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Supporting Information

Hole Transport in Sensitized CdS–NiO Nanoparticle Photocathode

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Fluorine-doped SnO_2 (FTO) substrates were used as the substrate for depositing NiO nanoparticle films. NiO was deposited by the spin casting a slurry of commercial NiO power (Aldrich, < 50 nm particle size) and then annealed at 450 °C for 1 h. The resulting film was about 1 µm thick. The CdS was deposited on the surface of the NiO by the chemical bath deposition as described previously.[9] In brief, the reaction solution, which contained 2 mM $CdSO_4$, 10 mM thiourea, and 1 M $NH_4(OH)_2$, was heated in a beaker to 60 °C. Next, the NiO sample was positioned vertically along the walls of the beaker. After 10 min the color of the solution turned from clear to orange, indicating the formation of CdS nanocrystallites. After a specific reaction time, which ranged from 5–25 min, the sample was removed from the bath and rinsed with water. The as-prepared CdS covered NiO film was calcined at 250 °C for 1 h under a dry nitrogen stream. The platinized FTO counter electrode and the CdS-NiO electrode were sealed together with 50 µm-thick thermal plastic. A small quantity of redox electrolyte solution containing 0.5 M Na_2S, 0.1 M S_8, and 0.2 M KCl in 7:3 H_2O:methanol (v/v) was introduced into the cell through one of the two drilled holes in the counter electrode. Another redox electrolyte solution investigated was $Co^{II/III}$ tris(4,4'-di-tert-butyl-2,2'-dipyridyl)perchlorate (0.1M/0.1M) and 0.1 M $LiClO_4$ in the propylene carbonate. The $Co^{II/III}$ redox mediator was prepared as described in the literature.[3] Transport and recombination time constants were measured, respectively, by intensity modulated photocurrent spectroscopy (IMPS) at short circuit and intensity modulated photovoltage spectroscopy (IMVS) at open circuit as described elsewhere.[21]

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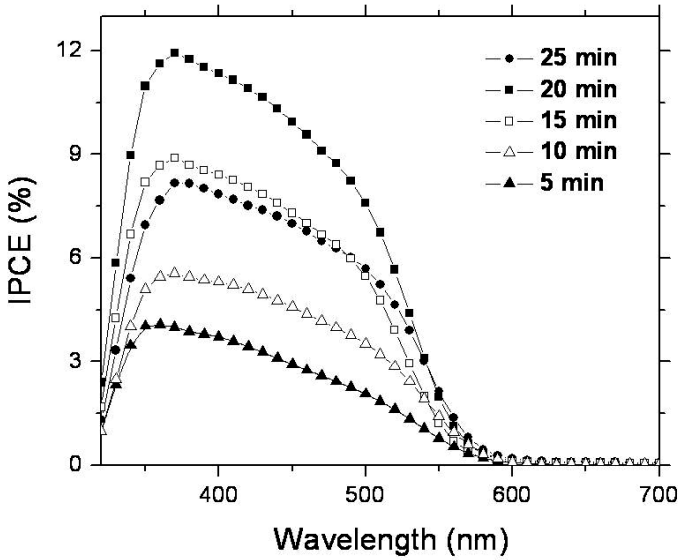

Figure S1. IPCE spectra of the CdS-NiO cell as a function of the reaction time used in the chemical bath deposition of CdS on the NiO particle surface.

The CdS was deposited on the NiO film by chemical bath deposition. The chemical bath contained 2 mM $CdSO_4$, 10 mM thiourea, and 1M NH_4OH and was held at a temperature of 60 °C. The highest the quantum efficiency (12 % at 370 nm) was obtained when the NiO film was exposed to the chemical bath for 20 min. Extending the time beyond 20 min lead to a decrease in the IPCE maximum (Figure S1) presumably due to blockage of the pores of NiO film by CdS.

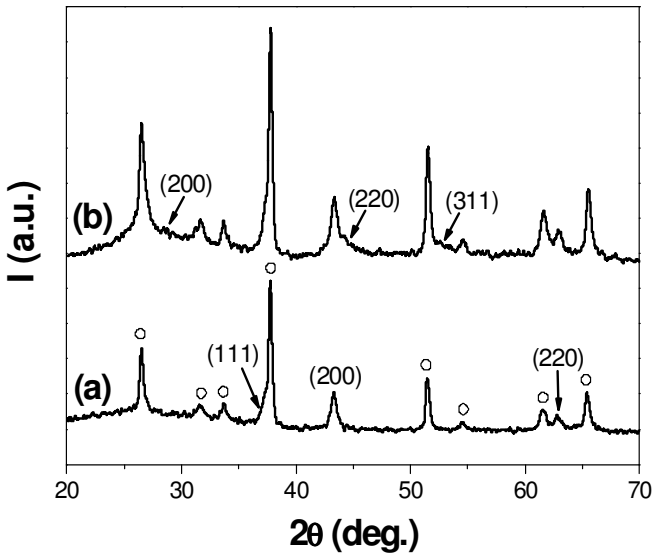

Figure S2. XRD spectra of (a) NiO and (b) CdS-NiO film. The open circles correspond to the fluorine-doped SnO_2 substrate.

