Supplementary Information

CdSe quantum dots/molecular cobalt catalyst co-grafted open porous NiO film as a photocathode for visible light driven H_2 evolution from neutral water

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Materials and instruments

Materials. Compounds glucose, ethanediol, sodium sulfite, selenium powder, sodium borohydride, cadmium nitrate, cadmium acetate, and selenium dioxide were purchased from local suppliers and used without further purification. Dimethylglyoxime, cobaltous chloride, and nickel nitrate were purchased from Aladdin and used as received. The water used as solvent in all photoelectrolysis experiments was deionized with a Millipore Milli-Q UF Plus system (15–18 MΩ-cm resistivity). The open porous NiO film was fabricated by using a recently reported green solvothermal synthesis protocol.[1] The reference planar NiO film was prepared by doctor-blading a NiO paste onto the FTO glass plate according to the literature method.[2] Cobalt catalyst, $[CoCl(dmgH)_2(pyridyl\text{-}4\text{-}hydrophosphonate)]^-$ (CoP, dmgH = dimethyloxime), was synthesized by using a literature procedure.[3]

Instruments. UV-Vis absorption measurements were carried out on an Evolution 220 spectrophotometer. ICP-OES analysis was recorded on an Optima 2000 DV spectrometer (Perkin Elmer Inc.). SEM images and EDX spectra were recorded with a NOVA NanoSEM 450 instrument operating at 3 kV and equipped with an OXFORD X-max EDX system operating at 20 kV. TEM images were obtained with a JEOL JEM2100 microscope at 200 kV and recorded by an ORIUS camera.

Preparation of photocathode

Grafting CdSe QDs to the porous NiO by the SILAR procedure. The SILAR procedure was made according to the literatures.[4,5] The NiO/CdSe QDs electrode was prepared by three SILAR cycles.

Grafting CdSe QDs to the porous NiO by the OPAR procedure.[6] Aqueous solutions of cadmium acetate (66.6 mg in 25 mL water) and thioglycolic acid (15 mg in 20 mL water) were mixed thoroughly by stirring. The freshly prepared sodium selenosulfate solution (2 mL), which was prepared by refluxing selenium powder (2 g) and sodium sulfite (4.83 g) in water (100 mL) for 10 h, was added to the cadmium acetate/thioglycolic acid mixed solution. Subsequentely, the NiO film was put into this solution at ~5 ºC for 2 days.

Grafting cobaloxime catalyst to the CdSe QDs sensitized porous NiO. The FTO glass decorated with the CdSe QD-sensitized porous NiO film was cut into 1 × 2 cm^2 pieces and the electrode was immersed in a methanol solution of the cobaloxime catalyst (1.0 mM) for 3 h under nitrogen atmosphere in the dark. The as-prepared electrode was washed with methanol and water for several times and dried in vacuum at room temperature. After that, the photocathode, NiO/CdSe/CoP or NiO/CdSe/Co, was stored under nitrogen in the dark and ready for further photoelectrochemical testing.

Electrocatalytic experiment

Electrochemical measurement. All electrochemical experiments were performed with a CH Instruments 650E or 630D potentiostats. Linear sweep voltammogram (LSV) of NiO and the as-prepared photocathodes were carried out in 0.1 M Na_2SO_4 solution at pH 6.8 in a standard three-electrode cell, using a Pt wire as counter electrode and Ag/AgCl in 3 M KCl as reference electrode. The scanning rate of CV tests was 100 mV s^{-1}. All potentials reported in this paper were converted to the NHE reference using $E(\mathrm{NHE}) = E(\mathrm{Ag/AgCl}) + 0.197$ V.

Photoelectrochemical measurement. Transient current responses of the as-prepared NiO/CdSe and NiO/CdSe/CoP photocathodes to on-off cycles of illumination on the electrode were carried out in a three-electrode PEC cell in 0.1 M Na_2SO_4 solution at pH 6.8, with a Pt wire as counter electrode and Ag/AgCl in 3 M KCl as reference electrode. Before the photoelectrochemical measurement, the aqueous solution was bubbled with nitrogen for 30 min. First, electrolysis of the sample photocathode in a 0.1 M Na_2SO_4 solution was conducted at a set-value of applied potential for 100 s without illumination; after that, the photocathode was exposed to illumination of a 300 W xenon lamp equipped with a $\lambda > 400$ nm cutoff filter for another 100 s; this was termed as one on-off cycle.

