Gram-Scale Synthesis of Catalytic Co$_9$S$_8$ Nanocrystal Ink as a Cathode Material for Spray-Deposited, Large-Area Dye-Sensitized Solar Cells

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ABSTRACT We report the development of Co$_9$S$_8$ nanocrystals as a cost-effective cathode material that can be readily combined with spraying techniques to fabricate large-area dye-sensitized solar cell (DSSC) devices and can be further connected with series or parallel cell architectures to obtain a relatively high output voltage or current. A gram-scale synthesis of Co$_9$S$_8$ nanocrystal is carried out via a noninjection reaction by mixing anhydrous CoCl$_2$ with trioctylphosphine (TOP), dodecanethiol and oleylamine (OLA) at 250 °C. The Co$_9$S$_8$ nanocrystals possess excellent catalytic ability with respect to I$^-$/I$_3^-$ redox reactions. The Co$_9$S$_8$ nanocrystals are prepared as naninks to fabricate uniform, crack-free Co$_9$S$_8$ thin films on different substrates by using a spray deposition technique. These Co$_9$S$_8$ films are used as counter electrodes assembled with dye-adsorbed TiO$_2$ photoanodes to fabricate DSSC devices having a working area of 2 cm$^2$ and an average power conversion efficiency (PCE) of 7.02 ± 0.18% under AM 1.5 solar illumination, which is comparable with the PCE of 7.2 ± 0.12% obtained using a Pt cathode. Furthermore, six 2 cm$^2$-sized DSSC devices connected in series output an open-circuit voltage of 4.2 V that can power a wide range of electronic devices such as LED arrays and can charge commercial lithium ion batteries.

KEYWORDS: cobalt sulfide · nanocrystals · cost-effective · large area · dye-sensitized solar cell · counter electrode

Ligand-stabilized colloidal nanocrystals exhibit stable dispersibility in solvents while strong solvation of the ligand’s tails generates a sufficient repulsive force against interparticle attraction that prevents sedimentation. The morphology of nanocrystals can be also controlled in the colloid synthetic chemistry.$^{1-3}$ Functional large-area device layers can be deposited from nanocrystal solutions, the so-called nanocrystal inks, using solution-based printing techniques, including spray deposition, blade coating, spin coating and drop casting. Device layers can be made via roll-to-roll, high-throughput (>20 m/min), and large-area (>150 m$^2$/h) solution-processed strategies using an established production line operated with a given set of parameters that is not achievable using vacuum-based deposition techniques. Complex devices made by assembly of nanostructure on various substrates can be also constructed.$^{4-6}$

Platinum (Pt) is the most commonly used cathode material for dye-sensitized solar cell (DSSC) because of its high conductivity, stability and catalytic activity with respect to iodine/triiodide (I$^-$/I$_3^-$) reduction.$^7$ However, the use of Pt is limitedly by its high cost. Thermal decomposition, sputtering, and electrochemical deposition are widely used for fabricating Pt counter electrodes.$^8-10$ However, the high-energy-consuming procedure works against the advantage of cost effectiveness. Inorganic nanomaterials outperform bulk micrometer-sized powders with respect to many catalytic reactions because of their significantly large exposure areas and can potentially serve as Pt-alternatives for a...
Metal chalcogenides nanomaterials represent important parts of topics being researched and are used in a wide range of applications.25–31 Co9S8 is a particularly good hydrosulfurization (HDS) catalyst with excellent activity for the oxygen reduction reaction (ORR) under acidic conditions.32,33 Co9S8 has a face-centered cubic (fcc) structure in the space group of Fm3m (225) with a lattice constant of 9.928 ± 0.001 Å.34 Because Co9S8 has a narrow homogeneity range and usually forms peritectically at high temperatures (~835 °C),35 the reaction conditions (e.g., reaction temperature and reaction time) are highly dependent on the formation of pure Co9S8. The bonding modes between metal and sulfur are typically complex and result in an intricate crystal structure.36 Binary cobalt sulfides exist in the form of various crystalline phases in a wide range of stoichiometries, including CoS, CoS2, Co8S9, and Co2S3, and in nonstoichiometric Co1+xS.37 The other challenge for forming pure Co9S8 is that the cobalt ion easily reacts with oxygen to form cobalt oxide or other cobalt-compound impurities.38 Thus far, there have been few reports on the synthesis of Co9S8 nanocrystals and many of these are based on two-step sulfuration reactions.39–41 For instance, Alivisatos et al. fabricated hollow Co9S8 nanocrystals by first forming cobalt nanocrystals followed by a sulfuration process.39 Recently, Co9S8–oleylamine hybrid nanosheets have been synthesized via an in-plane coassembly process.41 However, it is still challenging to use a one-step process for the synthesis of a considerably large amount of high-quality colloidal Co9S8 nanocrystals to meet application requirements. Furthermore, their performance with respect to their application to DSSC cathodes has not been investigated.

