FeS₂ Nanocrystal Ink as a Catalytic Electrode for Dye-Sensitized Solar Cells**

Ying-Chiao Wang, Di-Yan Wang, You-Ting Jiang, Hsin-An Chen, Chia-Chun Chen, Kuo-Chuan Ho, Hung-Lung Chou, and Chun-Wei Chen*

In the last decade, dye-sensitized solar cells (DSSCs) have attracted great interest for the fabrication of low-cost large-area photovoltaic devices as an alternative to conventional inorganic counterparts. The counter electrode (CE) is a critical component in DSSCs, where electrons are injected into the electrolyte to catalyze iodine reductions (I₃⁻ to I⁻). The most commonly used CE is based on indium-doped tin oxide (ITO)-coated glass loaded with platinum by sputtering. Platinum has a high catalytic activity for triiodide reduction and presents sufficient corrosion resistance. However, Pt is expensive because of its scarcity, and thus, the development of so-called Pt-free CEs for DSSCs using cheaper and abundant materials becomes technologically desirable. Recently, carbon-based materials, such as graphite, graphene, carbon nanotubes, and conducting polymers, have been used to replace Pt as electrocatalysts for triiodide reduction in DSSCs although these devices still suffer from poor thermal stability and weak corrosion resistance. Extensive research has been performed on using inorganic compounds such as transitional metal carbides, nitrides, oxides, and sulfides as a new class of alternative catalytic materials for Pt in DSSC systems. Therefore, pursuing low-cost and stable CE materials as alternatives to expensive Pt is crucial to make DSSC systems more competitive for future commercial applications.

Pyrite iron disulfide (FeS₂, so-called fool's gold) is an interesting next-generation photovoltaic material candidate that is abundant in nature and is nontoxic. It is ranked as having the highest material availability among 23 existing semiconducting photovoltaic systems that could potentially lead to lower costs compared to conventional silicon solar cells. Colloidal pyrite nanocrystals (NCs) were recently synthesized and characterized, providing great potential for developing low-cost fabrications of FeS₂-based photovoltaic devices using solution processes. We first demonstrated pyrite NC-based photodiode devices with a spectral response extended to near infrared (NIR) wavelengths because of its large optical absorption coefficient (> 10⁹ cm⁻¹) and broad band gap of 0.95 eV, which provided a crucial step toward success in producing colloidal pyrite NCs thin films as photovoltaic absorption layers. This study demonstrates an important photovoltaic application using FeS₂ nanocrystal pyrite ink to fabricate a cost-effective CE in DSSCs, which has the unique advantages of earth abundance and of being solution-processable. The DSSC device with the CE using the FeS₂ NC ink exhibits a promising power conversion efficiency of 7.31% comparable to that of the cell using the precious metal of Pt deposited by sputtering (7.52%), as well as remarkable electrochemical stability of greater than 500 consecutive cycle scans. Solution-processable and semi-transparent FeS₂ NC-based CEs also enable the fabrication of flexible and bifacial DSSCs. The results indicate that FeS₂ NC ink is an extremely promising candidate for replacing Pt to substantially reduce the cost of DSSCs in future commercial applications and have also shed light on employing the low-cost FeS₂ NC catalyst in other electrochemical cells.

