusion length $L$ and charge collection efficiency $\eta_{cc}$; (b) hole diffusion coefficient $D$ and conductivity $\sigma$. 

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The conductivity $\sigma$ of NiO film is rather invariant, as shown in Figure 2.11b. The hole diffusion coefficient $D$ is in the order of $10^{-7}$ cm$^2$ s$^{-1}$ at the whole voltage region. $D$ reflects the hole transport ability of the NiO material, but is also sensitive to the film quality, preparation method and microscopic morphology. The $D$ of NiO in the literature is around $10^{-8} \sim 10^{-7}$ cm$^2$ s$^{-1}$.44-45

2.3.4 Using EIS to study the effect of ALD blocking layer on interfacial charge transfer

In this section we show an example, using EIS to help investigate the charge transfer processes in p-DSCs. To reduce the recombination in p-DSCs, the surface of NiO could be coated with a thin blocking layer of an insulating material. Aluminum oxide (Al$_2$O$_3$), which has a large band gap of $\sim 9$ eV, has been used for blocking charge carrier recombination in n-DSCs and thus becomes a natural choice for us. EIS was performed on the nontreated and 1 cycle of ALD alumina-treated NiO-based DSCs to gauge the effect of the alumina coating on the fundamental charge carrier transfer in the cell.
Figure 2.12 (a) Nyquist plots of the untreated and alumina-deposited NiO based p-DSCs in dark condition, at 0.13 V bias potential. (b–d) Plots of chemical capacitance, charge carrier lifetime, and recombination resistance of the two types of cells against applied voltage, as obtained from numerical fitting of (a).

As the recombination process is voltage dependent, it is more meaningful to compare the recombination parameters on the same potential scale. Figure 2.12a shows the Nyquist plots of the untreated and alumina-treated cell in dark at the bias of 0.13 V. The equivalent circuit model in Figure 2.3b was used to fit the plots. The experimental data are plotted as dots, while the fits are plotted as lines. The chemical capacitance, the recombination resistance, and the hole lifetime of the two cells in the dark under different bias are plotted in Figure 2.12b-d. Clearly, the alumina coating imparts a much higher
resistance to the recombination of separated charge carriers. The chemical capacitance is found to decrease upon the coating of alumina (maybe due to the surface passivation); however, the overall product of the recombination resistance and chemical capacitance is higher for alumina-coated electrodes than the untreated ones. Consequently, the hole lifetime is increased in the alumina-coated NiO electrodes.

2.4 Conclusion

EIS is demonstrated as a powerful steady-state technique to study p-DSCs. Typically, two semicircles and a linear line \((R_t)\) were observed in the Nyquist plot. Equivalent circuits have been applied to extract pivotal parameters characterizing the hole transport and recombination at the NiO/electrolyte interface and the charge transfer reaction at the counter electrode. The recombination resistance and the hole lifetime of the p-DSC decrease exponentially with increasing voltage. The hole transport time is relatively constant at different bias condition. EIS analysis shows that both the recombination resistance and hole lifetime are higher for ALD alumina-treated DSCs, which demonstrates that ALD alumina acts as a recombination blocking layer.

References


37. Peter, L. Transport, trapping and interfacial transfer of electrons in dye-sensitized


(41), 16134-16139.
Chapter 3  Probing the low $FF$ of NiO p-DSCs: effect of interfacial recombination charge transfer

3.1 Introduction

A p-DSC works in a mode inverse to the traditional n-DSC, and can be integrated with an n-DSC to construct a tandem DSC, which holds great promise to overcome the efficiency bottleneck. A dye-sensitized photocathode also has the promising application in the production of solar fuels via artificial photosynthesis. Though lagging behind, the study of the p-DSC has attracted increasing attention recently. As a result, considerable progress has been made in the semiconductor materials, the sensitizer design and the exploration of novel redox mediators. However, the efficiencies of p-DSCs are still far from their n-type counterparts so far. As one of the key performance parameters, the $FF$ value of p-DSCs in most published papers is only 0.3–0.4, which is just half of that of the TiO$_2$-based n-DSC and severely limits the energy conversion efficiency.

The $FF$ is a measure of “squareness” in the $J$-$V$ curve. In conjunction with $V_{OC}$ and $J_{SC}$, it determines the maximum obtainable power of the cell. Generally, a p-n junction solar cell can be simulated using a basic diode model (Figure 3.1) including an ideal diode, shunt resistance $R_{sh}$, and series resistance $R_s$. Theoretically, $R_{sh}$ determines the flatness of the $J$-$V$ curve at SC, while $R_s$ determines the vertical sharpness of the $J$-$V$ curve at OC. A good $FF$ value calls for a large $R_{sh}$ and small $R_s$. Under the ideal condition with infinitely
large $R_{sh}$ and zero $R_s$, the theoretical maximum $FF$ for a solar cell is a function of $V_{OC}$ and ideality factor $m$:\textsuperscript{22-24}

$$\text{FF} = \frac{V_r - \ln(V_r + 0.72)}{V_r + 1}$$

(Equation 3.1)

in which $V_r = qV_{OC}/(mk_BT)$, and $m$ is the diode ideality factor. The basic diode model shown in Figure 3.1 can also be applied to DSCs, with the diode representing the semiconductor/electrolyte interface. The closest element to $R_{sh}$ is the resistance at substrate/electrolyte interface. It should be noted that this kind of interpretation is far from flawless, as pointed out by J. Bisquert in a recent book chapter,\textsuperscript{21} because both $R_{sh}$ and $R_s$ are voltage dependent for n-DSCs. Nevertheless, the general picture of the model holds true and the maximum $FF$ value can still be obtained from Equation 3.1.

Figure 3.1 A basic electrical model for solar cells.

According to Equation 3.1, a p-DSC with a $V_{OC}$ of ~150 mV and ideality factor $m$ of 1 should have a $FF$ of 0.58. Therefore, although the $V_{OC}$ of p-DSC is not high, the $FF$ should have much room for improvement. In previous papers, several authors noticed this
problem and speculated a couple of reasons for low $FF$. Zhang et al. pointed out that, besides the low $V_{OC}$ and the influence of ideality factor $m$, the short hole diffusion length and insufficient charge collection might account for the relatively low $FF$. They synthesized NiO nanorod to enhance the hole transport property and achieved a record $FF$ of 0.42 under 1 sun.\(^7\) Kang et al. suggested that the low $FF$ results from the high series resistance associated with the low hole conductivity in p-NiO.\(^25\) However, the $FF$ value was not improved even when the conductivity was enhanced by 2 orders of magnitude after CdS sensitization. In a recent review, Odobel et al. mentioned that back charge recombination and high dark current limit the $FF$ in p-DSCs.\(^5\) In general, all these concerns make sense to some extent, because high dark current and large series resistance resulting from large hole transport resistance are supposed to suppress $FF$ value. However, there lacks specialized, detailed and comprehensive study that focuses on analyzing the influence of different factors and giving a clear and unambiguous answer to this fundamental problem.

In this work, we report a systematic probing of NiO p-DSCs under full voltage regions and different illumination conditions using EIS. We aim at a better understanding of physical mechanisms involved in the cell performance for finding out the critical reasons for the low $FF$ and unsatisfactory efficiency. As shown in Chapter 2, EIS is a frequency-domain approach widely used to characterize ionic and electronic processes in a variety of solar cells,\(^22\) and different kinetic processes can be clearly decoupled and separated by their different responding frequency. Moreover, in the limit of zero frequency, the dc resistance
\( R_{dc} \), per area) obtained by EIS is the differential resistance of the steady state \( J-V \) curve\(^{20, 22, 26} \)

\[ R_{dc} = Z(\omega=0) = (dJ/dV)^{-1} \]  
(Equation 3.2)

In other words, \( R_{dc} \) determines the slope of \( J-V \) curve at each operating point. Under 1 sun illumination, by applying different bias, we can use EIS to track the trend of each type of resistance and obtain information responsible for the change of \( R_{dc} \) and thus the slope of \( J-V \) curve.

3.2 Experimental section

3.2.1 Cell preparation

Detailed procedures of preparation of Cell N2 are shown in Chapter 2.2.2.

3.2.2 Electrochemistry characterization and analysis

Photovoltaic measurements were performed using a solar simulator (Small-Area Class B, Solar Simulator, PV Measurements), which provides AM 1.5G illumination with an equivalent light intensity of 1000 Wm\(^{-2} \) (1 sun). The current-voltage curve was recorded using a CV-50W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN). The IR drop was corrected using the following equation (the notation used in this chapter is summarized in Chapter 3.5 for clarity):\(^{22} \)

\[ V = E_F - J \Box R_S \]  
(Equation 3.3)

in which \( R_S = r_s + R_{CE} + (1/3)R_t \).  
(Equation 3.4)
EIS was tested with an EIS600 potentiostat (Gamry Instruments, Warminster, PA) in the frequency range of $2 \times 10^5$–$1 \times 10^{-1}$ Hz. The working electrode was connected to the NiO electrode, and the counter and reference electrode were connected to the platinized counter electrode. The AC amplitude was 10 mV. The EIS data was analyzed using Gamry Echem Analyst software with the equivalent circuit shown in Figure 2.7a.

The impedance parameters were calculated using the Equations 2.5-2.8.\textsuperscript{20,27-29}

The $R_{rec,0}$ shown in Table 3.1 was calculated using the following equations:\textsuperscript{20,30-31}

For FTO: $J_0 = \frac{RT}{nF \cdot R_{rec,0}}$ (Equation 3.5)

and $n=2$;

For NiO: $J_0 = \frac{mRT}{F \cdot R_{rec,0}}$ (Equation 3.6)

and $m=0.93$ for Cell N2.

### 3.3 Results and discussions

#### 3.3.1 J-V curve and impedance results under 1 sun illumination

Figure 3.2 gives an example of the $J$-$V$ curve of a typical p-DSC Cell N2 under 1 sun illumination and in the dark. The corresponding values of $V_{OC}$, $J_{SC}$, $FF$ and energy conversion efficiency $\eta$ are listed in Table 3.2. The relatively low $V_{OC}$ (127 mV) is usually attributed to small energetic difference between the VB edge of NiO (+0.5 V vs. NHE) and redox potential of iodide/triiodide mediator (+0.35 V\textsuperscript{32} vs. NHE). The dark current clearly shows the diode feature.
Figure 3.2 J-V curve of a typical p-DSC Cell N2 under 1 sun illumination and in the dark. The inset shows the molecular structure of the sensitizer O2.

The basic EIS analysis of the cell N2 has been discussed in Chapter 2.3.3. The shape of the J-V curve is controlled by the dc resistance, $R_{dc}$. In p-DSCs, $R_{dc}$ can be expressed as \(^{22,33}\)

$$R_{dc} = r_s + R_{CE} + (1/3)R_t + R_{rec} \quad \text{(Equation 3.7)}$$

In order to identify which resistance dominates, we probed the cell’s impedance under 1 sun illumination with varying dc bias. As shown in Figure 3.3a, $R_{rec}$ is much larger than the other resistance in the whole range of bias. $R_t$ is almost constant in the whole voltage region. The small $R_t$ also means the quasi-Fermi level ($E_F$) is homogenous in NiO: even at SC the potential drop across the NiO film ($J_{SC} \cdot R_t / 3$) is only 10 mV. The error bars were calculated to be smaller than the data symbols and thus were omitted.
Figure 3.3b compares the $R_{dc}$ values obtained from EIS and the differential of the $J-V$ curve. The close agreement between the black squares and the red circles demonstrates the correlation between the impedance data measured at different dc bias under 1 sun illumination and the shape of the $J-V$ characteristic curve. The $R_{dc}$ of the cell in the dark is also presented in the figure, which is well correlated to the diode behavior of the dark $J-V$ curve shown in Figure 3.2.
Figure 3.3 Resistances as a function of bias: (a) $r_s$, $R_{CE}$, $R_t$ and $R_{rec}$ (under 1 sun illumination); (b) $R_{dc}$ determined from EIS (under 1 sun illumination and in the dark) and the slope of $J$-$V$ curve (under 1 sun illumination).
3.3.2 Recombination at NiO/dye/electrolyte interface

From the above discussion, the small $R_{\text{rec}}$ under 1 sun determines the small $R_{\text{dc}}$, and thus leads to the fan-shaped $J-V$ curve. Therefore, it is crucial to understand the processes controlling $R_{\text{rec}}$.

The $E_F$ of holes in NiO can be varied by potentiostatic control or manipulating the light intensity. In Figure 3.4, we compare the measured $R_{\text{rec}}$ of Cell N2 under three experimental conditions: (i) under different illumination intensities at $V_{\text{OC}}$, (ii) under 1 sun illumination applying different dc bias and (iii) in the dark. At $V_{\text{OC}}$, the $E_F$ is flat and there is no net current flowing in the cell. Under condition (ii) and (iii), $iR$ drop correction has been done to adjust the applied bias to the $E_F$ (vs. $E_{\text{redox}}$) for fair comparison.\textsuperscript{22,34} $R_t$ and $C_{\mu}$ values remain similar under the three conditions. Under condition (i), the dependence of $R_{\text{rec}}$ on the $V_{\text{OC}}$ follows an exponential function, with a slope of 39.5 mV dec\textsuperscript{-1}. The exponential dependence of $R_{\text{rec}}$ on the potential is as expected, because the hole density at VB of NiO increases exponentially when $E_F$ is tuned downwards, which augments the recombination rate. The slope here is related to the recombination mechanism and the reaction order of the hole.\textsuperscript{35}

However, the $R_{\text{rec}}$ measured under condition (ii), as also exhibited in Figure 3.3a, is much smaller and does not follow the monotonic exponential relationship. A saturation of $R_{\text{rec}}$ at only around 130 $\Omega$ cm\textsuperscript{2} indicates the existence of large recombination rates even near SC. It is worth mentioning that the exponential dependence of $R_{\text{rec}}$ on voltage is still well maintained under condition (ii) in TiO$_2$ n-DSCs,\textsuperscript{36} which illustrates that the remarkable difference we found here is unique to NiO p-DSCs.
Since light is the only different parameter under the three conditions, it is reasonable that an additional “photoinduced” recombination accounts for the significant decrease in $R_{\text{rec}}$ upon light illumination. Two possible mechanisms are responsible for the large recombination rates under an intense irradiation. One is the increased recombination with the photo-reduced dyes (designated as $R_{\text{rec-dye}}$), and the other is the increased recombination with the electrolyte (designated as $R_{\text{rec-el}}$) due to the increased local concentration of I$^-$.\textsuperscript{37-38}

It is not easy to directly probe the local concentration of I$^-$ in the pores of the semiconducting film experimentally. We notice that some insightful simulation studies of n-DSCs have been reported recently. Miettunen et al. developed a numerical 2D transient model of n-DSCs, and found the concentration of I$_3^-$ at the photoelectrode side increases from $\sim$30 mol m$^{-3}$ to $\sim$ 45 mol m$^{-3}$ in a working cell.\textsuperscript{39} Barnes et al. presented a complete numerical simulation of n-DSCs to assess the importance of different loss pathways under various operational conditions. At SC under 1 sun illumination, the concentration of I$_3^-$ in the 12.5 μm TiO$_2$ film increases from the initial 0.05 M to $\sim$0.12 M.\textsuperscript{40} The variation of local iodide concentration in our NiO p-DSCs should be smaller, because the net reaction at TiO$_2$ photoanode or NiO photocathode is the conversion between I$_3^-$ and I$^-$, and the photocurrent of the p-DSC is one order of magnitude lower. In addition, since $R_{\text{rec-el}}$ is inversely proportional to the concentration of I$^-$,\textsuperscript{21} a more than two orders of magnitude decrease of $R_{\text{rec}}$ at SC under condition (ii) calls for a 100-fold increase of local iodide concentration. Considering that the bulk concentration of iodide in the electrolyte of Cell A is already as high as 1 M, a concentration higher than 100 M is not realistic.
Therefore, the unique trend of $R_{\text{rec}}$ under condition (ii) in Figure 4 should be primarily ascribed to the existence of $R_{\text{rec-dye}}$, instead of significantly decreased $R_{\text{rec-el}}$. Under 1 sun, the resistance is dominated by the recombination with the reduced dye in the small voltage region, and by the recombination with the electrolyte in the high voltage region. The former resistance shows nearly no dependence on the voltage (the flat region in Figure 3.4); while the latter one shows an exponential dependence. The combined effect can then be described by a resistance in parallel with a diode. This will be discussed in details in Section 3.3.3. It is worth emphasizing that the flat $R_{\text{rec-dye}}$ seems anti-intuitive at first glance, because $R_{\text{rec-dye}}$ is also supposed to be inversely proportional to the hole density at VB of NiO. A possible explanation is that the recombination between NiO and dye anion takes place through localized surface states (i.e. surface Ni$^{3+}$).
Figure 3.4 $R_{\text{rec}}$ measured by EIS using two experimental configurations: (i) under different illumination at $V_{\text{OC}}$, (ii) under 1 sun illumination at different dc bias, and (iii) in the dark applying different bias. The voltages were corrected to $E_F$.