In this study, high-quality Co9S8 nanocrystals in gram-scale production are synthesized by a noninjection, one-pot reaction at ~250 °C. On the basis of the analysis of cyclic voltammetry data and the Tafel curve, we find that the Co9S8 nanocrystal cathode has excellent catalytic ability with respect to I-/I3− redox reactions, thereby proving that these nanocrystals are a promising avenue as cathode material for DSSCs. The nanocrystals exhibit stable dispersion in various nonpolar solvents that matches well with the criteria of nanocrystal inks. The nanocrystals are spray-deposited on various conductive substrates by an airbrush to fabricate uniform, large-area (~100 cm2) micrometer-thick films. For device performance evaluation, the DSSC devices are fabricated with a 2 cm2 (0.5 cm × 4 cm) working area, which is at least 5 times larger than the working areas (0.15–0.4 cm2) of the cells usually evaluated in the literature. The champion power conversion efficiency (PCE) of Co9S8/Mo counter electrode in our DSSC system is 7.24% under AM1.5 illumination, which is comparable to that of Pt with a PCE of 7.34%. The single cell delivers a short-circuit current of more than 28 mA with an open-circuit voltage of ~0.7 V, which is sufficient to drive electric devices. Higher voltage (>3 V) DSSC devices composed of six 2 cm2 cells connected in series are also applied to turn on devices requiring higher operation voltages.

RESULTS AND DISCUSSION

A noninjection, one-pot reaction was conducted as the synthetic approach for the production of Co9S8 nanocrystals since this method can be easily scaled up to obtain large quantities of the products. Co9S8 nanocrystals were prepared by combining a mixture of anhydrous CoCl2 with trioctylphosphine (TOP), dodecanethiol and oleylamine (OLA) at room temperature in an Ar atmosphere. Dodecanethiol served as the sulfur source42,43 and reduced the sulfuration temperature with cobalt precursors.44 The mixture was heated to 250 °C and was held at this temperature for 10 min. During this period, the color changed from blue (anhydrous cobalt(II) chloride) to dark black, indicating the formation of Co9S8 nanocrystals. One batch reaction could produce more than 1 g of the product with a yield of more than 90% (Figure 1a). The X-ray diffraction (XRD) result shown in Figure 1b indicates the as-prepared sample with peaks indexed perfectly with the Co9S8 FCC phase (JCPDS No. 86-2273) having the cell...
parameter $a = 9.92 \text{ Å}$. The inset of Figure 1b shows the unit cell of FCC Co$_9$S$_8$.

Co$_9$S$_8$ nanocrystals had facet shapes with an average particle size of $\sim 18 \text{ nm}$ as observed by transmission electron microscopy (TEM) (Figure 2a). The selected area electron diffraction (SAED) pattern (Figure 2b) verified that product was FCC Co$_9$S$_8$. Figure 2c–f shows HRTEM images with the associated fast Fourier transform (FFT) of Co$_9$S$_8$ nanocrystals. These nanoparticles had lattice fringe corresponding to Co$_9$S$_8$ and exhibited excellent crystallinity. The corresponding reciprocal lattice image could be indexed to the $[\{112\}]$ and $[\{111\}]$ zone axes of fcc Co$_9$S$_8$. From Figure 2c, the inter fringe distance of 0.286 and 0.351 nm corresponds to the (222) and (220) planes of the cubic Co$_9$S$_8$ phase, respectively. Further, the clear crystal fringe of 0.176 nm shows in Figure 2e was indexed to the (440) plane of Co$_9$S$_8$. Energy-dispersive X-ray spectroscopy (EDS) obtained from fields of nanocrystals indicated an average Co/S composition of 9:8, confirming the stoichiometry of Co$_9$S$_8$ (Figure 3a). X-ray photoelectron spectroscopy (XPS) is a surface-sensitive tool used for analyzing the chemical state of cobalt sulfide. The binding energy was corrected by referencing C 1s (284.60 eV). The measured cobalt 2p peaks were located at 778.5 and 793.9 eV, and the Co 2p spectrum had small asymmetric core electron peaks, which were identical with the literature value.45,46 The measured S 2p peaks were located at 161.2 and 162.3 eV with a split of 1.1 eV; this was in good agreement with the previous report.47