Determination of Faradaic efficiency.

The experiments were performed in a 0.1 M Na_2SO_4 solution at pH 6.8 and 25 °C with a NiO/CdSe/CoP photocathode as working electrode, a Pt foil as counter electrode, and Ag/AgCl in 3 M KCl as reference electrode in a gas-tight electrochemical cell at an applied potential of −0.2 V vs. NHE and under illumination ($\lambda > 400$ nm). Considering that a certain amount of hydrogen would be dissolved in the aqueous solution, the solution of Na_2SO_4 was saturated with H_2 through bubbling at 25 °C for 30 min prior to use. The gas in the headspace of the cell was analyzed by CEAULIGHT GC-7920 gas chromatographic (GC) instrument equipped with a 5 Å molecular sieve column (2 mm × 2 m) before and during 2 h photoelectrolysis. The amount of H_2 evolved was calculated by the difference in the H_2 contents. A Faradaic efficiency of about 81% was obtained by comparing the amount of hydrogen evolved with that calculated from consumed charge.

References

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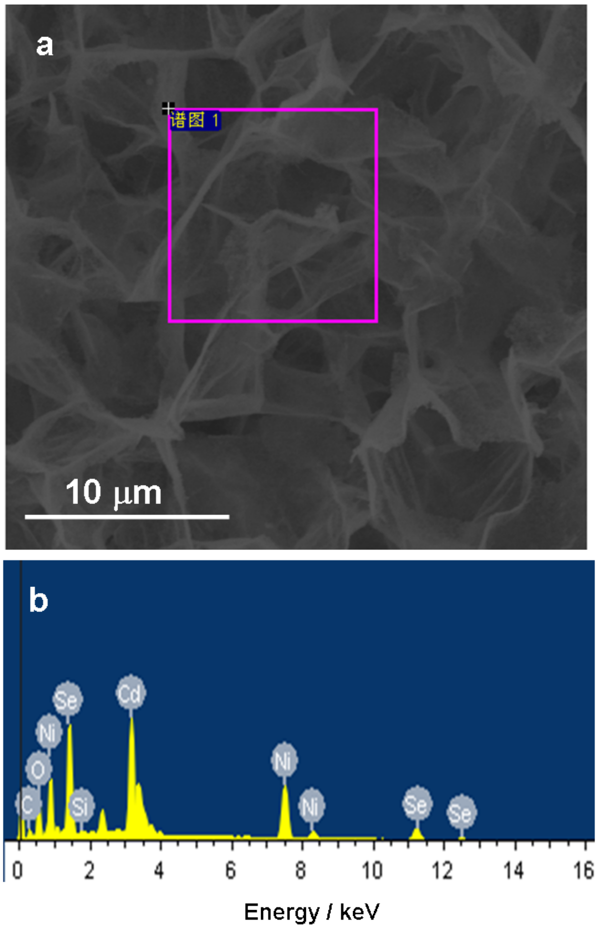
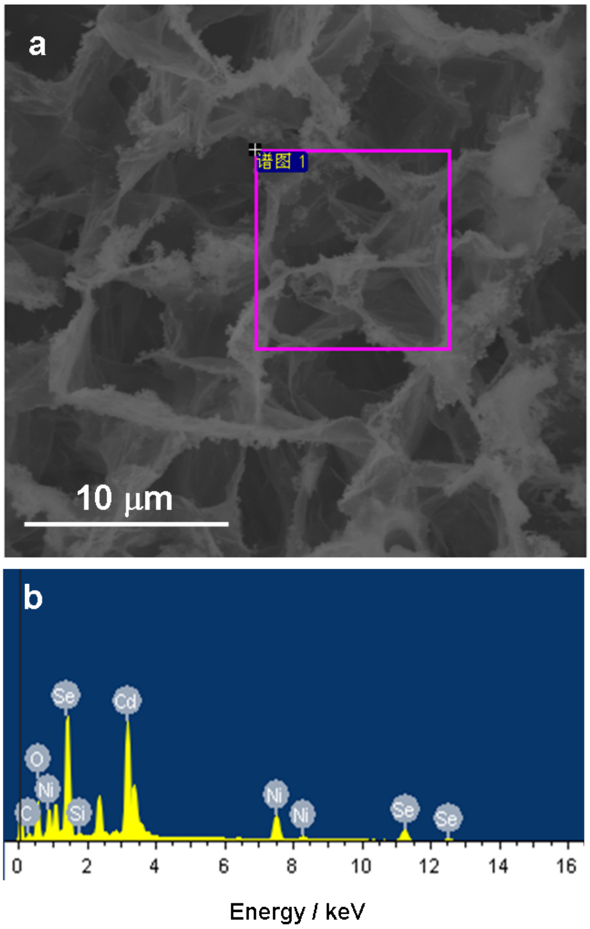