3.3.3 Shunt resistance and the electric circuit model

The FTO substrate/electrolyte interface is believed to be a major current leaking pathway under low bias in n-DSCs, and determines $R_{\text{sh}}$ in the diode model of n-DSC. However, Figure 3.5 clearly demonstrates that this is not the case for the NiO p-DSC. $R_{\text{rec}}$ of Cell N2 is much smaller than that of a blank FTO-Pt cell at equivalent voltage. Besides, the capacitance (data not shown) is several mF for Cell N2 and several μF for the blank cell. Thus, unlike TiO$_2$ which becomes an insulator at low bias, NiO is much more reactive with I$^-$ at the whole voltage region. The leaking current through the FTO/electrolyte interface is negligible in p-DSCs.
Figure 3.5 $R_{\text{rec}}$ of the NiO p-DSC Cell N2 and a blank FTO-Pt cell with identical electrolyte composition in the dark.

From the charge transfer resistance at zero bias $R_{\text{rec,0}}$, we can get the dark exchange current $J_0$. Table 3.1 compares $R_{\text{rec,0}}$ and $J_0$ for the TiO$_2$ based n-DSC, NiO based p-DSC and bare FTO, indicating that $J_0$ increases in the order TiO$_2$ < FTO < NiO. This observation has several implications. First, a compact NiO back layer seems not necessary for the p-DSC, because it facilitates, instead of blocking the recombination with electrolyte. There have been several papers using a thin NiO blocking layer to suppress recombination, so it is worth experimentally testing the effect of the blocking layer. In the dark, the cell with NiO UL (spin-coated 0.4 M nickel acetate before heating, 50 nm thick) shows higher dark current than FTO. NiO is more reactive with I$^-$ at the whole voltage region. Therefore, NiO UL would actually facilitate the recombination with electrolyte, although it might enhance
the contact between the film and FTO. Opposite condition is found in n-DSCs. The TiO$_2$ UL systematically lowers the recombination current at all voltages.$^{41}$

**Figure 3.6** Dark $J$-$V$ curve of a blank FTO cell and a cell with NiO UL

Secondly, according to the diode equation:$^{22}$

$$J_d = J_0(e^{qV/k_B T} - 1)$$

(Equation 3.8)

A large $J_0$ value makes for a high dark current $J_d$, which would suppress FF.

**Table 3.1** Comparison of $R_{rec,0}$ and $J_0$ of the n-DSC, p-DSC and bare FTO

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{rec,0}$ (Ω cm$^2$)</th>
<th>$J_0$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>$10^{-10}$ to $10^{-6}$ ref$^{[42]}$</td>
</tr>
<tr>
<td>FTO</td>
<td>$1.1 \times 10^6$</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>NiO</td>
<td>$3.2 \times 10^4$</td>
<td>$7.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
After analyzing the crucial interfaces, we can establish an electric circuit model adapted to NiO p-DSCs for the representation of $J-V$ curve (see Figure 3.7). The characteristic of $R_{\text{rec-el}}$ can still be described by a diode, which dominates at the high voltage region. $R_{\text{rec-dye}}$, which is often ignored in the model of n-DSCs, should lie in parallel with the diode at the same interface and actually plays a critical role to the cell performance at the low voltage region. $R_{\text{BL}}$ represents the FTO back layer/electrolyte interface. Because $R_{\text{BL}}$ is much larger than $R_{\text{rec-dye}}$ and $R_{\text{rec-el}}$, the resistance measured by EIS is $R_{\text{rec}} = R_{\text{rec-dye}} \parallel R_{\text{rec-el}}$. Compared with the classic solar cell model shown in Figure 3.1, the shunt resistant $R_{\text{sh}}$ is dominated by $R_{\text{rec-dye}}$.

Figure 3.7 An electric model adapted to the typical NiO p-DSC.

### 3.3.4 Theoretical maximum FF of the cell

The quantitative analysis of the influence of the different factors on cell performance is shown in Figure 3.8 and summarized in Table 3.2. After $R_s$ (total series resistance of the cell, $R_s = r_s + R_{\text{CE}} + (1/3)R_0$) subtraction, the $FF$ and $\eta$ are enhanced by 6%.
and 19%, respectively. As a comparison, Hamann et al. did similar correction for an N3 sensitized TiO$_2$ n-DSC using \([\text{Co}(t\text{-Bu}_2\text{bpy})_3]^{3+/2+}\) mediator and found that the $FF$ is increased from 0.49 to around 0.8.$^{43}$ Thus, the series resistance is not the limiting factor of low $FF$ in p-DSCs, probably because of the low current. Although the hole diffusion coefficient of NiO is not comparable to the electron diffusion coefficient of TiO$_2$, the $R_t$ is still quite small due to the thin film, and its influence on $FF$ is insignificant.

The net photocurrent of the cell can be formulated by

$$J_{\text{net}} = J_{\text{inj}} - J_{\text{rec}}$$

(Equation 3.9)

where $J_{\text{rec}}$ is the recombination current, an opposite flow that internally annihilates the moving carriers. For n-DSCs people often assume $J_{\text{inj}} = J_{\text{SC}}$, because recombination is minimum at SC. In p-DSCs, $J_{\text{inj}}$ must be higher than $J_{\text{SC}}$, because of the series recombination with dye. This is also confirmed by the $J$-$V$ curve shown in Figure 3.2 where current in negative bias is higher than $J_{\text{SC}}$. If we artificially eliminate the recombination with dye by assuming $J_{\text{rec}} = J_{\text{d}}$ (the potential scale has been corrected to $E_F$) and $J_{\text{inj}} = J_{\text{SC}}$, we can obtain a better-shaped $J$-$V$ curve (blue solid line). The $FF$ and $\eta$ are enhanced by 76% and 146%, respectively. In contrast, in a similar simulation on an n-DSC that shows incomplete dye regeneration at high bias,$^{44}$ the enhancement of efficiency is only 30%. These results suggest that the recombination with dye in p-DSCs is much more significant than that in n-DSCs. The light blue area in Figure 3.8 clear shows the difference in $J_{\text{net}}$ at equivalent $E_F$ as a result of difference in $J_{\text{rec}}$ and $J_{\text{d}}$. It should be kept in mind that $J_{\text{rec}}$ has already been scaled to zero at SC, so the actual difference is more pronounced. Moreover, even after all the corrections, the $FF$ of Cell A is only 0.60. According to Equation 3.1,
with a $V_{OC}$ of 160 mV and an ideality factor $m$ as 0.93 (see Figure 3.9), a cell can achieve a maximum $FF$ value of 0.61, which is in good agreement with our analysis.

**Figure 3.8** $J$-$V$ curve after eliminating the effect of series resistance and recombination with reduced dye.

<table>
<thead>
<tr>
<th>Note</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (mV)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>1.6</td>
<td>127</td>
<td>0.34</td>
<td>0.069</td>
</tr>
<tr>
<td>$R_s$ subtraction</td>
<td>1.8</td>
<td>127</td>
<td>0.36</td>
<td>0.082</td>
</tr>
<tr>
<td>$J = J_{SC} - J_d$</td>
<td>1.8</td>
<td>160</td>
<td>0.60</td>
<td>$1.7 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
Figure 3.9 Voltage dependence of log($J_d$) after $R_s$ correction. Red solid line shows the fitting result. $m=0.93$.

The serious hole recombination with dye molecule is a challenging issue for p-DSCs, while the reason is still not well understood. In TiO$_2$, 90% of the electrons fall into the trap states below the CB edge,$^{45}$ so these trap states can help slow down recombination. In NiO, holes might be mobile at localized surface states and thus are easy to recombine with the photo-reduced dyes. In addition, the lower dielectric constant of NiO means NiO is less effective in screening the Coulombic interaction between the charged dye and the carrier in semiconductor than TiO$_2$ (NiO: ~11.9; TiO$_2$: 30-170; ZnO: ~8).$^{46-48}$ Several strategies have been applied to suppress this undesirable recombination, including preparing high crystalline NiO with less surface defects,$^{10}$ synthesizing sensitizers with long lived charge separated state,$^2,^{13}$ and applying ultrathin barrier layer coating.$^{49-50}$ Considering these limitations of NiO and its nonoptimal band position, exploring
alternative p-type semiconductors that is as unsurpassed as TiO$_2$ in n-DSCs is a rewarding direction.$^{8-9}$

### 3.4 Conclusion

In conclusion, we report the first systematic study of NiO based p-DSCs for identifying the factors that induce the low $FF$ in these solar cells. Several observations are helpful in shedding light on their operation. First, the application of 1 sun illumination significantly reduces $R_{rec}$, which indicates that $R_{rec}$ is affected by both $R_{rec-el}$ and $R_{rec-dye}$, with the latter process dominating at the SC condition. Secondly, the small $R_{dc}$, mainly contributed from small $R_{rec}$, determines the fan-shaped steady-state $J-V$ curve. The substantial efficiency loss mainly due to recombination with reduced dye anions is as large as 1.5 times of the remained efficiency of the cell. Moreover, a new electric model is suggested for NiO p-DSCs. The main current loss is by virtue of recombining with the reduced dye anions, while the current leakage through the FTO substrate/electrolyte interface is negligible. The diagnostic method used in this paper can also be applied to other solar cells, for example, ZnO n-DSCs which also suffer from low $FF$. 
### 3.5 Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{dc}$</td>
<td>$\Omega$ cm$^2$</td>
<td>DC resistance of cell</td>
</tr>
<tr>
<td>$r_{rec}$</td>
<td>$\Omega$ cm$^3$</td>
<td>Recombination resistance per unit volume of the film</td>
</tr>
<tr>
<td>$R_{rec}$</td>
<td>$\Omega$ cm$^2$</td>
<td>Recombination resistance of the film ($R_{rec} = r_{rec} d$)</td>
</tr>
<tr>
<td>$R_{rec,0}$</td>
<td>$\Omega$ cm$^2$</td>
<td>Recombination resistance at zero bias</td>
</tr>
<tr>
<td>$r_t$</td>
<td>$\Omega$ cm</td>
<td>Transport resistance per unit length of the film</td>
</tr>
<tr>
<td>$R_t$</td>
<td>$\Omega$ cm$^2$</td>
<td>Transport resistance of the film ($R_t = r_t d$)</td>
</tr>
<tr>
<td>$R_{CE}$</td>
<td>$\Omega$ cm</td>
<td>Charge transfer resistance at counter electrode</td>
</tr>
<tr>
<td>$R_s$</td>
<td>$\Omega$ cm$^2$</td>
<td>Total series resistance of cell</td>
</tr>
<tr>
<td>$r_s$</td>
<td>$\Omega$ cm$^2$</td>
<td>Series resistance measured by impedance</td>
</tr>
<tr>
<td>$R_{rec-el}$</td>
<td>$\Omega$ cm$^2$</td>
<td>Recombination resistance with electrolyte</td>
</tr>
<tr>
<td>$R_{rec-dye}$</td>
<td>$\Omega$ cm$^2$</td>
<td>Recombination resistance with dye</td>
</tr>
<tr>
<td>$R_{sh}$</td>
<td>$\Omega$ cm$^2$</td>
<td>Shunt resistance of cell</td>
</tr>
<tr>
<td>$R_{BL}$</td>
<td>$\Omega$ cm$^2$</td>
<td>Recombination resistance from FTO back layer</td>
</tr>
<tr>
<td>$c_\mu$</td>
<td>mF cm$^{-3}$</td>
<td>Chemical capacitance per unit volume</td>
</tr>
<tr>
<td>$C_\mu$</td>
<td>mF cm$^{-2}$</td>
<td>Chemical capacitance ($C_\mu = c_\mu d$)</td>
</tr>
<tr>
<td>$C_{CE}$</td>
<td>mF cm$^{-2}$</td>
<td>Capacitance at counter electrode/electrolyte interface</td>
</tr>
<tr>
<td>$\tau_h$</td>
<td>ms</td>
<td>Hole lifetime</td>
</tr>
<tr>
<td>$\tau_tr$</td>
<td>ms</td>
<td>Hole transport time</td>
</tr>
<tr>
<td>$L$</td>
<td>$\mu$m</td>
<td>Hole diffusion length</td>
</tr>
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<td>$d$</td>
<td>$\mu$m</td>
<td>Film thickness</td>
</tr>
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<td>$\eta_{cc}$</td>
<td>-</td>
<td>Charge collection efficiency</td>
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<tr>
<td>$J_0$</td>
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<td>mA cm$^{-2}$</td>
<td>Net current density of cell</td>
</tr>
<tr>
<td>$J_{rec}$</td>
<td>mA cm$^{-2}$</td>
<td>Recombination current density of cell</td>
</tr>
<tr>
<td>$J_d$</td>
<td>mA cm$^{-2}$</td>
<td>Recombination current density of cell in the dark</td>
</tr>
</tbody>
</table>
References


248 (13-14), 1165-1179.
37. Wang, Q.; Moser, J. E.; Gratzel, M. Electrochemical impedance spectroscopic


Chapter 4  

Sensitized n-SCs for high-current photocathodes: effect of dye-controlled interfacial electron transfer

4.1 Introduction

Dye-sensitized nanoparticulate metal oxides hold great promise as photoactive electrodes for light-to-electricity conversion\(^1\) and light-to-chemical fuels transformation\(^2\)\(^-\)\(^3\). The nanoparticulate metal oxide functions as the scaffold for dye adsorption and the pathway for charge transport. As shown in Equation 4.1-4.3, theoretically the photoexcited dye (D) can be either oxidatively or reductively quenched by the semiconductor, in which photosensitization process the semiconductor acts as an electron acceptor or donor, respectively.

\[
\begin{align*}
D|SC + h\nu &\rightarrow D^*|SC & \text{Photoexcitation} & \quad (\text{Equation 4.1}) \\
D^*|SC &\rightarrow e^-(SC) + D^+ |SC & \text{Electron injection} & \quad (\text{Equation 4.2}) \\
D^*|SC &\rightarrow h^+(SC) + D^- |SC & \text{Hole injection} & \quad (\text{Equation 4.3})
\end{align*}
\]

Wide bandgap semiconductors, such as n-type TiO\(_2\)\(^4\), ZnO\(^5\) and SnO\(_2\)\(^6\), and p-type NiO\(^7\), have attracted a lot of research interests in this area. Among them, TiO\(_2\)-based n-DSCs are well-developed and produce high anodic photocurrents approaching 18 mA cm\(^{-2}\)\(^8\)\(^-\)\(^9\). In contrast, NiO suffers from parasitic absorption and slow hole diffusion\(^10\)-\(^11\) (which have been discussed in Chapter 2), leading to unsatisfactory photocurrents in p-DSCs (usually varying between 0.1-5.5 mA cm\(^{-2}\) (as summarized in Table 4.1).\(^{12}\) There are only
a few exceptions with $J_{SC} > 7.0 \text{ mA cm}^{-2}$. In addition, NiO is known to suffer from large pseudocapacitance, complex Ni(III)/Ni(II) surface states, electrochromic properties and easy dissolution in acids, which greatly limits its application for both fundamental mechanism investigation and practical DSPEC device optimization. Therefore, searching for novel cathode material alternative to NiO represents an elegant strategy to break the bottleneck. Recent efforts have focused on other wide bandgap p-SCs, e.g. Cu(I) based delafossite complex metal oxides. However, due to the difficulty of synthesizing small nanoparticles with high surface areas, the photocurrents of those cells are still limited by insufficient dye loading.