The Co$_9$S$_8$ nanocrystals exhibited stable solvent dispersion at high nanocrystal concentrations (>20 mg/mL) without sedimentation for several months in many nonpolar solvents. The Co$_9$S$_8$ nanoinks can be carried by the inert gas traveling through the inkjet nozzle and sprayed onto the substrate to form a thin film. Figure 4a depicts a sketch of the spraying experimental setup. (see Movie S1 in the Supporting Information for fabrication process). In the case of spray deposition, the film quality is associated with nozzle geometry, ink properties, substrate temperature and the pressure of the process gas.48 The dispersion stability of inks is critical for this process. If a nanoink is not stable, the inkjet nozzles get clogged frequently by the aggregated particles, which results in unstable ejection. Figure 4b shows a photograph of Co$_9$S$_8$ nanocrystals dispersed in hexane at a concentration of 20 mg/mL. FTO- and Mo-coated glasses were used as substrates for the Co$_9$S$_8$ nanocrystal deposition. A 100 cm$^2$ uniform film composed of spray-deposited Co$_9$S$_8$ nanocrystals was fabricated in 5 min by spraying the inks (Figure 4e). The as-deposited films were annealed at 350 °C in an Ar atmosphere for 2 h. This annealing procedure improved mechanical strength and adhesion to the substrates; furthermore, the surfactants that were capped on the Co$_9$S$_8$ nanocrystal surface could be removed to increase conductivity and crystallinity without any phase change. (Figure S1 in the Supporting Information for XRD characterization). Figure 4d shows the cross-sectional and the plan view of the annealed Co$_9$S$_8$ film. The scanning electron microscopy (SEM) images revealed that the film was dense and no obvious crack was formed. The thickness of the cobalt sulfide layer was in the range of 0.9–1.2 μm, which could be controlled by tuning the concentration of nanoinks, pressure of the carrier gas and the spraying time. The Co$_9$S$_8$ nanocrystals were also deposited on the Mo substrates; the cross-sectional image of the Co$_9$S$_8$ film is shown in Figure S2 in the Supporting Information.

In our system, I$^-$/I$_3^-$ redox couple was considered as a redox mediator. The nanocrystal films had more reaction sites for I$^-$/I$_3^-$ reduction reactions in the electrolyte because of the large specific surface area.

Figure 2. (a) TEM image of cobalt sulfide nanocrystals and (b) their corresponding SAED pattern; (c–f) HRTEM images of cobalt sulfide nanocrystals and their corresponding FFT pattern.
which increased effective active area. Figure 5a shows the cyclic voltammograms in an acetonitrile solution with 10.0 mM LiI, 1.0 mM I₂, and 0.1 M LiClO₄ for Pt, Co₉S₈ on FTO substrate (Co₉S₈/FTO), and Co₉S₈ on Mo substrate (Co₉S₈/Mo) at a scanning rate of 20 mV/s. Two pairs of oxidation and reduction peaks were predominantly observed in three curves. The result indicated that both cobalt sulphide and Pt had good electrocatalytic activity for the I⁻/I₃⁻ system. The anodic peaks shown in Figure 5a are denoted as (I) and (II), and the reverse cathode peaks are denoted as (I') and (II'), respectively. According to the literature, iodine is oxidized to triiodide (peak I) and then to iodine (peak II) by reactions 1 and 2, respectively.

\[
3I^- \rightarrow I_3^- + 2e^- \tag{1}
\]

\[
2I_3^- \rightarrow 3I_2 + 2e^- \tag{2}
\]

In the reverse process, iodine is first reduced to triiodide (peak II'), then to iodide (peak I') corresponding to the reactions 3 and 4, respectively.

\[
3I_2 + 2e^- \rightarrow 2I_3^- \tag{3}
\]

\[
I_3^- + 2e^- \rightarrow 3I^- \tag{4}
\]