The FeS₂ NCs were prepared using wet solution-phase chemical synthesis with a number of modifications according to our previous reports. Figure 1a shows a high-resolution transmission electron microscopy (HR-TEM) image of an FeS₂ NC with a diameter of 15 ± 3 nm. The clear lattice fringes of the FeS₂ NCs with a lattice spacing of 0.31 nm matched the (111) plane of pyrite. The fast Fourier transform (FFT) patterns shown in Figure 1b exhibited various index facets, including [210], [211], and [311] on the NC, showing typical signatures of a pyrite-phased crystal structure. Figure 1c shows a photograph of the FeS₂ NCs ink. For fabricating the FeS₂ NC CE, FeS₂ NC ink of concentration 4000 rpm was spun-coated onto an ITO glass substrate at 4000 rpm for 20 s, as shown in Figure 1d. Because as-
The synthesized FeS$_2$ NCs are typically passivated with circa 2.5 nm long alkyl ligands (that is, oleic acid (OA) and oleylamine (OLA)), this can prevent close nanocrystal packing of FeS$_2$ thin films, thus impeding charge transport. The FeS$_2$ NC films were subsequently dipped in 15 mM ethanedi-thiol (EDT) in an acetonitrile solution for 20 s and spun (at 8000 rpm for 20 s) to remove the long chain ligands from the NC surfaces and to reduce the interparticle spaces of NCs. A nearly 20-fold increase in the conductivity (5.4 x 10$^{-3}$ S cm$^{-1}$) of the FeS$_2$ NC thin film with EDT treatment was obtained, compared to the 2.6 x 10$^{-3}$ S cm$^{-1}$ of the film without treatment. Figures 1e and f show the top and cross-sectional scanning electron microscopy (SEM) images of the densely packed FeS$_2$ NC thin film on the ITO glass.

Figure 2 shows the current density-voltage (J–V) curves of the DSSCs with various CEs under AM 1.5 illumination at 100 mW cm$^{-2}$. The detailed parameters of the photovoltaic device performances are summarized in Table 1. These three devices showed two pairs of redox peaks where the redox couple at lower potential peaks (that is, between 0.4 and 0.1 V vs. Ag/Ag$^+$) corresponded to the reaction (1) of I$_3^-$ $+$ 2e$^-$$\rightarrow$3I$^-$, and the redox couple at higher potential peaks (that is, between 0.2 and 0.6 V vs. Ag/Ag$^+$) corresponded to the reaction (2) of 3I$^-$$+$2e$^-$ $\rightarrow$2I$_2$ $+$ 2I$^-$. According to the reaction (1), the CV curve showed an anodic peak current density ($J_{pa1}$) and a cathodic peak current density ($J_{pc1}$) at the left pair of redox peaks, corresponding to the oxidation of the I$^-$ ions and the reduction of the I$_3^-$ ions, respectively. For the FeS$_2$ NC CE, the result was comparable to the performance of the reference DSSC device using the conventional Pt CE with a $J_{sc}$ of 15.37 mA cm$^{-2}$, a FF of 0.69, and an $\eta$ value of 7.52%. In contrast, the DSSC device using the FeS$_2$ NC-based CE without EDT treatment showed a lower device performance $\eta$ of 5.74% with a $J_{sc}$ of 12.63 mA cm$^{-2}$ and a FF of 0.64 because of the long alkyl ligands passivated on the FeS$_2$ NC surfaces. These results suggest that earth-abundant FeS$_2$ NC ink is a promising alternative to the precious Pt metal as an efficient electrocatalyst in DSSCs.

Table 1: Photovoltaic performance obtained from DSSCs with various CEs under AM 1.5 illumination at 100 mW cm$^{-2}$, parameters of EIS and Tafel polarization, and corresponding surface roughness of various CEs.

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>$R_{ct}$ [$\Omega$ cm$^{-2}$]</th>
<th>CPE $^{[c]}$ [m$^{-1}$]</th>
<th>$R_{ms}^{[b]}$ [nm]</th>
<th>$J_{sc}^{[d]}$ [mA cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.71</td>
<td>15.37</td>
<td>0.69</td>
<td>7.52</td>
<td>1.47</td>
<td>11.67</td>
<td>13.6</td>
</tr>
<tr>
<td>FeS$_2$ (with EDT treatment)</td>
<td>0.71</td>
<td>15.14</td>
<td>0.68</td>
<td>7.31</td>
<td>1.60</td>
<td>18.74</td>
<td>10.67</td>
</tr>
<tr>
<td>FeS$_2$ (without EDT treatment)</td>
<td>0.71</td>
<td>12.63</td>
<td>0.64</td>
<td>5.74</td>
<td>4.54</td>
<td>37.21</td>
<td>10.28</td>
</tr>
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</table>