ITO is a degenerate n-SC with a bandgap around 3.7-3.8 eV. Due to its superior conductivity and high transparency in the visible light region, planar ITO thin film has been widely used as the transparent conductive substrate in organic photovoltaic devices and organic light-emitting diodes (OLEDs). In addition, nanostructured ITO films have served as high-surface-area scaffolds for supporting TiO$_2$ and hematite in photoelectrochemical devices, and electrochemical catalysts such as photosystem II, water oxidation catalyst and hydrogen evolution catalyst.

Dye-sensitized ITO as photoelectrodes have been reported in a few instances and the photocurrents were generally very low. Both anodic and cathodic photocurrents have been observed. For example, Hupp et al. observed a μA-scale cathodic current from a multilayer porphyrin-sensitized flat ITO soaked in an aqueous I$_3$/I$_{-}$solution. Laberty-Robert et al. reported that sensitization of mesoporous ITO by a complex [Ru(bpy)$_2$(4,4'- (CH$_2$PO$_3$H$_2$)$_2$-bpy)]Cl$_2$ (bpy is 2,2'-bipyridyl) can generate up to 50 μA cm$^{-2}$ cathodic
photocurrents in the presence of an electron acceptor in the electrolyte.\textsuperscript{44} Very recently, Meyer \textit{et al.} observed electron injection from surface-bound $[\text{Ru(bpy)}_2(\text{dcb})]^2^+$(dcb is 4,4'-\(\text{COOH}\)\(_2\)-2,2'-bipyridyl) into \textit{nano}ITO films with the rate constant at the order of 10\textsuperscript{10} s\(^{-1}\), which indicates that the sensitized ITO films can be potentially used as photoanodes.\textsuperscript{45}

\textbf{Table 4.1} Summary of $J_{\text{SC}}$ of NiO based p-type DSCs in published papers

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$J_{\text{SC}}$ (mA/cm(^2))</th>
<th>NiO film thickness (μm)</th>
<th>Reference/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPPC</td>
<td>0.079</td>
<td>1</td>
<td>20/1999</td>
</tr>
<tr>
<td>Coumarin 343</td>
<td>1.7</td>
<td>5</td>
<td>21/2009</td>
</tr>
<tr>
<td>P1</td>
<td>5.48</td>
<td>1.1-1.2</td>
<td>22/2010</td>
</tr>
<tr>
<td>P2</td>
<td>3.37</td>
<td>Not reported (n.r.)</td>
<td>23/2010</td>
</tr>
<tr>
<td>P3</td>
<td>1.36</td>
<td>n.r.</td>
<td>23/2010</td>
</tr>
<tr>
<td>P7</td>
<td>3.37</td>
<td>n.r.</td>
<td>23/2010</td>
</tr>
<tr>
<td>PMI-2T-TPA</td>
<td>2.06</td>
<td>2.3</td>
<td>24/2010</td>
</tr>
<tr>
<td>PMI-4T-TPA</td>
<td>3.40</td>
<td>2.3</td>
<td>24/2010</td>
</tr>
<tr>
<td>PMI-6T-TPA</td>
<td>5.35</td>
<td>2.3</td>
<td>24/2010</td>
</tr>
<tr>
<td>PMI-NDI</td>
<td>2.65</td>
<td>2</td>
<td>25/2011</td>
</tr>
<tr>
<td>O2</td>
<td>1.43</td>
<td>0.6</td>
<td>26/2011</td>
</tr>
<tr>
<td>O6</td>
<td>1.04</td>
<td>0.6</td>
<td>26/2011</td>
</tr>
<tr>
<td>O7</td>
<td>1.74</td>
<td>0.6</td>
<td>26/2011</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">\text{Ru(bpy)}_2(4,4'-(\text{CH}_2\text{PO}_3\text{H}_2)_2\text{bpy})</a>_2$</td>
<td>0.78</td>
<td>n.r.</td>
<td>27/2011</td>
</tr>
<tr>
<td>O8</td>
<td>0.44</td>
<td>0.6</td>
<td>28/2012</td>
</tr>
<tr>
<td>O11</td>
<td>1.16</td>
<td>0.6</td>
<td>28/2012</td>
</tr>
<tr>
<td>O12</td>
<td>1.84</td>
<td>0.6</td>
<td>28/2012</td>
</tr>
<tr>
<td>PMI-6T-TPA</td>
<td>7.0</td>
<td>6.0 (microballs)</td>
<td>29/2012</td>
</tr>
<tr>
<td>O3</td>
<td>3.04</td>
<td>2</td>
<td>30/2013</td>
</tr>
<tr>
<td>O13</td>
<td>2.66</td>
<td>2</td>
<td>30/2013</td>
</tr>
<tr>
<td>O17</td>
<td>2.69</td>
<td>2</td>
<td>30/2013</td>
</tr>
<tr>
<td>bodipy dye 1</td>
<td>3.15</td>
<td>n.r.</td>
<td>31/2013</td>
</tr>
<tr>
<td>O18</td>
<td>3.43</td>
<td>2.3</td>
<td>32/2014</td>
</tr>
<tr>
<td>zxx-op1-2</td>
<td>7.57</td>
<td>3.1</td>
<td>34/2014</td>
</tr>
<tr>
<td>BH-2</td>
<td>4.3</td>
<td>2.0-2.5</td>
<td>33/2014</td>
</tr>
<tr>
<td>BH-4</td>
<td>7.4</td>
<td>2.0-2.5</td>
<td>33/2014</td>
</tr>
</tbody>
</table>
Tin oxide (SnO$_2$) is an abundant and low cost metal oxide. It is a native wide bandgap non-degenerate n-SC, which makes it a natural choice for the photoanode. Because of its low-lying conduction band ($E_{CB} \approx 0$ V vs. NHE), it can accept electrons from many of the sensitizers (e.g. far-red-absorbing chromophores) that are generally unable to sensitize TiO$_2$ ($E_{CB} \approx -0.5$ V vs. NHE). Significant advances have been made in the anodic photosensitization of SnO$_2$, with the development of various types of sensitizers, including organometallic compounds (e.g. ruthenium-based dyes)$^{46-50}$, organic molecules$^{51-52}$, quantum dots$^{53}$, conjugated polymers$^{54}$, and the emerging inorganic-organic hybrid perovskite materials$^{55-57}$.

DSCs are majority carrier devices. Conventional wisdom uses n-SCs for n-DSCs and p-SCs for p-DSCs. Cathodic photosensitization of an n-SC seems against common wisdom and remains a formidable challenge. Herein, we report the incorporation of an n-SC as an efficient photocathode in which the hole is conducted through the CB of the n-SC, instead of the VB of the conventional p-SC. As a demonstration, two n-SCs, mesoporous ITO and SnO$_2$ films, sensitized by energy-aligned cyclometalated ruthenium (II) complexes, can generate remarkable cathodic photocurrents in a DSC configuration. The superior conductivity and transparency of the photoelectrode enable the use of thick films (over 10 μm), which is a big advantage over NiO (optimal film thickness around 2-3 μm). The photocurrent generation mechanism was investigated by transient absorption spectroscopy (TAS), which demonstrated that the cathodic photocurrent results from reduction of the photoexcited sensitizer by electrons of the semiconductor.
4.2 Experimental section

4.2.1 General information

All reagents were purchased from Sigma-Aldrich except where otherwise indicated. Dyes O18, O3, O2 and PMI-2T-TPA were synthesized following published procedures in references.

4.2.2 Film preparation and characterization

1.2 g of commercial ITO nanopowder (indium tin oxide, NanoTek, 99.5%, Alfa Aesar) was dispersed in 10 ml ethanol via sonication. 2 ml of 10 w.t.% ethyl cellulose ethanolic solution and 4 ml terpineol were added to the initial suspension. After a homogeneous paste was obtained, ethanol was removed from the paste on a rotary evaporator. The film was deposited onto FTO substrates (Hartford Glass Co., Inc) by doctor-blading method and dried at 50 °C in a vacuum oven. For thick films, multiple layers were deposited by repeating the doctor-blading and drying process. The films were then calcinated at 450 °C for 30 min. For SnO2, the recipe was the same. TiO2 films were prepared using reported method. The active film area is 0.25 cm². The thickness of the film is measured by Alpha-Step D-100 Profilometer (KLA-Tencor). The transmittance spectra of bare semiconductor and dye-sensitized films were recorded using Perkin Elmer Lambda 950 spectrometer with an integrating sphere.

4.2.3 Solar cell fabrication and characterization

The films were immersed in the dye solution (O18, O3, O2: 0.14 mM in acetonitrile; PMI-2T-TPA: 0.2 mM in N,N-dimethylformamide) for overnight. The counter electrodes
were platinized by thermal decomposition of H₂PtCl₆ from isopropanol on a FTO at 385 °C for 20 min. A 60-µm thick Surlyn 60 hotmelt foil (Solaronix) was used as the primary sealing material. Then, an electrolyte composed of 1.0 M LiI and 0.1 M I₂ in acetonitrile was injected through a hole predrilled on the counter electrode. The hole was sealed afterward with a glass cover slide.

Photovoltaic measurements were performed using a solar simulator (Small-Area Class B, Solar Simulator, PV Measurements), which provides standard AM 1.5G illumination with an equivalent light intensity of 1000 W m⁻² (1 Sun). The J-V measurements were carried out by Reference 600 potentiostat (Gamry Instruments, Warminster, PA). The working electrode lead was connected to the FTO substrate with the metal oxide film on it, and the counter and reference electrodes were connected to the Pt counter electrode. The cathodic current is defined as negative, and the anodic current is defined as positive. The scan rate of LSV was 1 mV s⁻¹.

The incident photon-to-current conversion efficiency (IPCE) spectra were recorded using the QEX7 quantum efficiency measurement systems (PV Measurements, Inc.). Prior each measurement, a standard silicon photodiode was used to calibrate the system. The chopping frequency was set to 4 Hz and no bias light was used.

IMVS/IMPS was tested under white light, using a CompactStat electrochemical analyzer and programmable modulated light (Ivium Technologies). IMPS and IMVS were usually carried out under the SC and OC condition, respectively. We were able to test IMPS and IMVS at any (J, V) point (from SC to OC) on the J-V curve measured under the same light intensity, by setting the specific potentiostat potential or galvanostat current.
respectively. The time constant was identified from the peak frequency in the corresponding imaginary part vs. frequency plot.\textsuperscript{11} The diffusion coefficient $D$ was calculated based on Equation 4.4.\textsuperscript{60-61}

$$
\tau_{ir} = \frac{d^2}{(2.35D)} \quad \text{(Equation 4.4)}
$$

\textit{4.2.4 TAS}

Experiments were carried out at the Center of Nanoscale Materials (CNM) of Argonne National Laboratory. Solutions of 0.1 mM O3 and 0.1 mM O3/0.1 mM tetrabutylammonium triiodide (TBAI\textsubscript{3}) in acetonitrile were prepared. An amplified Ti:Sapphire laser system (Spectra Physics, Spitfire-Pro) and an automated data acquisition system (Ultrafast Systems, EOS for 0-1 ms range) were used. The amplifier was seeded with the 120 fs output from the oscillator (Spectra Physics, Tsunami) and was operated at 1.0 kHz for EOS measurements. The amplifier output was split and 90% of the output was used to pump an optical parametric amplifier (TOPAS). This generated the pump beam. For EOS, a supercontinuum light source (Ultrafast Systems) was used for the probe. O3 and O3/ TBAI\textsubscript{3} solutions were pumped at 505 nm with the power of ~500 $\mu$W. The ground state recovery kinetics was fitted at 556 nm by a single exponential decay with offset (Equation 4.5).

$$
A = A_1 e^{-(t-t_0)} \quad \text{(Equation 4.5)}
$$
4.3 Results and discussions

4.3.1 Sensitized ITO photocathode

4.3.1.1 Film characterization and cell performance

The mesoporous ITO film consisted of ITO nanoparticles with size 30-50 nm (Figure 4.1). The ITO films after annealing in the air were pale yellow (Figure 4.2b) with near-UV absorption tailing into the visible light spectrum (see dotted lines in Figure 4.2a). The bare FTO substrate, the 3.5 μm thick ITO film, and the 11.2 μm thick ITO film have a transmittance of 81.07%, 55.3% and 29.9% at 600 nm, respectively.

Figure 4.1 Scanning electron microscopy (SEM) image of the ITO film.
Figure 4.2 (a) Transmittance spectra of the 3.5 μm (blue) and 11.2 μm (red) thick ITO films before (dot lines) and after (solid lines) sensitization; Digital images of the 3.5 μm thick ITO film (b) before and (c) after sensitization.

The molecular structure and the energy levels of the sensitizers used in this work are depicted in Figure 4.3. The calculation of the reduced potential of the excited and ground state dyes are summarized in Table 4.2.
Figure 4.3 (a) Structures of dyes used in this work. (b) energy diagrams of the ITO conduction band and dyes.
Table 4.2 Summary of the energy levels of the sensitizers used in this paper

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$E (D^*/D^-)$ (V vs NHE)$^a$</th>
<th>$E (D/D^-)$ (V vs NHE)$^b$</th>
<th>$E_{0-0}$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>0.46</td>
<td>-1.49</td>
<td>1.95$^c$</td>
<td>[30]</td>
</tr>
<tr>
<td>O18</td>
<td>0.49</td>
<td>-1.18</td>
<td>1.67$^d$</td>
<td>[32]</td>
</tr>
<tr>
<td>PMI-2T-TPA</td>
<td>0.94</td>
<td>-0.80</td>
<td>1.74$^e$</td>
<td>[62]</td>
</tr>
<tr>
<td>O2</td>
<td>1.41</td>
<td>-0.78</td>
<td>2.19$^d$</td>
<td>[26]</td>
</tr>
</tbody>
</table>

Notes:

a. $E(D^*/D^-) = E(D/D^-) + E_{0-0}$;
b. $E(D/D^-)$ is obtained from the first reduction potential (for O3, O18 and O2) or the onset reduction potential (for PMI-2T-TPA) in cyclic voltammograms;
c. this value is estimated from the absorption onset in the UV-Vis absorption spectrum;
d. this value is obtained from the intersection of the normalized absorption and emission spectra;
e. this value is calculated from the energy gap between the onset reduction and oxidation potential in cyclic voltammograms.

For the sensitizers, we start with O18, which is a panchromatic cyclometalated Ru(II) dye recently reported by our group for NiO-based p-DSCs. It features intense absorption in the visible to near IR region, with the absorption tail extending to 800 nm.
After being immersed in 0.14 mM O18 dye solution for overnight, the ITO film became completely black (Figure 4.2c). For the 11.2-μm thick film, the transmittance was almost zero below 600 nm wavelength (see Figure 4.2a).

**Figure 4.4** $J-V$ curves of O18-sensitized 3.5 (blue) and 11.2 μm (red) thick ITO solar cells, and a blank ITO cell (green), under standard 1 sun illumination (solid line) and in the dark (dotted line).