The current density of the oxidation and reduction for three electrodes was almost identical. This suggested that the electrocatalytic ability of Co₉S₈ toward I⁻/I₃⁻ redox couple was comparable to that of Pt. It is explained that the charge-transfer resistance in the I⁻/I₃⁻ redox reaction for the three electrodes was very close. The electrocatalytic ability was reconfirmed by a Tafel polarization measurement, which is a powerful electrochemical characterization method for examining the interfacial charge-transfer properties on the electrode surface. The Tafel curve can be separated into three zones: polarization zone (low potential), Tafel zone (intermediate potential with a sharp slope), and diffusion zone (high potential). The Tafel polarization curves by symmetrical dummy cell are shown in figure 5b. In the Tafel zone, both Co₉S₈/Mo and Co₉S₈/FTO exhibited a little larger exchange current density (J₀) than the Pt electrode, which could be obtained by intersecting the cathodic branch and the equilibrium potential line (Figure S3 in the Supporting Information). The Rct value could be calculated using eq 5, where \( R \) denotes the gas constant; \( T \), the temperature; \( F \), Faraday's constant; \( n \), the total number of electrons involved in the reaction; and \( R_{ct} \) the charge transfer resistance. Using this equation, we found that the Rct value of Pt was a little larger than that of Co₉S₈/Mo and Co₉S₈/FTO.

\[
J_0 = \frac{RT}{nFR_{ct}} \tag{5}
\]

The DSSC devices had a working area of 2 cm² (4 cm × 0.5 cm) and used the Co₉S₈ layer as the cathode and the N719 adsorbed mesoporous TiO₂ film as the anode. Figure 6a shows a photograph of a 2 cm² DSSC device. Figure 6b shows the \( J-V \) curves of the DSSC using Pt, Co₉S₈/FTO and Co₉S₈/Mo counter...
electrodes. The photovoltaic parameters are summarized in the Table 1. Under the completely same experimental conditions, the catalytic ability between Co$_9$S$_8$/FTO and Co$_9$S$_8$/Mo was found to be similar, and the slight differences between the two electrodes attributed to the uniformity of Co$_9$S$_8$ film. The Co$_9$S$_8$/FTO—DSSC and Co$_9$S$_8$/Mo—DSSC yielded power conversion efficiencies (PCEs) of 6.91% and 7.00% under AM 1.5 illumination, respectively. The results were a slightly lower than those obtained for the Pt PCE. The open-circuit voltage ($V_{oc}$) values of the three cells were around 0.71–0.72 V. However, the fill factors of Pt-DSSC were smaller than those of the others, which was attributed to the larger $R_{ct}$. The short-circuit current density ($J_{sc}$) values of Co$_9$S$_8$/FTO and Co$_9$S$_8$/Mo were found to be 14.75 and 13.98 mA/cm$^2$, respectively, which were close to value of 14.21 mA/cm$^2$ for a Pt electrode. Typically, the redox reaction at the counter electrode/electrolyte interface can divided into three stages: (1) the $I_3^-$ diffusion from the bulk solution to the vicinity of counter electrode, (2) the adsorption of $I_3^-$ on the surface of the counter electrode, and (3) the charge transfer from and the $I^-$ removal from the surface of the counter electrode. The rate of the redox reaction was significantly

![Figure 5](image1.png)  
Figure 5. (a) Cyclic voltammograms of the Pt, Co$_9$S$_8$ on FTO substrate, and Co$_9$S$_8$ on Mo substrate for $I^-/I_3^-$ species. The peak I and peak I' represent $3I^- \rightarrow I_3^+ + 2e^-$; peak II and peak II' represent $2I_3^- \rightarrow 3I^- + 2e^-$, respectively. (b) Tafel polarization curves of the $I^-/I_3^-$ symmetrical cells of the Pt on FTO substrate, Co$_9$S$_8$ on FTO substrate, and Co$_9$S$_8$ on Mo substrate.