Figure S2 show XRD patterns of the NiO and CdS-NiO after they were annealed. The characteristic peaks of the NiO (111), (200), and (220) crystal planes, corresponding to the cubic structure, can be observed in the XRD patterns (Figure 2S).[1] Besides the NiO diffraction pattern, the XRD spectrum of CdS-NiO also contains peaks of the CdS (200), (220) and (311) crystal planes, which are indicative of cubic structure.[2]

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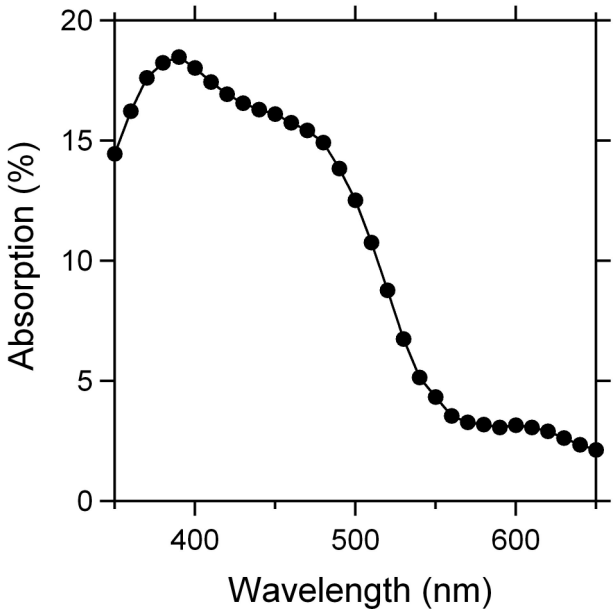

Figure S3. The absorption spectrum of CdS coated on the NiO nanoparticle film.

Figure S3 shows the absorption spectrum of CdS that is coated on the NiO nanoparticle film by chemical bath deposition followed by annealing at 250 °C for 1 h under N_2. The absorption of CdS is increased substantially when the wavelength is decreased below 550 nm, consistent with the IPCE spectrum of NiO-CdS photocathode (Figure 2).

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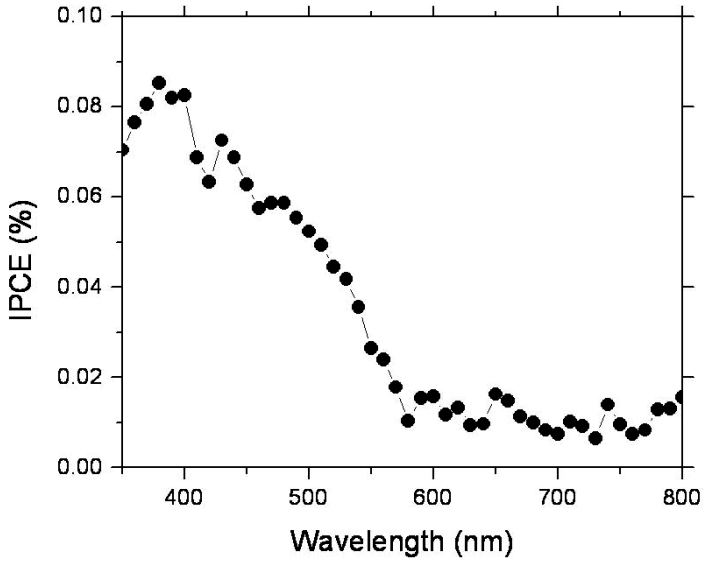

Figure S4. IPCE spectrum of a CdS-sensitized NiO nanoparticle film containing $Co^{II/III}$ tris(4,4'-di-tert-butyl-2,2'-dipyridyl)perchlorate (0.1 M/0.1M) and 0.1 M $LiClO_4$ in the propylene carbonate.

Figure S4 shows the IPCE spectrum of the CdS-sensitized NiO photocathode incorporating the $Co^{II/III}$ tris(4,4'-di-tert-butyl-2,2'-dipyridyl)perchlorate in propylene carbonate. The CdS/NiO cell containing the cobalt-based electrolyte yields a significantly reduced IPCE response compared to the CdS/NiO cell containing a polysulfide-based electrolyte for reasoned discussed in connection with Figure 2.

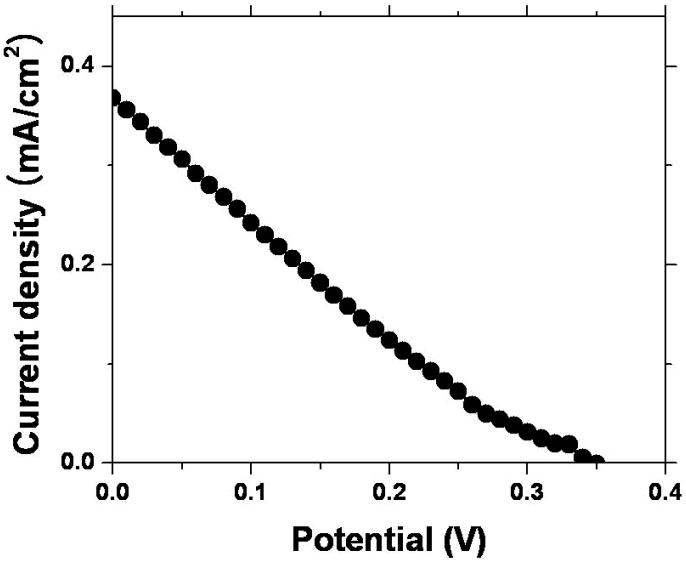

Figure S5. J-V curve of CdS-sensitized NiO film in a 7:3 H_2O:methanol (vol./vol.) solution containing 0.5 M Na_2S, 0.1 M S_8, and 0.2 M KCl under simulated AM 1.5 solar irradiance (100 mW/cm^2).

Figure S5 shows the photoresponse of the CdS-sensitized NiO film exhibited a short-circuit photocurrent density (J_{sc}) of 0.38 mA/cm^2 (geometric area: 0.3 cm^2), an open-circuit photovoltage (V_{oc}) of 0.35 V, and a fill factor (FF) of 0.21, corresponding to a solar conversion efficiency of 0.027 %.

References

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