The photovoltaic performance of the sandwich type solar cells based on O18-sensitized ITO films were systematically studied. Figure 4.4 shows the $J-V$ characteristic curve for the cells with 3.5 and 11.2μm film. The $V_{OC}$ is around 100 mV, which is similar to the dye-sensitized NiO cells with I$_2$/LiI redox shuttle.\textsuperscript{63-64} The $V_{OC}$ seems to be limited by high dark current density (e.g. 2.5 mA cm$^{-2}$ for the 11.2 μm thick film at 120 mV bias). As a control, a non-sensitized ITO cell was fabricated and tested under 1 sun illumination.
(green solid line in Figure 4.4). Only negligible $V_{OC}$ (3 mV) and $J_{SC}$ (0.16 mA cm$^{-2}$) were observed. This also confirms that the high current and moderate voltage come from dye sensitization. Besides, the dark current is linear (green dot line) and orders of magnitude higher when dye is absent, indicating that the dye molecules greatly block the recombination between the ITO film and the redox shuttle.

![Figure 4.5](image.png)

**Figure 4.5** Dependence of $J_{sc}$ on the thickness of the ITO film for O3 and O18 sensitized cell.

The $V_{OC}$ of the ITO cell is comparable to that of the NiO p-DSC with the I$_2$/LiI redox, but lower than that of the normal TiO$_2$ based n-DSC. The $V_{OC}$ is limited by the high dark current (e.g. 2.5 mA cm$^2$ for the 11.2 μm thick film at 120 mV bias), which originates from the back electron transfer from I$^-$ to ITO. This is also suggested by our investigation of the hole lifetime and transport property of ITO electrodes (as detailed in Figure 4.8).
The lifetime drops exponentially with increasing voltages, leading to low charge collection efficiencies at high voltages. The current leaking from this channel can potentially be suppressed by surface blocking techniques.\textsuperscript{65-66} On the other hand, the sensitized ITO photocathode has very promising applications for solar fuels, and high photovoltage is not crucial in the scenario of water and CO\textsubscript{2} reductions.

A striking feature is that high cathodic photocurrents were observed for these solar cells. The dependence of the $J_{\text{SC}}$ on the film thickness is shown in Figure 4.5. $J_{\text{SC}}$ increases from 2.67 mA cm\textsuperscript{-2} for the cell made from a thin film (3.5 μm) to 5.96±0.19 mA cm\textsuperscript{-2} for those from thick films with the thickness of 11.1±0.2 μm (data from four cells). This photocurrent density is two to three orders of magnitude higher than that reported in literature using sensitized ITO as the photoelectrode\textsuperscript{42-44}, and is close to the highest record for p-DSCs (see Table 4.1). The $J_{\text{SC}}$ increases as the film gets thicker, but the enhancement gradually declines. This is because that the thicker film provides more surface area for dye loading, but also suffers from lower charge collection efficiency, and lower transmittance of the bare film due to the light scattering.

Figure 4.6 shows the IPCE spectra of the cells made from the 3.5 μm and 11.2 μm thick ITO film. The IPCE spectra of both cells resemble the panchromatic absorption profile of O18, indicating that the photocurrent indeed results from dye sensitization. For the 11.2-μm thick cell, the IPCE maintains around 25%-28% from 450 nm to 650 nm. The integrated currents are 2.93 and 5.77 mA cm\textsuperscript{-2}, respectively, which are in close agreement with the results shown in Figure 4.5.
Figure 4.6 IPCE spectra of O18 sensitized 3.5 μm and 11.2 μm thick ITO solar cells.

IMVS/IMPS was used to probe the charge collection property of the 11.2-μm thick cell. The $J-V$ curve under the white light is shown in Figure 4.7. IMVS/IMPS was measured at certain $(J,V)$ points marked as the red circles in Figure 4.7, by setting the specific potentiostat potential or galvanostat current, respectively. As shown in Figure 4.8, both transport time and hole lifetime decrease as bias increases, probably owing to the higher hole density. The hole lifetime shows a clear exponential dependence on the voltage, while the change of transport time is not significant. The charge collection efficiency is calculated to be 77% at SC condition.
Figure 4.7 $J$-$V$ curve of the O18 sensitized 11.2-μm thick cell under the white light in IMPS/IMVS measurement. IMVS/IMPS was measured at certain $(J,V)$ points marked as the red circles.

We also studied the effect of sensitizer on photocurrents by replacing O18 with other sensitizers designed for efficient hole injection, i.e. O3, O2 and PMI-2T-TPA. The cyclometalated ruthenium dye O3 works well in this system. It generates a cathodic $J_{SC}$ of 4.89 mA cm$^{-2}$ for a 10.5-μm thick film, which performs only slightly worse than O18 (comparison shown in Figure 4.5). This is probably because of the narrower absorption spectrum of O3 compared with O18. PMI-2T-TPA and O2 are organic push-pull dyes. A limited cathodic $J_{SC}$ of 0.30 mA cm$^{-2}$ and anodic $J_{SC}$ of 0.43 mA cm$^{-2}$ were observed for PMI-2T-TPA and O2 sensitized cell with 10-μm thick ITO film, respectively.
Figure 4.8 Hole transport time and lifetime measured by IMPS and IMVS at different bias potential/current.

4.3.1.2 TAS study and mechanism discussion

Large cathodic photocurrents from O18 and O3-sensitized cells unambiguously demonstrate the hole transfer to the ITO electrode. However, the key question is how the ITO acts as a photoelectrode—whether the hole injection is from the excited or oxidized dye. Two possible mechanisms are illustrated in Figure 4.9. Mechanism I involves, as a primary step, hole injection from the photoexcited dye D* into CB of ITO, which is analogous to the first step in p-DSCs and DSPECs. Alternatively, the oxidative quenching of the excited dye by the electron acceptor in the electrolyte (triiodide) can occur first, followed by thermal interfacial hole transfer from the oxidized dye D⁺ to ITO. We call this Mechanism II, which corresponds to a typical photogalvanic cell.⁶⁷
TAS was used to study the charge transfer steps in the O3 dye/ triiodide electrolyte interface. Two solutions, O3 and O3/tetrabutylammonium triiodide (TBAI\textsubscript{3}), were pumped at 505 nm to selectively excite O3 and probed of the absorption change. The resulting transient difference spectra (Figure 4.10a) are almost identical for both solutions: the bleaching of MLCT absorption at 525-618 nm and growth of absorption at 618-750 nm, indicating the presence of identical photoexcited products. The normalized temporal absorbance changes at 556 nm of both solutions in the μs-scale are compared in Figure 4.10b. Their ground state recovery kinetics can be adequately fitted with a single exponential decay equation (Equation 4.5). The time constant is 14.3 ns for O3/TBAI\textsubscript{3} and 13.6 ns for O3. Because of the very similar kinetic processes observed in both O3 and O3/TBAI\textsubscript{3} solution, and no new spectroscopic features corresponding to charge separated species in O3/TBAI\textsubscript{3}, I\textsuperscript{-} is unable to efficiently oxidatively quench O3\textsuperscript{*}. Therefore, the likelihood of Mechanism II is excluded.
Figure 4.10 (a) Transient difference absorption spectra of O3 and O3/TBAI$_3$ in acetonitrile; (b) fitting of the normalized absorbance difference at 556 nm of O3 and O3/TBAI$_3$ in acetonitrile.

Herein we provide more discussions of photogalvanic cell. A “photogalvanic cell” generally refers to an electrochemical cell in which current or voltage changes result from
photochemically generated changes in the relative concentrations of reactants in an oxidation-reduction couple.\textsuperscript{67} Two types of photogalvanic cells might be related to our dye-sensitized ITO solar cells.

(1) a photo-driven concentration cell

In this proposed cell, the concentration gradient of redox shuttles between two electrodes is generated upon illumination. The potential of each electrode is determined by Nernst potential of the redox shuttle at the electrode surface. If our dye-sensitized ITO solar cells work in this way, the photoelectrode would photoreduce triiodide at the ITO surface, which depletes triiodide and generates a high local concentration of iodide. If this effect is significant enough to generate any potential difference, the potential of the ITO electrode should be more negative than that of the counter electrode (according to the Nernst equation), which leads to a photoanode. This completely contradicts our observed cathodic photocurrent. Therefore, this scenario can be ruled out.

(2) a dye-sensitized photogalvanic cell\textsuperscript{68}

A dye-sensitized photogalvanic cell is theoretically possible in our case, in which hole injection occurs as a thermal charge transfer process after the excited dye is oxidatively quenched by triiodide. In this case, the counter electrode is poised at the triiodide/iodide potential, and the photovoltage results from the positive shift of the $E_F$ of ITO after accepting holes. The mechanism is illustrated as Mechanism II in Figure 4.9. However, our TAS results didn't show the formation of charge-separated products resulting from the oxidative quenching of the photoexcited dye by triiodide.
Since Mechanism II has already been excluded, the cathodic photocurrent outputs from our O3 and O18-sensitized ITO solar cells necessitate the hole injection process (as shown in Mechanism I). Therefore the photocurrent modulation should take place at the dye/ITO interface, instead of the dye/electrolyte interface.

It should be noted that the electron injection is also thermodynamically possible at dye/ITO interfaces. An example is the anodic photocurrent outputs from our O2-sensitized ITO solar cells. Another example is a recent report of the electron injection process in [Ru(bpy)$_2$(dcb)]$_2^{2+}$ (dcb is 4,4'-(COOH)$_2$-2,2'-bipyridyl)-sensitized nanITO films. The electron injection rate constant is at the order of $10^{10}$ s$^{-1}$. In our opinion, the lack of electron injection process at the O3/ITO interface can be attributed to the remote location of the LUMO of O3 from ITO. LUMO of O3 is mainly localized on bpy ligands which are far away from the ITO surface. This results in inefficient overlap of O3 LUMO with the unoccupied density of states (DOS) of ITO, as well as long electron tunneling distance. Therefore, the electron injection process is prohibited.

As a degenerate semiconductor, the Fermi level of ITO (~0.2 V vs. NHE)$^{69}$ cuts through its CB, resulting in free electrons in CB and the quasi-metallic behavior. When ITO is in contact with the electrolyte, its $E_F$ reaches equilibrium with the Nernst potential of the redox couple (~0.3 V vs. NHE). Upon illumination, an excited dye extracts one free electron from the ITO CB (hole injection process), and the reduced dye is regenerated by the redox couple afterwards. The consumption of the electrons lowers the $E_F$ of ITO and generates the positive $V_{OC}$. 

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The above mechanism indicates the importance of the energy level alignment at the ITO-sensitizer interface. According to Gerischer’s interfacial electron transfer theory,\textsuperscript{70-71} efficient charge transfer at metal oxide/sensitizer interface depends critically on the overlap of the sensitizer excited-state distribution function with the DOS of the semiconductor. Efficient electron transfer occurs when the electronic acceptor level of the excited molecule has effective overlap with the ITO CB (Figure 4.11a). In contrast, if the HOMO of the dye lies in the bandgap of ITO with minimal DOS (Figure 4.11b), the electron transfer is retarded. The working principle illustrated in Figure 4.11 well explains the dye-selectivity in our cells. Figure 4.11a represents the cases of O18 and O3, whose HOMO (0.49 V and 0.46 V) overlaps with ITO CB. Figure 4.11b represents the case of O2. O2’s HOMO (1.40 V)\textsuperscript{26} is much more positive than that of O18 and lies deeply in the bandgap of ITO. Its LUMO locates at -0.78 V, allowing for efficient electron injection. PMI-2T-TPA’s HOMO locates at 0.94 V, which is between that of O18 and O2. Therefore, a limited cathodic $J_{SC}$ of 0.30 mA cm$^{-2}$ was obtained.
Figure 4.11 Working principle for dye-sensitized ITO as a photocathode: (a) efficient electron transfer when energy is matched, as in O18 and O3-sensitized cells; and (b) hindered electron transfer when energy is not matched, as in O2-sensitized cells.

4.3.2 Sensitized SnO$_2$ photocathode

Figure 4.12 shows the SEM image of the as-made SnO$_2$ film. The mesoporous film consists of homogeneously distributed SnO$_2$ nanoparticles with a uniform size of 20-30 nm (the scale bar is 200 nm), which makes for high surface area and excellent film transparency. The transmittance at 600 nm remains as high as 76.98% for the 11.0 μm-thick SnO$_2$ film, which is only slightly lower than that of the bare FTO substrate (81.07%, see Figure 4.13). The transmittance spectra of a 2.0 μm-thick NiO film is also plotted in the figure for a direct comparison. The 2.0 μm-thick NiO film absorbs much more light than the 11.0 μm-thick SnO$_2$ film, with a transmittance of only 37.06% at 600 nm. It can be clearly seen that NiO suffers from its parasitic light absorption, while the SnO$_2$ film is highly transparent.
Figure 4.12 SEM image of the as-made SnO$_2$ film. The scale bar is 200 nm.

Figure 4.13 Transmittance spectra of the bare FTO substrate (black), 11.0 μm thick SnO$_2$ film before (red) and after O18 sensitization (blue), and the 2.0 μm thick NiO film (green dash curve).
Numerous sensitizers have been reported for successful anodic photosensitization of SnO\textsubscript{2}. Here we choose three dyes which are well-designed for efficient hole injection, and have never been studied on the SnO\textsubscript{2} film. After being immersed in 0.14 mM O18 dye solution for overnight, the SnO\textsubscript{2} film turned completely black (see the blue curve in Figure 4.13), which proves the excellent dye loading on SnO\textsubscript{2} and the panchromatic absorption of the O18 sensitizer.

We tested these photoelectrodes using a conventional sandwich type DSC structure with the I\textsubscript{2}/LiI redox couple in acetonitrile solvent ($E_{\text{Red}} \approx 0.3$ V vs. NHE). The photovoltaic performance is shown in Figure 4.14. Striking cathodic photocurrents were observed for the three O18 sensitized SnO\textsubscript{2} solar cells (Cell 1-3, film thickness 11.0±0.1 μm) under standard AM1.5 1 sun illumination. The $J_{SC}$ is as high as 7.91 ± 0.17 mA cm\textsuperscript{-2}, which outperforms the O18-sensitized NiO p-DSC (3.43 ± 0.13 mA cm\textsuperscript{-2}) and O18-sensitized ITO DSC (5.96 ± 0.19 mA cm\textsuperscript{-2}), and is among the highest in sensitized photocathodes.\textsuperscript{13-14,72} The $V_{OC}$ is around 100 mV, which is similar to that of the NiO based p-DSC with the I\textsubscript{2}/LiI redox shuttle,\textsuperscript{73-74} but lower than that of the general SnO\textsubscript{2} based n-DSCs (30-470 mV for bare SnO\textsubscript{2} particle electrode with similar redox mediator, higher voltages with additional surface coating).\textsuperscript{48,50,61,75-76} The $V_{OC}$ of our SnO\textsubscript{2} p-DSC seems limited by the high dark current, which can potentially be suppressed by surface blocking techniques.\textsuperscript{50,65,77} It should also be noted that the $V_{oc}$ in a DSC is in part determined by the Nernst potential of the redox shuttle, so the photovoltage will be different for DSPEC application.
Figure 4.14 J-V curves of O18-sensitized SnO₂ solar cells under standard AM1.5 1 Sun irradiation. Dark currents are shown with dash lines.

Figure 4.15 Transmittance spectra of the 11.0 μm thick SnO₂ film before (black) and after (red) O3 sensitization.
Figure 4.16 $J-V$ curves of the O3 sensitized SnO$_2$ solar cell under standard AM1.5 1 Sun irradiation. Dark currents are shown with dash lines.