![Figure 6](image2.png)  
Figure 6. (a) Photograph of a DSSC cell with 2 cm$^2$ working area; (b) $J-V$ curves of the DSSCs with the Pt, Co$_9$S$_8$ on FTO, and Co$_9$S$_8$ on Mo counter electrode measured under AM1.5 illumination; (c) Nyquist plots of DSSCs with the Pt, Co$_9$S$_8$ on FTO, and Co$_9$S$_8$ on Mo counter electrode.

| TABLE 1. Photovoltaic Performances of DSSCs Using Pt, Co$_9$S$_8$/FTO, and Co$_9$S$_8$/Mo as Counter Electrodes |
|----------|----------|-----|-----|-------|-------|
| $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) | $R_s$ (Ω) | $R_{ct1}$ (Ω) |
| Pt       | 0.72     | 14.75 | 0.67 | 7.13  | 0.58  | 0.17  |
| Co$_9$S$_8$/FTO | 0.71     | 14.21 | 0.69 | 7.00  | 0.59  | 0.14  |
| Co$_9$S$_8$/Mo | 0.72     | 13.98 | 0.69 | 6.91  | 0.71  | 0.13  |
influenced by the effective active site at which the Co9S8 films might be larger than the Pt film. Therefore, the charge-transfer resistance at the Co9S8/Mo and Co9S8/FTO counter electrodes/electrolyte interface was smaller than that obtained in the case of Pt in our experiment. More PCEs values obtained from Co9S8/Mo—DSSC and Co9S8/FTO—DSSC under similar conditions are listed in the Supporting Information. The DSSC device with a Co9S8 nanocrystal counter electrode exhibited the highest PCE of 7.24% with an average value of 7.02 ± 0.18%.

The DSSC cells (Figure 7a) were used for powering a wide range of electronic devices. The 2 cm²-DSSC device produced a short-circuit current of more than 28 mA, which is sufficient to turn on an electric fan (Figure 7b). The electric fan remains running while the cell is under continuous illumination (see Movie S2 in the Supporting Information). However, most of the electronic devices cannot be powered by this low voltage (≈0.6 V). Six DSSCs with Co9S8 electrodes were connected in series to achieve an open circuit voltage of 4.2 V (Figure 7c). This series-connected DSSC devices could directly power numerous electronic devices, for example, calculators (1.5 V), yellow and red LEDs (2 V), and remote controllers (3 V), and charge lithium ion batteries (LIBs) (>3.5 V). As a demonstration, LED arrays containing more than 90 LED bulbs were lit without fading in real time by the DSSC devices as shown in Figure 7d (see Movie S3 in the Supporting Information). The series-connected DSSC devices could charge energy storage devices. An empty commercial LIB (Model: 16340, 880 mAh) with a voltage of 2.8 V was charged by 6 DSSCs for 30 min until the voltage increased to 3.3 V. Then, it was discharged by using a potentiostat system (VMP3); the discharge Q—t curve is shown in Figure 7e. A capacity of approximately 3 mAh was obtained, which was considerably smaller than the expected value of 12–14 mAh. The reason for the low capacity was the large resistance in LIB that consumed some energy. Therefore, DSSC devices using Co9S8 cathodes could potentially be extended to systems having a parallel connection of large area cells (>100 cm²) to obtain high current of more than 1.5 A for high-rate charging. On the other hand, modules with more than 25 series-connected cells can achieve a high voltage of 12 V to drive automobile starter motors.

CONCLUSION

Gram-scale Co9S8 nanocrystal synthesis was achieved using a facile noninjection one-pot approach. The Co9S8 nanocrystals exhibited highly catalytic properties with respect to I−/I3− redox reactions which has made them excellent for use as cathode materials for DSSC. The well-dispersed Co9S8 nanocrystal inks could be spray-deposited on different substrates to create dense cathode films for DSSC applications. The spray printing process could be used for fabricating a large-area nanocrystal film on substrates at a roll-to-roll process at a speed of up to 20 m/min. Single 2 cm²-sized DSSC using Co9S8 counter electrodes assembled with TiO2 photoanodes gave an average PCE of 7.02 ± 0.18% that was comparable to the value of 7.2 ± 0.12% obtained in the case of the Pt electrodes. We described
the performance of series-connected DSSCs to power electric fans, light up LED arrays, and charge energy storage devices. In the future, a coordinated design of DSSC modules can be developed to achieve higher output voltage and higher output current for a wide range of applications. This study advances the development of catalytic Co$_9$S$_8$ nanocrystal inks which hold immense potential as a cost-effective cathode material for large-area, solution-based processing DSSC module applications.