Next, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) measurements, and Tafel curves were performed to analyze the correlation between the electrocatalytic activity of the FeS$_2$ NC CEs and the photocurrent generation. Figure 3a shows the three CVs of the devices using the reference Pt CE and FeS$_2$ NC CEs with and without EDT treatment, respectively, which consisted of a typical three-electrode cell structure. Each CV curve showed two pairs of redox peaks where the redox couple at lower potential peaks (that is, between −0.4 and 0.1 V vs. Ag/Ag$^+$) corresponded to the reaction (1) of I$_3^-$ $+$ 2e$^-$$\rightarrow$3I$^-$, and the redox couple at higher potential peaks (that is, between 0.2 and 0.6 V vs. Ag/Ag$^+$) corresponded to the reaction (2) of 3I$^-$$+$2e$^-$ $\rightarrow$2I$_2$ $+$ 2I$^-$. According to the reaction (1), the CV curve showed an anodic peak current density ($J_{pa1}$) and a cathodic peak current density ($J_{pc1}$) at the left pair of redox peaks, corresponding to the oxidation of the I$^-$ ions and the reduction of the I$_3^-$ ions, respectively. For the FeS$_2$ NC CE...
with EDT treatment, the CV profile and \( J_{pa1} \) were similar to those of the Pt CE counterpart, indicating that FeS\(_2\) NCs are as effective as Pt in catalyzing the reduction of triiodide to iodide. In contrast, the magnitude \( J_{pa1} \) of the device using FeS\(_2\) CE without EDT treatment was much lower compared to that of the FeS\(_2\) CE with treatment. Figure 3b shows the CV profile curves and the corresponding \( J_{pa1} \) and \( J_{pc1} \) of the device using the FeS\(_2\) CE with EDT treatment following 500 consecutive cycle scans. The nearly unaltered curve shape and nearly constant peak current density demonstrated the excellent electrochemical stability of the FeS\(_2\) CE in the I\(_2\)/C\(_0\)/I\(_3\)/C\(_0\)-based electrolyte.

Figure 4a shows the Nyquist plots of the devices from the EIS measurement. The devices consisted of a symmetric sandwich-like structure (that is, CE/electrolyte/CE) fabricated using FeS\(_2\) NCs and Pt electrodes, where two identical electrodes were separated between an ionomer resin spacer (Surlyn, SX1170-25). The charge transfer resistance \( R_{ct} \) was obtained by fitting the semicircle in the high-frequency region (leftmost semicircle), which corresponded to the charge-transfer process at the electrolyte/electrode interfaces, and the right-hand semicircle in the low-frequency range indicated the Nernst diffusion impedance within the electrolyte.[10,29] The charge-transfer resistance \( R_{ct} \) for the FeS\(_2\) NCs with EDT treatment was 1.60 \( \Omega \) cm\(^2\), which was close to that of the reference Pt electrode (1.47 \( \Omega \) cm\(^2\)), indicating that FeS\(_2\) NCs have excellent catalytic activity. The increased \( R_{ct} \) value for the FeS\(_2\) NC device without EDT treatment was attributed to the long alkyl ligands on the NC surface, which may have impeded the charge transfer rate. The corresponding constant phase-angle element (CPE) values for the FeS\(_2\) CE with and without EDT treatment were 38.74 and 37.21 mF, respectively, which were significantly higher than that of the Pt CE with a CPE value of 11.67 mF, which is presumably due to the increased electrochemically active areas of the FeS\(_2\) NC CEs with large surface roughness.[30] The root-mean-square roughness (\( R_{rms} \)) values determined from atomic force microscopy (AFM) topography images were 1.36 nm (Pt), 10.67 nm (FeS\(_2\) NC with EDT treatment), and 10.28 nm (FeS\(_2\) NC without EDT treatment), as shown in the Supporting Information, Figure S2. The exchange current density (\( J_0 \)), which is equal to \( J_0 = \frac{RT}{nF}\sqrt{R_{ct}} \)[16,31] is directly related to the electrochemical catalytic activity of the electrode, where \( R \) is the gas constant, \( T \) is the absolute temperature in K, \( n \) is number of electrons involved in the electrochemical reduction reaction, \( F \) is the Faraday constant, and \( R_{ct} \) is the charge transfer resistance. Consequently, the exchange current densities (\( J_0 \)) obtained from these impedance spectroscopy data were 17.45, 16.03, and 5.66 mA cm\(^{-2}\) for the Pt CE and FeS\(_2\) NC CEs with and without EDT treatment, respectively. Figure 4b shows the Tafel polarization measurement of the logarithmic current density (log \( J \)) as a function of voltage (\( U/V \)) for the oxidation/reduction of the I\(_2\)/I\(_3\)-redox couple with a similar device structure to that used in the Nyquist plot measurement. The exchange current densities (\( J_0 \)), which can
be estimated from the extrapolated intercepts of the cathodic branches of the corresponding Tafel plots,[31] were in the consistent order of Pt > FeS₂ NC (with EDT treatment) > FeS₂ NC (without EDT treatment). Furthermore, the limiting current density \( J_{\text{lim}} \) which was determined by the diffusion of ionic carriers between the two electrodes, was directly proportional to the diffusion coefficient (\( D \)) of the triiodide species. The \( J_{\text{lim}} \) value of the device using the FeS₂ NC (with EDT treatment) electrodes was similar to that using Pt. All of the CV, EIS, and Tafel polarization measurement results showed good consistency with the corresponding photovoltaic performances of DSSC devices using various CE electrodes.