Figure 4.17 $J-V$ curves of the PMI-2T-TPA sensitized SnO$_2$ solar cell under standard AM1.5 1 Sun irradiation. Dark currents are shown with dash lines.
Other sensitizers (O3 and PMI-2T-TPA) were also probed in this system, and the $J-V$ curves are shown in Figure 4.16-4.17. As summarized in the bar chart (inset of Figure 4.18, cathodic current defined as negative), the O3-sensitized SnO$_2$ photoelectrode produces a remarkable cathodic $J_{SC}$ of 7.52 mA cm$^{-2}$, while the PMI-2T-TPA-sensitized SnO$_2$ photoelectrode shows an anodic $J_{SC}$ of 0.86 mA cm$^{-2}$. The IPCE spectra (at 1 sun intensity) of O18 and O3 sensitized SnO$_2$ cell are plotted in Figure 4.18 as a function of excitation wavelength. The IPCE of the O18 cell is red shifted by about 100 nm compared with the O3 cell, which consists with the sensitized film absorption spectra (Figure 4.13 and Figure 4.15), and is owing to the extended conjugation of $\pi$ system. The IPCE of O18 cell maintains above 40.0% from 390 nm to 630 nm. In addition, the integrated $J_{SC}$ reaches 8.8 mA cm$^{-2}$, which is in close agreement with the results of the $J-V$ measurements. The IPCE spectra of both cells resemble the absorption profile of the sensitizer, which clearly demonstrates that the photocurrent originates from the excited sensitizer.
Figure 4.18 IPCE spectra of O18 (black) and O3 (red) sensitized cell. The inset compares the $J_{SC}$ of O18 (black), O3 (red) and PMI-2T-TPA (blue) sensitized cell. (Cathodic current is defined as negative.)

The charge transport, recombination, and collection properties of the O18-sensitized SnO$_2$ photocathode were carefully probed by IMVS/IMPS$^{78}$. IMVS/IMPS was measured at certain $(J,V)$ points along the $J-V$ curve, by setting the specific potentiostat potential or galvanostat current, respectively. As shown in Figure 4.19, both “hole” lifetime and transport time decrease as bias increases, probably due to the enhanced hole concentration in SnO$_2$. The lifetime has an exponential dependence on the voltage, while the change of the transport time is not very significant. Compared with NiO, although the SnO$_2$ film is much thicker (11 μm vs. 2μm), the transport time (3-6 ms) is one order of magnitude shorter than that of general NiO p-DSC$^{79-80}$. At the short circuit condition, the
charge collection efficiency is 66%; the charge carrier diffusion coefficient is calculated to be $8.8 \times 10^{-5}$ cm$^2$s$^{-1}$, which is about 2-3 orders of magnitude higher than that of NiO.$^{80-81}$

![Figure 4.19](image.png)

**Figure 4.19** Hole transport time and lifetime measured by IMPS and IMVS at different bias potential/current.

Since there have been extensive studies on SnO$_2$ photoanode, it is insightful to compare the charge carrier collection properties of those SnO$_2$ photoanodes with our unique photocathode. The electron mobility of SnO$_2$ is reported to be 1-2 orders of magnitude higher than that of TiO$_2$, and the reported electron diffusion coefficient for SnO$_2$ n-DSC is close to our result ($10^{-5}$ cm$^2$s$^{-1}$ scale$^{61}$). The result makes sense because the charge transport channel is similar for both photoelectrodes, although the direction opposes. The charge carrier lifetime depends on the charge density of the semiconductor, redox mediator concentration, surface treatment of the electrode, sensitizer, etc. Therefore
it is hard to make a perfect comparison. A general problem for the SnO$_2$ photoanode is the high dark current and fast recombination (with redox shuttle or oxidized sensitizer), which was also observed by us.

It should be noted that theoretically the photocurrent in this kind of system can be assigned to the sensitizer excited state interaction with either the semiconductor or the redox couple. In Chapter 4.3.1$^{83}$, we carried out transient absorption spectroscopy (TAS) studies to convincingly demonstrate that the efficient oxidative quenching of the MLCT excited states of O3 by triiodide is not possible. Since one pathway has been clearly ruled out, the cathodic photocurrent should unambiguously result from efficient reductive quenching of the excited dye by SnO$_2$.

In Chapter 4.3.1, we reported that ITO can either oxidatively or reductively quench the excited state of the dye, and the efficient hole injection process relies on sufficient energy overlap of the $E(D^*/D^-)$ of the dye with the electron donor states of ITO. The sensitizer-induced photocurrent modulation/switching effect on the SnO$_2$ photoelectrode can generally be explained by similar theory. However, different from the semi-metallic ITO which might bear electron Fermi-level pinning characteristics, SnO$_2$ is a normal n-SC with a simpler band structure picture. Its CB lies at around 0 V vs. NHE, while our probing bias is at ~0.3 V vs. NHE. The cathodic photocurrent originates from the reduction of the excited dye by the electrons of the SnO$_2$ film. The electron thermal population on these density of states (DOS) has an exponential dependence on the $E_F$ position: $^{38,39}$

$$n = N_C \exp[(E_F-E_C)/k_B T] \quad \text{(Equation 4.6)}$$

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in which $E_C$ is CB edge potential, $N_C$ is the effective DOS at the level $E_C$, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. In addition, SnO$_2$ is found to have intraband states with high reactivity$^{50,53}$ just below CB. In the photosensitization process, the consumption of the electrons in the CB and intraband states lowers down the quasi-$E_F$ of SnO$_2$ and generates the positive photovoltage.

DSC is basically a kinetically determined solar cell. Here the electron injection from the excited dye to SnO$_2$ is also theoretically possible, however, the remote LUMO location from the metal oxide surface results in insufficient overlap of LUMO with the unoccupied DOS of SnO$_2$, as well as long electron tunneling distance, which can suppress the electron injection. For the sensitizer PMI-2T-TPA, $E(D^*/D^-)$ is very positive and lies deeply in the bandgap of SnO$_2$, which limits the hole injection due to insufficient overlap with DOS of SnO$_2$. As a result, limited anodic photocurrent was observed.

We also extended our study to other n-type semiconductors. As a comparison, TiO$_2$ films (10.0 μm) were investigated using the same solar cell structure and electrolyte. O$_3$-sensitized TiO$_2$ cell shows very limited cathodic photocurrent while the PMI-2T-TPA sensitized one shows decent anodic photocurrent ($J_{SC} = 0.87$ mA cm$^{-2}$, $V_{oc} = 397$ mV, see Figure 4.20-4.21). The different performance between TiO$_2$ and SnO$_2$ can be rationalized by their different CB positions. At an $E_F$ of $\sim$0.3 V vs. NHE, SnO$_2$ has sufficient electrons in its CB and intraband states just below CB to reduce the excited dye, while TiO$_2$ is still quite insulating.
Figure 4.20 $J-V$ curves of the O3 sensitized TiO$_2$ solar cell under standard AM1.5 1 Sun irradiation. Dark currents are shown with dash lines.

Figure 4.21 $J-V$ curves of the PMI-2T-TPA sensitized TiO$_2$ solar cell under standard AM1.5 1 Sun irradiation. Dark currents are shown with dash lines.
4.4 Conclusion

In summary, we report an efficient dye-sensitized photocathode system by the careful design of the energy level of the sensitizer and the introduction of highly transparent and conductive n-type semiconductors. As a demonstration, unprecedentedly high cathodic photocurrents from Ru^{II} complexes-sensitized mesoporous ITO and SnO$_2$ films in the LiI/I$_2$ electrolyte have been achieved. Our TAS results confirm that the high cathodic photocurrent is attributed to the fast hole injection process from the excited dye into ITO. This novel type of photocathode can potentially break the current bottleneck and achieve wide applications in DSCs and solar fuels. This work makes it even possible to build the tandem DSC and DSPEC with the n-SC as both anode and cathode material. In addition, the photocurrent direction and magnitude on ITO and SnO$_2$ electrode can be modulated by tuning the reducing potential of the excited sensitizer.

References


3. Swierk, J. R.; Mallouk, T. E. Design and development of photoanodes for water-


31. Lefebvre, J. F.; Sun, X. Z.; Calladine, J. A.; George, M. W.; Gibson, E. A. Promoting


2013, 7 (3), 2396-2405.


44. Hamd, W.; Chavarot-Kerlidou, M.; Fize, J.; Muller, G.; Leyris, A.; Matheron, M.; Courtin, E.; Fontecave, M.; Sanchez, C.; Artero, V.; Laberty-Robert, C. Dye-sensitized nanostructured crystalline mesoporous tin-doped indium oxide films with tunable


58. Cremer, J. Novel Head-to-tail Coupled Oligo(3-hexylthiophene) Derivatives for


65. Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R. Control of Charge Recombination Dynamics in Dye Sensitized Solar Cells by the Use of Conformally


73. He, M.; Ji, Z.; Huang, Z.; Wu, Y. Molecular Orbital Engineering of a Panchromatic


Chapter 5  
Dimeric [Mo$_2$S$_{12}$]$^{2-}$ cluster: a molecular analog of MoS$_2$ edges for superior hydrogen-evolution electrocatalysis

5.1 Introduction

Hydrogen has the highest energy density by weight among all chemical fuels. In recent decades, this has sparked intense research interests in generating hydrogen from water splitting. To date, the best HER electrocatalysts are the Pt-group metals. However, the low abundance and concomitant high cost make them undesirable for large-scale hydrogen production. Therefore, finding alternative and inexpensive HER catalysts is of paramount importance. According to the Sabatier principle\textsuperscript{1}, the crucial requirement for an optimal HER catalyst is a moderate binding of hydrogen on the catalytic site, which is reflected by near-zero Gibbs free energy for atomic hydrogen adsorption ($\Delta G_{\text{ads}}(H) \approx 0$).\textsuperscript{2-5} A state-of-the-art HER catalyst such as Pt (111) has a $\Delta G_{\text{ads}}(H)$ of only -0.09 eV.\textsuperscript{6}

Promising advances in finding alternative HER catalysts have been made in recent years. One landmark example is MoS$_2$. The seminal computational and experimental studies have shown that the edge sites of the MoS$_2$ planes have excellent catalytic activity for HER ($\Delta G_{\text{ads}}(H) = 0.08$ eV), while the (0001) basal planes are inert.\textsuperscript{2,6} Thus, considerable efforts have been focused on developing nanostructured MoS$_2$ with maximally exposed edge sites.\textsuperscript{7-15}
A fundamentally revolutionary approach is to directly design Mo-S based molecules and clusters which vividly mimic the MoS$_2$ edge sites. Besides maximizing the edge density, these molecular mimics also provide an attractive strategy to freely create, precisely probe, and systematically investigate the various types of active sites. It is well-known that transition metal-sulfur complexes are involved in a lot of catalytic centers of hydrogen evolving enzymes in nature. Also, Mo-S based complex was reported for the homogeneous HER electrocatalysis and related mechanism study by the early work.$^{16}$ The center of Figure 1 shows a single MoS$_2$ layer with sulfur-rich edges. Different molecular mimics can potentially be designed, depending on which way the MoS$_2$ sheet is cropped. For example, a discrete analog was reported by Karunadasa et al., who were able to integrate the single “Mo-S$_2$” triangular functional unit into a molecular catalyst for homogeneous HER.$^{17}$ The polymeric analogs are also possible when polynuclear Mo-S based clusters are introduced. The cluster [Mo$_3$S$_{13}$]$^2^-$ has been reported to be an advanced heterogeneous HER catalyst very recently,$^{18}$ which we view as a trimer analog. However, compared with the numerous efforts in developing nanostructured MoS$_2$, $^{19-28}$ there are generally very few MoS$_2$ molecular catalysts reported.

The general term “edge site” of MoS$_2$ include various types, with different sulfur percentage coverage on Mo or S edges. The left part of Figure 2 shows a single MoS$_2$ layer with two types of sulfur-rich edge sites: (i) 100% sulfur covered (10-10) Mo edges (top side) and (ii) sulfur saturated (-1010) S edges (left side). These two types of edges are analogous to the terminal and bridging S$_2$ ligands in molecules, respectively. A thorough comprehension of the catalytic chemistry and mechanism of these sites is of paramount
importance for both fundamental research and practical catalyst optimization. Designing
the molecular mimics containing these sites thus becomes an attractive strategy to
understand the reaction mechanism and improve their activities. Since a dimer structure is
the smallest unite to include both bridging and terminal S₂, herein we conceptually design
a bi-nuclear analog [Mo₂S₁₂]²⁻ (see the right part of Figure 2) in the form of
(NH₄)₂[Mo₂(S₂)₆]·2H₂O, by revisiting classical cluster chemistry.²⁹

Figure 5.1 Scheme of the relations of the Mo-S based molecular HER catalysts. Monolayer
MoS₂ with sulfur-rich edges (center), the discrete analog [(PY₅Me₂)MoS₂]²⁺ (top), the
trimeric analog [Mo₃S₁₃]²⁻ cluster (right) and our dimeric analog [Mo₂S₁₂]²⁻ cluster (left).
**Figure 5.2** Scheme of the relation between the $[\text{Mo}_2\text{S}_{12}]^{2-}$ cluster and the MoS$_2$ edge sites. The $[\text{Mo}_2\text{S}_{12}]^{2-}$ cluster is the smallest molecular analog of MoS$_2$ possessing both bridging and terminal disulfide (S$_2$) ligands (highlighted by blue and red dotted rectangular frame, respectively).

The electrochemical tests show that $[\text{Mo}_2\text{S}_{12}]^{2-}$ is an advanced and stable heterogeneous HER catalyst under acidic conditions. The measured small Tafel slope of ~40 mV dec$^{-1}$ suggests that the HER process goes through Volmer-Heyrovsky microscopic steps. The comparison of the overpotential at 10 mA cm$^{-2}$ and turnover frequency at 200 mV overpotential proves the superiority of our $[\text{Mo}_2\text{S}_{12}]^{2-}$ among the Mo-S based electrocatalysts. We also report a series of computational investigations of the HER energetics on the $[\text{Mo}_2\text{S}_{12}]^{2-}$ cluster. The calculated thermoneutral H binding affinity ($\Delta G_{\text{ads}}(H) = -0.05$ eV) is consistent with the high HER catalytic activity.
5.2 Experimental section

5.2.1 Synthesis of \((\text{NH}_4)_2[\text{Mo}_2(S_2)_{6}]\cdot2\text{H}_2\text{O}\)

The \((\text{NH}_4)_2[\text{Mo}_2(S_2)_{6}]\cdot2\text{H}_2\text{O}\) clusters were prepared based on the method of Müller \textit{et al.}\textsuperscript{30-33}, but with some important modifications. 2.0 g of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\) (Sigma-Aldrich) and 1.5 g of \(\text{NH}_2\text{OH}\cdot\text{HCl}\) (Sigma-Aldrich) were dissolved in 30 ml deionized (DI) water (> 18.0 MΩ cm) to form a reddish brown solution, to which a 30 ml of dark red \((\text{NH}_4)_2\text{S}_x\) solution was added afterwards. The mixed solution was warmed at 50°C for 1 hr, then cooled to room temperature and filtered. The filtrate was heated at 90°C for another 4 hrs and filtered again after being cooled down. Then, 10 ml \((\text{NH}_4)_2\text{S}_x\) solution was added to the reddish brown filtrate under magnetic stirring at room temperature. The resulting solution in a 100 ml Erlenmeyer flask was transferred to a sealed box filled with Ar gas. After overnight reaction, the black rod-shaped crystals of \((\text{NH}_4)_2[\text{Mo}_2(S_2)_{6}]\cdot2\text{H}_2\text{O}\) precipitated out from the solution, which were collected by filtration afterwards. The black crystals were further purified by wash with 10 ml ice-cold water, 20 ml 2-propanol, 15 ml carbon disulfide, and 20 ml diethyl ether for a couple of times. The sample was dried in the vacuum oven at room temperature, and then stored in the glovebox. The identity and purity of the sample were confirmed by synchrotron-radiated single-crystal XRD and powder XRD measurements.