MATERIALS AND METHODS

Materials. All chemicals were used as received from the Aldrich chemical, including cobalt(III) chloride (CoCl$_2$, anhydrous 97%), trietylphosphine ((CH$_3$)$_3$P)$_3$P, 90%), dodecanethiol (C$_{12}$H$_{25}$SH, >98%), oleylamine (CH$_3$(CH$_2$)$_7$CH$_2$NH$_2$, 70%), hexane, and ethanol (ACS reagent grade, >99.5%).

Cobalt Sulfide Nanocrystal Synthesis. In the synthesis of Co$_9$S$_8$ nanocrystals, 5 mL of TOP and 0.25 mmol of CoCl$_2$ (0.0328 g) were added to a 50 mL three-neck flask placed on a heating plate; one neck was connected to a temperature sensor and stopcock valve was connected to a Schlenk line system; the other neck was sealed by a rubber septum. Next, 5 mL of dodecanethiol and 5 mL of oleylamine (OLA) were injected into the three-neck flask with intensely stirring. The three-neck flask was purged using argon for 35 min. The temperature of reaction was instantly raised to 250 °C, which was kept at 250 °C for 10 min with vigorous stirring. Then, the flask was cooled instantly to room temperature by a cold water bath. Five milliliters of hexane and 15 mL of ethanol were added to the flask. The cobalt sulfide nanocrystals were washed by centrifugation at 8000 rpm for 10 min, whereas byproducts and unreacted precursors were discarded. For large-scale production of Co$_9$S$_8$ nanocrystals, all of the reactants were scaled up to 10 times in volume or in moles than the above recipe with 500 mL flask.

Counter-Electrode Fabrication. Cobalt Sulfide Counter-Electrode. Mo-coated glass substrate was fabricated by DC magnetron sputtering with a film thickness of 500 nm. A thin layer of Co$_9$S$_8$ was deposited by spraying coating method. The Co$_9$S$_8$ nanoink was prepared by Co$_9$S$_8$ nanocrystals dispersed in hexane with a concentration of 20 mg/mL. The nanoink was sprayed onto the FTO glass substrate (SnO$_2$:F glass, 8 Ω/sq) and Mo-coated glass substrate by using a airbrush (KUSING BD-130, 0.3 mm) at 0.8 psig of head pressure. Both kind of electrodes together with a spacer between the two electrodes were assembled by clipping two electrodes with an Oxford INCA EDS detector for EDS analysis, respectively.

Characterization of Cobalt Sulfide Nanocrystals. TEM images were obtained on JEOL JEM-1200 at an accelerating voltage of 100 kV for low resolution imaging and on a JEOL JEM-3000F at an accelerating voltage of 300 kV equipped with an Oxford INCA EDS detector for EDS analysis, respectively. SEM images were obtained on UM-6500. XRD data were obtained by Rigaku Ultima IV X-ray diffractometer using a Cu radiation source (λ = 1.54 Å). XPS analysis was performed on ULVAC-PHI XPS.

Cyclic Voltammetry Measurement. Cyclic voltammetry (CV) was recorded with a three electrode system on a multichannel electrochemical analyzer (Bio-Logic-Science Instruments, VMP3). Pt was used as the counter electrode, and Ag/AgCl was used as the reference electrode. An argon-purged solution of 10.0 mM LiI, 1.0 mM I$_2$, and 0.1 M LiClO$_4$ in acetonitrile served as the electrolyte. CV curves were recorded in the range of 1.0 to −1.0 V at a scan rate of 20 mV/s.

Tafel Polarization Measurement. Tafel-polarization measurements were employed with an electrochemical workstation system (VMP3) in a symmetrical dummy cell. The electrolyte was as the same of the electrolyte of DSSC. The scan rate was 20 mV/s.

Photocurrent–Voltage (J–V) Characteristic Curves and EIS Measurement. The J–V performance of the DSSCs was measured under solar simulator (AM 1.5, 100 mW/cm$^2$). Electrochemical impedance spectrometer (Autolab) was employed to determine the charge transfer resistance (R$_{ct}$), which was taken under solar illumination in the frequency range of 10$^{-2}$–10$^{-4}$ Hz. The spectra were fitted by the Zview software.

Supporting Information Available: XRD pattern and SEM images of Co$_9$S$_8$ nanocrystal films; other photocurrent–voltage (J–V) plots of DSSC devices; movies (MPG) showing the fabrication of spray-deposited Co$_9$S$_8$ DSSC cathodes and various electronic devices powered by the DSSCs. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