Along with replacing Pt as a low-cost CE material, solution-processable FeS₂ NC ink has the advantage that it can be printed onto various substrates which are heat sensitive or flexible for large-area roll-to-roll production. Figure 5a shows the device performance of the DSSC with a flexible CE using the FeS₂ NCs ink cast onto an ITO/PET substrate. The device exhibited a power conversion efficiency (\( \eta \)) of 6.36\% with a short-circuit current density (\( J_{\text{sc}} \)) of 14.93 mA\,cm⁻², an open-circuit voltage (\( V_{\text{oc}} \)) of 0.71 V, and a fill factor (FF) of 0.60 (under AM1.5 illumination at 100 mW\,cm⁻²). Furthermore, the semi-transparency of the FeS₂ NC-based CE enabled the fabrication of a bifacially active DSSC (Supporting Information, Figure S4b), which had the advantage of harvesting incident light from both sides (that is, front or rear sides). The inset of Figure 5b shows the transmission spectrum of the semi-transparent FeS₂ NC-based CE that had a transmittance of 50–70\% ranging from 300 to 800 nm compared to that of nearly 15\% for the reference Pt CE with low transparency and high reflectivity. Figure 5b shows the current-density–voltage characteristics of the DSSCs using the FeS₂ NC and Pt CEs as illuminated from the rear side. The DSSC device consisting of the FeS₂ NC CE exhibited an efficiency of 4.17\%, which was approximately 57\% of that from the front illumination. In contrast, the reference device using the opaque Pt CE, as illuminated from the rear side, only had an efficiency of 1.06\%. These results suggest the potential application of FeS₂ NC-based semi-transparent DSSCs in bifacial photovoltaic devices because of their capabilities for utilizing incident light from both sides to further reduce the cost of energy production.

In summary, this study demonstrated that FeS₂ NC ink is a promising alternative to the expensive Pt CE and exhibits excellent electrochemical catalytic activity and remarkable stability in catalyzing the reduction of triiodide to iodide in DSSCs. Solution-processable and semi-transparent FeS₂ NC-based CEs also enable the fabrication of flexible or bifacial DSSCs. The breakthrough of using earth-abundant FeS₂ NC ink to replace the precious metal Pt as a low-cost CE material may foster development to further bring down the cost of energy production in DSSCs. The results have also tremendous implications for future development in the low-cost nanoscale Fe-based electrocatalysts.

Keywords: dyes/pigments · electrocatalysis · iron disulfide · nanomaterials · solar cells

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