5.2.2 Synthesis of \((\text{NH}_4)_2[\text{Mo}_3\text{S}(S_2)_{6}]\cdot\text{H}_2\text{O}\)

\((\text{NH}_4)_2[\text{Mo}_3\text{S}(S_2)_{6}]\cdot\text{H}_2\text{O}\) was prepared according to the method of Müller \textit{et al.}\textsuperscript{30,32} 4.0 g \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\) (Sigma-Aldrich) dissolved in 30 ml DI water was mixed with
80 ml of (NH₄)₂Sₓ solution, and then heated at 90°C in a glass Erlenmeyer flask for 15 hrs. The Dark-red crystals of (NH₄)₂[Mo₃S(S₂)₆]∙H₂O were collected by filtration, and then washed successively with 300 ml water, 25 ml ethanol, 20 ml carbon disulfide (three times), and 20 ml diethyl ether, and finally dried in the vacuum oven at room temperature. The identity of the crystals confirmed by powder XRD (Figure 5.7c).

5.2.3 Physical characterization

For the synchrotron-radiated single-crystal X-ray diffraction (XRD) measurement, intensity data were collected at 150 K on a D8 goniostat equipped with a Bruker PHOTON100 CMOS detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ=0.7749 Å. For data collection, frames were measured for a duration of 4 s for data at 0.5° intervals of ω with a maximum 2θ value of ~60°. The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.

The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Kratos Axis Ultra XPS with monochromatic Al X-ray source, at an operation voltage as 12 kV and a current as 10 mA. All the XPS spectra were calibrated with C 1s at 284.6 eV. The SEM (FEI/Philips Sirion Field Emission SEM) was used to obtain the morphology of the crystal. The elemental mapping was acquired by Energy Dispersive Spectrometer using X-rays (EDS) that incorporated on the SEM. The Raman spectra were collected on Renishaw microscope Raman spectrometer with a 514 nm excitation wavelength at 50X zoom. The
power of the laser was 0.6 mW to avoid sample damage, and the acquisition time was 20s. Raw data were used without further data processing. FTIR spectra was recorded using a Perkin-Elmer Frontier Dual-Range FIR/MidIR spectrometer in an argon-filled glovebox. The UV-Vis absorption spectrum was recorded by Perkin Elmer Lambda 950 spectrometer.

5.2.4 Electrode preparation

Submonolayer of catalyst was loaded via lay-by-layer deposition method with the help of a commonly used polycation poly(diallyldimethylammonium chloride) (PDDA). Glass pieces (2.5×2.5×0.3 cm³) coated with fluorine-doped tin oxide (FTO) (Hartford Glass Co.) were cleaned by sonication in soap water, DI water, ethanol and acetone solution, respectively. After being dried, the FTO substrates were soaked in diluted PDDA solution (MW<100000, 0.035 w.t.% in water) for 8 min, washed by H₂O (4 min), and then soaked in 0.05 mM methanolic Mo₂ solution for another 8 min, washed by methanol (2 min) and H₂O (2 min), and then completely dried for electrochemistry test. Massive loading on FTO was done by directly drop-casting 1 mM Mo₂ DMF solution and vacuum-dried. To determine the amount of sub-monolayer loading, the loaded catalysts on FTO was washed off by sonicating in 15 ml 0.1 M NaOH solution for 1 hr and immersing in the solution for overnight. The concentration of Mo in the resulted solution was measured by inductively coupled plasma (ICP) measurement. The amount for sub-monolayer loading of Mo₂ is determined to be 0.17 nmol cm⁻² on FTO.

The Glassy carbon (GC) electrode (CHI, d= 3.0 mm, A= 0.071 cm²) was polished to a mirror finish with aqueous slurry of 0.05 μm alumina powder on a polishing microcloth (BUEHLER), cleaned with deionized (DI) water and acetone, and dried before each use.
A homogeneous ink was made from fresh DMF solution, 30 mg/mL of Super P® Li carbon and 80 μL/L of 5 wt% Nafion solution. The paste was drop-casted on the GC electrode surface through micropipette, and then dried in the vacuum oven. Various amount of Mo2 was loaded by control the concentration of the paste and the loading volume.

5.2.5 Electrochemistry measurements

The electrochemical tests were carried out by Reference 600 potentiostat (Gamry Instruments, Warminster, PA) in a custom made three-electrode electrochemical cell, with 0.5 M H₂SO₄ (pH~0) as the electrolyte solution sparged with Ar gas. GC electrode modified by different catalyst/loading was used as the working electrode, and the counter electrode was a graphite rod. The Ag/AgCl reference electrode (3 M NaCl, BASI) was calibrated to the reversible hydrogen electrode (RHE) potential with Pt meshes being both working and counter electrodes in the same 0.5 M H₂SO₄ solution purged with high purity H₂. The shift was -0.239 V vs. RHE. The polarization curves were measured by LSV with a scan rate of 5 mV s⁻¹. The j-V curve shown in the paper are all iR corrected. The EIS were performed at different DC bias with the frequency range of 2 ×10⁵ ~ 1 ×10⁻¹ Hz and the AC amplitude of 10 mV. The accelerated stability test was applied through cyclic voltammetry at 0.2 V ~ -0.25 V vs. RHE with a scan rate of 100 mV/s. The chronoamperometry (CA) test was performed using a GC rotating disk electrode (Pine Instrument, d= 5.0 mm, A= 0.196 cm²) with a rotating rate of 2500 r.p.m, which can help remove the in-situ generated H₂ bubble. The electrochemical tests with FTO working electrode were carried out in a custom made three-electrode electrochemical cell with FTO sealed by the O-ring.
5.2.6 Turnover frequency (TOF) calculation

During comparison, the TOF is normalized to per Mo atom in the catalyst. For various Mo-S based catalysts with the molecular formula of Mo\textsubscript{x}S\textsubscript{y} and certain catalyst loading mass,

\[
\text{TOF} = \frac{\text{hydrogen turnover numbers per area}}{\text{Mo atom numbers per area}} = 5.18 \times 10^{-3} \text{ s}^{-1} \times J (\text{per mA cm}^{-2}) \times \text{Mw} / [(\text{loading mass (per µg cm}^{-2}) \times x] \quad (\text{Equation 5.1})
\]

Here the current densities at -0.2 V vs. RHE were used for estimation.

5.2.7 DFT calculation

The calculation of \(\Delta G_{\text{ads}}(H)\) were performed using the Vienna \textit{Ab initio} Simulation Package (VASP\textsuperscript{34-35}, with plane wave cutoff energy of 400 eV. Pseudopotentials implemented in the projector augmented-wave (PAW) method were used to model core electrons\textsuperscript{36}. The Perdew–Burke–Ernzerhof (PBE)\textsuperscript{36-37} form of the generalized gradient approximation (GGA) was selected to represent the exchange-correlation functional. Fermi-level smearing with a Gaussian width of 0.1 eV was used to accelerate the self-consistent total-energy iterations. All structures were relaxed using a limited memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS)\textsuperscript{38} algorithm until forces on all atoms are less than 0.03 eV/Å. Spin polarization was included in all calculations. The system was modeled using periodically repeated Mo\textsubscript{2}S\textsubscript{12} clusters, with the unit cell size of 15×15×15 Å. Each unit cell contains one Mo\textsubscript{2}S\textsubscript{12} cluster, and there is at least 9 Å distance between one cluster and its nearest periodic image. The Brillouin zone was sampled at the Γ-point. The support effects from the glassy carbon are not included and we have tested that this will not affect the results (details are provided in the next section).
We calculated the adsorption of H on the clusters, the differential adsorption energy $E_{\text{ads}}$ of the n-th H atom on Mo$_2$S$_{12}$ (labeled as Mo2) is defined as:

$$\Delta E_{\text{ads}}[H] = E[nH^*-\text{Mo2}] - E[(n-1)H^*-\text{Mo2}] - \frac{1}{2}E[H_2]$$  \hspace{1cm} (Equation 5.2)

In the special case of the first H adsorption, it becomes:

$$\Delta E_{\text{ads}}[H] = E[H^*-\text{Mo2}] - E[\text{Mo2}] - \frac{1}{2}E[H_2]$$  \hspace{1cm} (Equation 5.3)

We also calculated the adsorption free energy of H, which has a similar definition:

$$\Delta G_{\text{ads}}[H] = G[nH^*-\text{Mo2}] - G[(n-1)H^*-\text{Mo2}] - \frac{1}{2}G[H_2]$$  \hspace{1cm} (Equation 5.4)

We considered the contributions to Gibbs free energy from the zero-points energies, $-T \Delta S$ and $\int_0^{300} K C_v dT$. Each term was calculated using standard thermodynamics methods$^{39}$. Vibrational frequencies for H$_2$ and nH-Mo2 needed in free energy calculations were obtained from normal mode analysis after we relaxed the corresponding structures using VASP.

In this study the carbon support was not explicitly modeled, but we have examined the effects of carbon support by placing a layer of graphene under the Mo2 clusters. DFT calculations show that Mo2 was stabilized on the carbon support only by dispersion effects. Even with the dispersion correction included in our DFT calculation using Grimme’s DFT-D3 method$^{40}$, Mo2 still binds weakly with carbon and keep an equilibrium distance of around 3 Å away from the support. As a result, we found that the adsorption energy of H on Mo2 is the same regardless of the presence of the carbon support (-0.293 vs. -0.296 eV, with or without the carbon support). Therefore we conclude that even with the carbon support included in our model, the observations in this study will still be the same.
5.3 Results and discussions

5.3.1 Physical characterization

(NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O was synthesized and purified based on a modified Müller method.$^{29-31, 33}$ (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O was prepared and separated as crystalline black needles/rods with length varying from 10-100 μm (Figure 3b). Synchrotron-radiated single-crystal XRD analysis shows that (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O crystallizes in the orthorhombic space group Pnna with a =21.2927(11) Å, b =13.0408(7) Å, c = 12.6064(7) Å, and a multiplicity of 8 (unit cell depicted in Figure 3c). Figure 2a shows that each Mo center is coordinated to four S$_2$ units, with two bridging S$_2$ having a short average S-S bond length of 2.034(5) Å, and two terminal S$_2$ having a long average S-S bond length of 2.053(2) Å. The details of the single crystal data, bond angle and bond length are listed in Table 5.1-5.3.
Figure 5.3 Structure of (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]·2H$_2$O. (a) Structure of a single molecule, position determined by synchrotron-radiated single-crystal XRD. (b) Optical microscopic image of the black rods on a glass slide. Inset shows the digital image of the bulk powder in the vial. (c) The corresponding (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]·2H$_2$O crystal structure, viewed from c axis.
**Figure 5.4** (a) SEM image of the (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]$\cdot$2H$_2$O rod; (b) and (c): spatial distribution of Mo and S elements shown by EDS.

Figure 5.4 displays one crystalline (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]$\cdot$2H$_2$O rod with the length of tens of micrometers and the width of several micrometers. EDS maps (Figure 5.4b and 5.4c) show the spatial distribution of Mo and S on our sample.
Figure 5.5 Powder XRD pattern of (NH₄)₂[Mo₂S₁₂]·2H₂O (black: experimental result; red: simulation based on the single crystal structure; blue: signal from substrate tape).

The powder XRD of the bulk sample (Figure 5.5) is also consistent with the (NH₄)₂[Mo₂(S₂)₆]·2H₂O phase, proving that our synthesis produces a single-phase product. The experimentally measured (black curve) and simulated patterns (red curve) of (NH₄)₂[Mo₂S₁₂]·2H₂O agree well, both with (220) being the strongest peak.

Figure 5.6 shows the IR spectrum of the (NH₄)₂[Mo₂(S₂)₆]·2H₂O powder. The peak at 1380 cm⁻¹ is assigned to the vibration of NH₄⁺, and the intense peak at 522 cm⁻¹ is ascribed to the S-S stretching of the terminal S₂. The result consists well with the literature.²⁹,⁴¹ The band due to the vibration of the bridging S₂ (541 cm⁻¹) has a much lower
IR intensity. The peak position, peak intensity and the vibrational mode agree well with the simulated result.

Figure 5.6 IR spectrum of (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]·2H$_2$O. (a) experimental spectrum (the inset shows the 450–600 cm$^{-1}$ region); (b) the simulated spectrum at 400-600 cm$^{-1}$ region.
#### Table 5.1 Crystal Data and Structure Refinement for (NH₄)₂Mo₂S₁₂·2H₂O

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<th>Property</th>
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<tr>
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</tr>
<tr>
<td>( \lambda / \text{Å} )</td>
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</tr>
<tr>
<td>( T / \text{K} )</td>
<td>150(2)</td>
</tr>
<tr>
<td>Crystal dimensions/mm</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
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</tr>
<tr>
<td>( b / \text{Å} )</td>
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</tr>
<tr>
<td>( c / \text{Å} )</td>
<td>12.6064(7)</td>
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</tr>
<tr>
<td>( \beta/° )</td>
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<tr>
<td>( \gamma/° )</td>
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<td>( V / \text{Å}^3 )</td>
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<td>( D_c / \text{g cm}^{-3} )</td>
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<td>Absorption coefficient/mm⁻¹</td>
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<td>( F(000) )</td>
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<td>( \theta ) Range/°</td>
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<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Completeness</td>
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<tr>
<td>( R_{int} )</td>
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<tr>
<td>( R_1(I &gt; 2\sigma(I)) ) (^a)</td>
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</tr>
<tr>
<td>( wR_2(I &gt; 2\sigma(I)) ) (^a)</td>
<td>0.0666</td>
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<tr>
<td>Goodness-of-fit on ( F^2 )</td>
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<tr>
<td>( \Delta \rho_{\text{max, min}} / \text{e Å}^{-3} )</td>
<td>0.726, -0.453</td>
</tr>
</tbody>
</table>

\(^a\) \( R1 = \sum ||F_0| - |F_c||/\sum |F_0|; \ wR_2 = \sum [w(F_0^2 - F_C^2)^2]/\sum [w(F_0^2)]^{1/2} \)
Table 5.2 Selected bond lengths (Å) of \((\text{NH}_4)_2\text{Mo}_2\text{S}_{12} \cdot 2\text{H}_2\text{O}\)

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<th>Bond</th>
<th>Distance (Å)</th>
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<tr>
<td>Mo(1)-S(1)</td>
<td>2.3753(16)</td>
</tr>
<tr>
<td>Mo(1)-S(10)</td>
<td>2.4386(15)</td>
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<tr>
<td>Mo(1)-S(10)#1</td>
<td>2.4387(15)</td>
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<tr>
<td>Mo(1)-S(7)</td>
<td>2.4652(16)</td>
</tr>
<tr>
<td>Mo(1)-S(7)#1</td>
<td>2.4652(16)</td>
</tr>
<tr>
<td>Mo(1)-S(6)#1</td>
<td>2.5024(16)</td>
</tr>
<tr>
<td>Mo(1)-S(6)</td>
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<tr>
<td>Mo(3)-S(5)#2</td>
<td>2.3907(16)</td>
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<tr>
<td>Mo(3)-S(2)</td>
<td>2.3946(16)</td>
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<tr>
<td>Mo(3)-S(11)</td>
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<td>Mo(3)-S(12)</td>
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<td>Mo(3)-S(3)</td>
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<td>Mo(3)-S(5)</td>
<td>2.4756(16)</td>
</tr>
<tr>
<td>Mo(3)-S(9)</td>
<td>2.4805(17)</td>
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<tr>
<td>Mo(3)-S(2)#2</td>
<td>2.4891(16)</td>
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<tr>
<td>Mo(3)-Mo(3)#2</td>
<td>2.8177(10)</td>
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</table>

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1,z   #2 x,-y+1/2,-z+3/2
Table 5.3 Selected bond angles (°) of (NH₄)₂Mo₂S₁₂·2H₂O

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
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<tr>
<td>S(1)#1-Mo(1)-S(1)</td>
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<td>S(6)-Mo(2)-S(8)</td>
<td>94.22(5)</td>
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<td>S(1)#1-Mo(1)-S(10)</td>
<td>126.68(5)</td>
<td>S(6)-Mo(2)-S(1)</td>
<td>49.10(5)</td>
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<td>S(1)#1-Mo(1)-S(10)#1</td>
<td>86.28(5)</td>
<td>S(6)-Mo(2)-S(1)#1</td>
<td>89.01(5)</td>
</tr>
<tr>
<td>S(1)#1-Mo(1)-S(7)</td>
<td>135.65(5)</td>
<td>S(6)-Mo(2)-Mo(1)</td>
<td>56.47(4)</td>
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<td>S(1)#1-Mo(1)-S(7)#1</td>
<td>95.31(5)</td>
<td>S(5)#2-Mo(3)-S(2)</td>
<td>112.36(6)</td>
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<tr>
<td>S(1)#1-Mo(1)-S(6)#1</td>
<td>49.20(5)</td>
<td>S(5)#2-Mo(3)-S(11)</td>
<td>87.21(5)</td>
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<td>89.28(5)</td>
<td>S(5)#2-Mo(3)-S(12)</td>
<td>126.68(6)</td>
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<td>S(1)#1-Mo(1)-Mo(2)</td>
<td>56.41(4)</td>
<td>S(5)#2-Mo(3)-S(3)</td>
<td>93.23(6)</td>
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<td>112.93(8)</td>
<td>S(5)#2-Mo(3)-S(5)</td>
<td>90.24(6)</td>
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<td>S(6)-Mo(2)-S(4)</td>
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<td>S(5)#2-Mo(3)-S(9)</td>
<td>136.35(6)</td>
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<td>S(5)#2-Mo(3)-S(2)#2</td>
<td>49.24(5)</td>
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<tr>
<td>S(6)-Mo(2)-S(8)#1</td>
<td>135.62(5)</td>
<td>S(5)#2-Mo(3)-Mo(3)#2</td>
<td>56.04(4)</td>
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</table>

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1,z   #2 x,-y+1/2,-z+3/2
Figure 5.7 Characterization of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O. (a) SEM image; (b) digital image of powder sample; (c) powder XRD pattern (black: experimental result; red: simulation based on the single crystal structure; blue: signal from substrate tape).

The characterization of the as-synthesized (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O crystals is shown in Figure 5.7. The SEM image (Figure 5.7a) shows the block-shaped (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O crystals with micrometer size. The experimentally measured XRD pattern (black curve in Figure 5.7c) of the dark-red powders (Figure 5.7b) consists with the simulated one (red curve) and the reported one in literature. The strongest peak is (110).
The magnetic properties of the (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O and (NH$_4$)$_2$[Mo$_2$S$_{12}$]·2H$_2$O compound were investigated by SQUID magnetometer. Figure 5.8 shows the Curie plot in the temperature region of 3-300 K under the magnetic field of 200 Oe. The diamagnetic nature of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O and (NH$_4$)$_2$[Mo$_2$S$_{12}$]·2H$_2$O was unambiguously confirmed by the negative susceptibility value. The diamagnetism of the two compounds are consistent with the literature.$^{29,42}$

Figure 5.9 shows the UV-Vis absorption spectra of the 0.2 mM [Mo$_2$S$_{12}$]$^{2-}$ in degassed DMF solution. The five absorption peaks (including shoulder peaks) in DMF are not very characteristic, but all agree very well with the reported ones in methanol (with slight red-shift).$^{33}$ The assignments of the peaks remain obscure.
**Figure 5.9** UV-Vis absorption spectra of 0.2 mM $[\text{Mo}_2\text{S}_{12}]^{2-}$ DMF solution.

**Figure 5.10** XPS spectra of $[\text{Mo}_2\text{S}_{12}]^{2-}$ solid powder and the deposited film. (a) Deconvolution of the Mo 3d region. (b) The S 2p spectra consist of three different doublets (S 2p1/2 and S 2p3/2).
The clusters can be deposited on an electrode surface by facile drop-casting methods. Figure 5.10 shows the XPS of Mo 3d and S 2p region for the as-synthesized crystalline powder sample and the deposited film on FTO by drop-casting fresh 1 mM [Mo₂S₁₂]²⁻ DMF solution (Figure 5.11a). The binding energy (BE) is 229.4 eV and 232.6 eV for Mo 3d₅/₂ and Mo 3d₃/₂, respectively. In the literature of (NH₄)₂[Mo₂(S₂)₆]·2H₂O, the BEs of Mo 3d doublets were reported to be 230.3 eV and 233.4 eV. The separation between the two peaks is similar for our study and reference. However, it is hard to compare the absolute BE value because the reported study calibrated N 1s of NH₄⁺ to 403.0 V, which should normally appear at lower binding energies. The broad S 2p spectra consist of three different doublets (S 2p₃/₂ and S 2p₁/₂): (i) one at (161.8 eV, 163.0 eV) ascribed to the terminal S₂ ligands, (ii) one at (163.1 eV, 164.2 eV) due to the bridging S₂ ligands, and (iii) one at higher BE contributed from trace amount (<5%) of residual polysulfides. The clear separation of the spectra of the terminal and bridging S₂ ligands differentiate it from those MoS₂ and amorphous MoSₓ materials. The ratio of terminal to bridging sulfur at the surface was slightly lower than the theoretical value (2:1), but remained the same for both the crystalline powder and the deposited film sample (1.3:1), respectively. Therefore we conclude that the structure of the anionic cluster on the electrode surface is unchanged.
**Figure 5.11** Image of (a) 1.0 mM [Mo$_3$S$_{13}$]$^{2-}$ and [Mo$_2$S$_{12}$]$^{2-}$ DMF solution. (b) large hydrogen bubble accumulating at RDE surface in the CA test in 0.5 M H$_2$SO$_4$.

5.3.2 Electrochemistry measurement

**Figure 5.12** Polarization curves with different [Mo$_3$S$_{12}$]$^{2-}$ catalyst loading. The inset shows the performance of sub-monolayer deposited cluster on FTO electrode.

The HER electrocatalytic activities were investigated in 0.5 M H$_2$SO$_4$ solution (Ar saturated) with a typical three-electrode setup. The scan rate of all LSV tests was 5 mV s$^{-1}$. 

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1. Submonolayer of catalyst was loaded via the lay-by-layer self-assembly method on FTO substrates with the help of a commonly used polycation poly(diallyldimethylammonium chloride)\textsuperscript{46}. The amount for sub-monolayer loading is 0.17 nmol cm\textsuperscript{-2}, as determined by ICP measurement. The FTO does not show any detectable transmittance change after one cycle of catalyst loading, however the polarization curve (inset of Figure 5.12) clearly demonstrates the activity of the submonolayer of catalyst. Higher amount of catalyst was loaded on glassy carbon (GC) electrode by drop-casting a homogeneous ink consisting of fresh [Mo\textsubscript{2}S\textsubscript{12}]\textsuperscript{2-} (labelled as Mo2) DMF solution, carbon powder and Nafion. The polarization curves of Mo2 with various catalyst loading amount are displayed in Figure 5.12. The bare carbon powder on GC electrode was relatively inert to HER, with a negligible background current and an overpotential over 600 mV. When Mo2 was present, the polarization curve showed a low overpotential of 100~150 mV, beyond which the current density rise very rapidly. The cathodic current density enhances with the increasing amount of catalyst loading at a given potential.
Figure 5.13 Polarization curves with $[\text{Mo}_2\text{S}_{12}]^{2-}$, $[\text{Mo}_3\text{S}_{13}]^{2-}$ and bulk MoS$_2$.

The HER electrocatalytic activity of Mo2 was compared with that of the commercial bulk MoS$_2$ powder and the state-of-the-art catalyst $[\text{Mo}_3\text{S}_{13}]^{2-}$ (labelled as Mo3, Figure 5.7) in Figure 5.13. Our performance of Mo3 resembles the early-reported value (10 nmol cm$^{-2}$ is $\sim$7.6 μg cm$^{-2}$). Furthermore, Figure 3b clearly illustrates that the catalytic activity of Mo2 is superior to that of Mo3 with equivalent mole of catalyst loading. The bulk MoS$_2$ offers negligible H$_2$-evolving activity.

Tafel plots can help to elucidate the electron transfer kinetics. Three possible elementary steps have been suggested for HER in acidic solutions.$^{47}$ The first step is an initial discharge step (Volmer reaction):

$$\text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O} \quad \text{(Equation 5.5)}$$

followed by either an electrochemical desorption step (Heyrovsky reaction),

$$\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O} \quad \text{(Equation 5.6)}$$
Or a recombination step (Tafel reaction)

\[ \text{H}_\text{ads} + \text{H}_\text{ads} \rightarrow \text{H}_2 \]  

(Equation 5.7)

The HER reaction involves steps of either (5.5)-(5.6) or (5.5)-(5.7). Assuming the symmetric coefficient is 0.5, the Tafel slope should be around 120, 40 or 30 mV dec\(^{-1}\), if the rate limiting step is (1), (2) or (3), respectively.

The Tafel slope is 40 and 39 mV dec\(^{-1}\) for our Mo3 and Mo2 sample, respectively (Figure 5.14). The result of Mo3 agrees with the literature.\(^{18}\) Beyond the linear region, the current density deviates from the exponential relationship at higher overpotential, which might be due to the diffusion limit or block of the catalytic site by generated hydrogen bubbles.\(^{18}\) The Tafel slope of \(~40\) mV dec\(^{-1}\) indicates that both clusters proceed via the Volmer-Heyrovsky (step 1-2) mechanism, and the electrochemical desorption step (Heyrovsky reaction) is the rate limiting step. Tafel slopes of the reported advanced alternative HER catalysts were summarized in Table 5.4. Mo2 is among the types of clusters with small Tafel slope, which means that significant enhancement of the catalytic current can be obtained with only a moderate increase of the overpotential. The only alternative HER catalyst with an apparently smaller Tafel slope is the polypyrrole and MoS\(_x\) copolymer film (29 mV dec\(^{-1}\)).\(^{48}\)
Table 5.4 Summary of the Tafel slopes of HER heterogeneous catalysts

<table>
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<tr>
<th>Catalyst type</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>Reference</th>
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<tr>
<td>nanoparticulate MoS₂</td>
<td>120</td>
<td>49</td>
</tr>
<tr>
<td>Co-promoted MoS₂</td>
<td>101</td>
<td>49</td>
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<tr>
<td>double-gyroid MoS₂</td>
<td>50</td>
<td>12</td>
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<td>1T-MoS₂ nanosheet</td>
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<td>8</td>
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<tr>
<td>UHV MoS₂</td>
<td>Au</td>
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<tr>
<td>monodispersed MoS₂</td>
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<td>69</td>
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<tr>
<td>MoS₂</td>
<td>RGO</td>
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<tr>
<td>O-incorporated MoS₂</td>
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<td>13</td>
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<td>MoS₃</td>
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<td>Li-MoS₂</td>
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<td>[Mo₃S₄]⁴⁺</td>
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<td>Cu centered MOF (with 8 w.t.% GO)</td>
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<td>Ni</td>
<td>NiO</td>
<td>CoSe₂</td>
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<tr>
<td>Ni₂P</td>
<td>46</td>
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<tr>
<td>C₃N₄</td>
<td>N-Graphene</td>
<td>52</td>
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</table>
EIS was used to probe the electrochemical and ionic process at the electrode/electrolyte interface. We performed EIS under different dc bias along the $j-V$ curve. Representative Nyquist plots (bias: -0.165 V) are presented in Figure 3d, and the width of the semicircle indicates the total Faradic resistance of the HER process. The Faradic resistances of Mo2 (10 nmol cm$^{-2}$) under different overpotential (after $iR$ correction) are displayed in the inset of Figure 5.15. The Faradic resistance drops exponentially as the overpotential increases, and the slope is in excellent agreement with the Tafel slope.
Figure 5.15 Nyquist plots at the bias of -0.165 V. The inset shows the exponential dependence of $R_F$ with overpotential.

For comparing the HER activity of different heterogeneous catalysts, Jaramillo et al. suggested the overpotential at 10 mA cm$^{-2}$ electrode as a crucial parameter for evaluation.\textsuperscript{26} As displayed in Figure 5.16, Mo2 only requires an overpotential of 161 mV to reach a $J$ of 10 mA cm$^{-2}$, outperforming other cluster-type catalysts such as [Mo$_3$S$_4$]$^{4+}$ (240 mV)\textsuperscript{53} and Mo3 (178 mV in this work and 174 mV in literature\textsuperscript{18}), and most MoS$_2$ or MoS$_3$ based materials\textsuperscript{19, 22, 27, 51-52, 66-68} (Figure 5.16). We also compare the TOF of these catalysts at a 200 mV overpotential (Table 5.5). The TOF is normalized to per Mo atom in the catalyst based on the loading mass, because Mo is at least 100 times more expensive than S, and the accurate definition and evaluation of the exact amount of the “active catalytic site” is complicated for different reported results. Mo2 shows a TOF of 3.27 ±
0.15 s\(^{-1}\) per Mo (from three independent measurements) with the catalyst loading amount of 6.5 μg cm\(^{-2}\), which is higher than most of the Mo-S based catalysts with similar loading mass. The highest TOF so far is obtained from MoS\(_2\) nanoparticles on precious metal electrode Au (111),\(^{2,24}\) which is marginally higher than that of Mo2.

**Figure 5.16** Comparison of the overpotential at 10 mA cm\(^{-2}\) for various Mo-S based catalysts.
Table 5.5 Comparison of TOF (H₂ s⁻¹) at 200 mV overpotential per Mo atom for various advanced Mo-S based HER catalysts in 0.5 M H₂SO₄

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading amount</th>
<th>TOF (H₂ s⁻¹) at 200 mV overpotential per Mo atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo₂S₁₂]²⁻</td>
<td>6.5 µg cm⁻²</td>
<td>3.27 ± 0.15 (from three measurements)</td>
</tr>
<tr>
<td>[Mo₃S₁₃]²⁻ (this paper)</td>
<td>7.6 µg cm⁻²</td>
<td>0.86 ± 0.04 (from three measurements)</td>
</tr>
<tr>
<td>[Mo₃S₁₃]²⁻ (literature)¹⁸</td>
<td>10 µg cm⁻²</td>
<td>~0.60</td>
</tr>
<tr>
<td>[Mo₃S₄]⁴⁺ (2nd scan curve)³⁵</td>
<td>Sub monolayer</td>
<td>1.0</td>
</tr>
<tr>
<td>MoS₂ /RGO</td>
<td>285 µg cm⁻²</td>
<td>~0.1</td>
</tr>
<tr>
<td>Lithiated MoS₂ nanofilm¹⁰</td>
<td>22 µg cm⁻²</td>
<td>0.25</td>
</tr>
<tr>
<td>Monodispersed MoS₂ /Au¹¹</td>
<td>1.03 µg cm⁻²</td>
<td>~3.6</td>
</tr>
<tr>
<td>MoS₃</td>
<td>8 µg cm⁻²</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu₂MoS₄</td>
<td>41.6 µg cm⁻²</td>
<td>~0.044</td>
</tr>
</tbody>
</table>

Stability is also an important parameter for practical application. We applied accelerated cyclic potential scan from 0.2 V to –0.25 V at a scan rate of 100 mV s⁻¹. Only marginal activity loss was observed for Mo2 (10 nmol cm⁻²) modified GC electrode: the overpotential at 10 mA cm⁻² increased by 1 and 13 mV for the scan after 100 and 1000 potential cycles, respectively (Figure 5.17). This stability is similar to that of [Mo₃S₁₃]²⁻, which witnessed an increase by 13 mV in the similar stability test protocol.²⁶ CA test was...
performed on an RDE with 20 nmol cm$^{-2}$ of Mo2 at a bias of -0.2 V. Even at a rotating speed of 2500 r.p.m, hydrogen bubbles kept accumulating in situ (Figure 5.11b) due to the remarkable current, which blocked the electrode surface and lead to the fluctuation of the current (bubble growing/bursting). The overall trend shows the decent retention of performance.

**Figure 5.17** Polarization curves recorded before/after 100 and 1000 cycles of accelerated stability scan. The inset shows the $J$-$t$ response in a chronoamperometry test.
Figure 5.18 XPS spectra of the deposited $[\text{Mo}_2\text{S}_{12}]^{2-}$ film after 1 hr CA measurement. (a) Deconvolution of the Mo 3d region. (b) The S 2p spectra of $[\text{Mo}_2\text{S}_{12}]^{2-}$ consist of three different doublets (S2p$_{1/2}$ and S2p$_{3/2}$): the terminal S$_2$ ligands and the bridging S$_2$ ligands.

The chemical stability of the catalyst after 1 hr CA test on the FTO electrode was carefully investigated by XPS (Figure 5.18) and Raman spectra (Figure 5.19). Figure 5.18 shows the Mo 3d and S 2p spectra of the Mo2 film on FTO after 1 hr of CA test (bias: -0.2 V vs. RHE) in 0.5 M $\text{H}_2\text{SO}_4$. The Mo 3d spectra remained similar (peak position difference < 0.1 eV), except a small peak arising from S 2s of $\text{H}_2\text{SO}_4$ electrolyte left on the electrode surface. For S 2p spectra, the doublet of polysulfide residue disappeared, which consists with what was reported for $[\text{Mo}_3\text{S}_{13}]^{2-}$. The peak positions of terminal (161.8 eV, 163.0 eV) and bridging S$_2$ (163.1 eV, 164.2 eV) remained exactly unchanged. The Mo to S (from terminal and bridging S$_2$) ratio from XPS is 1:6.4, which clearly demonstrates that sulfur was not kicked out in the HER catalytic cycle.
Figure 5.19 Raman spectra of the $[\text{Mo}_2\text{S}_{12}]^{2-}$ cluster (powder sample, film on FTO, film after HER CA test for 1hr).

$(\text{NH}_4)_2[\text{Mo}_2(\text{S}_2)_6]\cdot2\text{H}_2\text{O}$ has been reported to be quite sensitive to thermal decomposition,$^{41}$ therefore only very weak laser power (e.g. 0.6 mW) can be used for probe. Nevertheless, the spectrum still shows valuable information for compound identification. Generally the spectrum is different from other Mo-S materials, e.g. MoS$_2$. The broad peak at 510–550 cm$^{-1}$ are assigned to S-S vibration. This consists with the two bridging S-S vibration modes (542, 536 cm$^{-1}$) and four terminal S-S vibration modes (525, 524, 521, 520 cm$^{-1}$) predicted by our DFT modeling. The trend of bridging and terminal S$_2$ also agrees with that of the S-S bond length (shorter by about 0.02 Å for bridging S$_2$). The characteristic peaks at ~360 cm$^{-1}$ is ascribed to the Mo-S vibration, which is both reported in literature$^{71}$ and observed by our DFT modeling. In addition, we did not observe any peaks corresponding to Mo-O vibration at 900-1000 cm$^{-1}$ region. Raman spectra probes the
vibrational mode of the chemical bonds of the cluster. The spectra were almost the same for these samples, which indicates that the cluster structure did not change after film deposition and HER test. The decent cyclability, and the similarity of the XPS and Raman spectra of the electrode before and after stability test demonstrate that Mo2 is a stable HER catalyst in acidic solution.

5.3.3 Simulation

Figure 5.20 Energetics of HER process on different catalysts: Mo$_2$S$_{12}$, MoS$_2$ nanoparticle and Pt. The insets shows the preferred geometries of 1H adsorption on Mo$_2$S$_{12}$. The adsorption sits are highlighted by red dotted circles.

Nørskov and co-workers illustrated that the binding affinity of H is an excellent descriptor of the HER activity of materials.\textsuperscript{5, 72-73} Here the origin of the excellent HER activity of our catalyst is studied by density functional theory (DFT) calculations. We
systematically explored the adsorption of H on various sites of Mo2. The catalytic paths through Mo-H or S-H intermediates have both been reported for Mo-S based materials.\textsuperscript{74-77} Our Mo atom has a high coordination number environment, making the Mo-H binding not preferable. The preferred hydrogen binding position is suggested to be bridging S\textsubscript{2} (inset of Figure 5.20) with $\Delta G_{\text{ads}}$ (H) of -0.05 eV (compared to 0.02 eV for terminal S\textsubscript{2}, see Figure 5.21a).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_21.png}
\caption{(a) Three most favorable H adsorption configurations on Mo2. (b) Three most favorable 2H adsorption configurations on Mo2. Their associated $E_{\text{ads}}$ and $G_{\text{ads}}$ values are listed below each structure. For clarity, depths cues are used in these pictures (atoms that are further away from the reader appear more transparent).}
\end{figure}
We have examined the H adsorption on Mo2 by comparing all possible adsorption sites. Both the terminal and bridging S₂ can be the binding site of H, however we found that H binding with the bridging S₂ is more stable by 0.07 eV in Gibbs free energy. We have also considered the possibility that H may bond directly with Mo by testing multiple initial structures where H is placed in vicinity of a Mo atom. However we could never find a stable structure with a Mo-H bond. Instead, we found that H always binds with S atoms. This indicates that H does not prefer the direct bonding with Mo, probably due to the high coordination number of Mo in this molecule. Figure 5.21 compares the geometry of three most stable H adsorption configurations on Mo2, together with their associated ΔE\text{ads} and ΔG\text{ads}.

Since multiple H adsorption sites exist, we also examined the possibility of the second (and further) H adsorption on Mo2. We found that the adsorption of the second H will increase the free energy of the system by at least 0.19 eV (Figure 5.21b), which is much higher than the potential necessary to desorb the first H atom through reaction: H-Mo2 + H⁺ + e⁻ → Mo2 + H₂ (ΔG = 0.05 eV). Since the second (and further) H adsorption is endothermic, we would expect only one H adsorbed in the catalytic cycle at ~ 0 V vs. RHE. The preference of the 1 H adsorption catalytic pathway over 2 H adsorption model is revealed in the scheme in Figure 5.22. This observation also suggests that the Tafel step is not favored compared with Heyrovsky reaction because the former requires at least two adsorbed H. Even at more negative bias, the Tafel step needs a large activation energy barrier of 0.91 eV (Figure 5.22), therefore the Volmer-Heyrovsky mechanism should dominates, which is consistent with the experimental Tafel plot (Figure 5.14).
Figure 5.22 Reaction paths and energies of the HER on Mo2 with two different reaction mechanisms (Volmer-Heyrovsky reaction or Volmer-Tafel reaction).

The free energy changes during HER are shown in the energy diagram in Figure 5.20. The HER process goes through three states, an initial state (H⁺ + e⁻), an intermediate adsorbed H*, and the final product H₂. Mo2 shows a close-to-zero ΔG_ads (H) of -0.05 eV, similar to MoS₂ nanoparticles (0.08 eV)⁷⁴ and Pt (111) (-0.09 eV)⁵. The |ΔG_ads (H)| of Mo2 is smaller than other reported moderate metallic catalysts⁵ and the recently reported advanced catalysts (-0.19 eV for C₃N₄@NG and 0.40 eV for MoS₄)⁶⁴,⁷⁸. Furthermore, the rate limiting step is likely to be Heyrovsky reaction since this step is energetically uphill and has a higher kinetic barrier than the Volmer reaction step.
5.4 Conclusions

To summarize, the [Mo$_2$S$_{12}$]$^{2-}$ cluster is reported as an advanced heterogeneous HER electrocatalyst and the simplest molecular model for the mimic and investigation of the terminal and bridging S$_2$. The crystal structure of the (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O microrod was well characterized by synchrotron-radiated single-crystal XRD. The catalyst can be loaded on GC and FTO electrodes by the drop-casting method. The small tafel slope of $\sim$40 mV dec$^{-1}$ suggests that the HER process goes through Volmer-Heyrovsky microscopic steps, with the Heyrovsky reaction as the rate limiting step. The comparison of the overpotential and turnover frequency indicates the superiority of (NH$_4$)$_2$[Mo$_2$(S$_2$)$_6$]-2H$_2$O over most of the other Mo-S based catalysts. The hydrogen adsorption energy is calculated to be only -0.05 eV on the bridging S$_2$, which is the best among all the reported non-metallic HER catalysts. These results indicate that the [Mo$_2$S$_{12}$]$^{2-}$ cluster has promising HER applications in the electrolysis and photoelectrolysis of water. Furthermore, rich chemistry can be applied in the MoS$_2$ molecular mimics, for the creative design and precise investigation of different types of active sites. We think our study is helpful shedding light on the rational design of HER catalysts and biomimetics of hydrogen evolving enzymes.

References


2. Jaramillo, T. F.; Jorgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff,


2005, 127 (36), 12717-12726.

Chapter 6 Conclusion

6.1 Summary of the research work

The past few decades have witnessed an incredible number of technological advances in the energy conversion devices that have changed our lifestyle. A comprehensive understanding of the charge transfer processes in key interfaces of these devices (e.g. solar cells, water splitting cells, etc.) is of paramount importance to both the fundamental science development and the practical device optimization. My efforts were directed toward elucidating interfacial charge transfer process related to dye-sensitized photocathodes and heterogeneous hydrogen evolution catalysis electrodes.

First, I carried out a fundamental and systematic investigation of NiO based p-DSCs using EIS and IMPS/IMVS technique. By varying the electrocatalytic properties of the counter electrode and the illumination intensities, I have unambiguously assigned the semicircles in the impedance Nyquist plot and generated a comprehensive equivalent circuit for p-DSCs. Key recombination parameters, including the hole transport resistance, recombination resistance, chemical capacitance, and the hole transport time and the hole lifetime, have been obtained and thoroughly discussed.

Then I went one step further to probe the low $FFs$ and unsatisfactory efficiencies of NiO p-DSCs via investigating the interfacial charge transfer processes using EIS. NiO p-DSCs were systematically probed under various bias and illumination conditions. Under
the constant 1 sun illumination, the $R_{rec}$ of the cell deviates from an exponential relationship with the potential and saturates at $\sim 130 \, \Omega \, \text{cm}^2$ under the short circuit condition, which is ascribed to the overwhelming recombination with the reduced dye anions. Such a small $R_{rec}$ results in the small dc resistance, which decreases the “flatness” of the $J-V$ curve. The quantitative analysis demonstrates that the $FF$ value is largely attenuated by the recombination of holes in NiO with the reduced dyes. Our analysis also shows that if this recombination can be eliminated, then an FF value of 0.6 can be reached, which agrees with the theoretical calculation with a $V_{OC}$ of 160 mV.

After pointing out the drawbacks of NiO, I focused on investigate alternative materials for sensitized photocathodes. Sensitized photocathodes are highly desired for solar fuels and tandem solar cells, yet the development is hindered by the scarcity of suitable p-type semiconductors. I have firstly reported the dye-controlled interfacial charge transfer, and demonstrated the generation of high cathodic photocurrents via sensitizing a conducting n-type semiconductor: ITO or tin oxide, which is against the common wisdom. The sensitized mesoporous ITO and tin oxide electrodes deliver unprecedented cathodic photocurrents, which is realized by the rational design of dyes with appropriate energy alignment with the conduction band of the semiconductor. This revolutionary study reveals a new perspective toward the selection of electrode materials for sensitized photocathodes.

The photoelectrode and electrocatalyst can be integrated into solar fuel production devices. I also studied the heterogeneous hydrogen evolution electrocatalysis. Proton reduction is one of the most fundamental and important reactions in nature. MoS$_2$ edges have been identified as the active sites for hydrogen evolution reaction (HER)
electrocatalysis. I conceptually designed a dimeric molecular analog \([\text{Mo}_2\text{S}_{12}]^{2-}\), as the smallest unit possessing both the terminal and bridging disulfide ligands. I performed the electrochemical tests, showing that \([\text{Mo}_2\text{S}_{12}]^{2-}\) is a superior heterogeneous HER catalyst under acidic conditions. Computations suggest that the bridging disulfide ligand of \([\text{Mo}_2\text{S}_{12}]^{2-}\) exhibits a hydrogen adsorption free energy near zero (-0.05 eV). The work helps shed light on the rational design of HER catalysts and biomimetics of hydrogen evolving enzymes.

6.2 Future work

Compatible photoelectrode and electrocatalysts can be integrated into solar fuel production devices to realize the solar water splitting. The Mo-S clusters can be deposited on our novel and efficient ITO and tin oxide photocathodes for proton reduction. Because the LUMO of O3 and O18 is very negative, the photocathode can be coupled with other catalysts for solar fuel production (e.g. CO\(_2\) reduction) and organic molecule synthesis.
Chapter 1


42. Natu, G.; Hasin, P.; Huang, Z. J.; Ji, Z. Q.; He, M. F.; Wu, Y. Y. Valence Band-Edge Engineering of Nickel Oxide Nanoparticles via Cobalt Doping for Application in p-Type

**Chapter 2**


**Chapter 3**


34. Barnes, P. R.; Anderson, A. Y.; Juozapavicius, M.; Liu, L.; Li, X.; Palomares, E.


Chapter 4


41. Muresan, N. M.; Willkomm, J.; Mersch, D.; Vaynzof, Y.; Reisner, E. Immobilization of a Molecular Cobaloxime Catalyst for Hydrogen Evolution on a


55. Ke, W. J.; Fang, G. J.; Liu, Q.; Xiong, L. B.; Qin, P. L.; Tao, H.; Wang, J.; Lei, H.


69. Helander, M. G.; Wang, Z.; Qiu, J.; Greiner, M. T.; Puzzo, D. P.; Liu, Z.; Lu, Z. Chlorinated Indium Tin Oxide Electrodes with High Work Function for Organic Device


77. Sewvandi, G. A.; Tao, Z. Q.; Kusunose, T.; Tanaka, Y.; Nakanishi, S.; Feng, Q. Modification of TiO2 Electrode with Organic Silane Interposed Layer for High-


**Chapter 5**


30. Müller, A.; Bhattacharyya, R. G.; Pfefferkorn, B. Eine einfache Darstellung der


parametrization of density functional dispersion correction (DFT-D) for the 94 elements

decomposition reactions of the ammonium thiomolybdates, (NH4)2Mo2S12·2H2O and
(NH4)2Mo3S13·2H2O. *J. Mater. Chem.*, **2001**, *11* (10), 2607-2614.

42. Müller, A.; Jostes, R.; Jaegermann, W.; Bhattacharyya, R. G. Spectroscopic
Investigations on the Molecular and Electronic-Structure of [Mo3S13]2−, a Discrete Binary

43. Olefjord, I.; Wegrelius, L. The influence of nitrogen on the passivation of stainless

44. Nagai, M.; Irisawa, A.; Omi, S. XPS study of the deactivation and sulfiding of
nitrided molybdena-alumina catalyst during the hydrodesulfurization of dibenzothiophene.

45. Xia, X.; Hao, Q.; Lei, W.; Wang, W.; Wang, H.; Wang, X. Reduced-graphene
oxide/molybdenum oxide/polyaniline ternary composite for high energy density

46. Fukumoto, H.; Yonezawa, Y. Layer-by-layer self-assembly of polyelectrolyte and

47. Conway, B. E.; Tilak, B. V. Interfacial processes involving electrocatalytic
(22-23), 3571-3594.