Element	Mass ratio	Molar ratio	Cd/Se atomic ratio
C K	5.66	18.49	
O K	17.84	43.74	
Si K	0.42	0.58	
Ni K	23.20	15.50	
Se L	21.96	10.90	
Cd L	30.92	10.79	Cd/Se = 1:1.01

Fig. S1 (a) SEM image and (b) EDX historgramand data of theCdSe/NiO sample made by OPAR method.



Element	Mass percentage	Atomic percentage	Cd/Se atomic ratio
C K	4.85	15.15	
O K	19.12	44.86	
Si K	0.58	0.77	
Ni K	39.20	25.07	
Se L	15.17	7.21	
Cd L	15.85	5.29	Cd/Se = 1: 1.36
Sn L	5.24	1.66	

Fig. S2 (a) SEM image and (b) EDX historgramand data of theCdSe/NiO sample made by SILAR method.

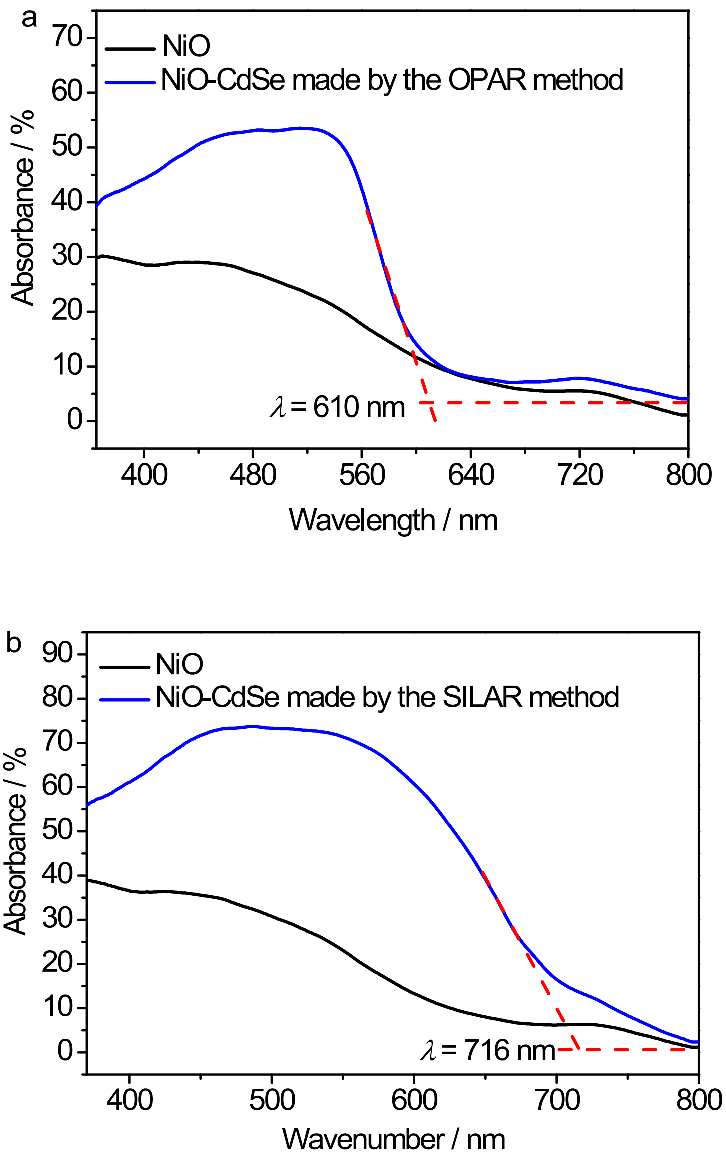


Fig. S3 Solid UV-vis spectra of the bare NiO and CdSe-sensitized NiO films made by the OPAR (a) and SILAR (b) methods.

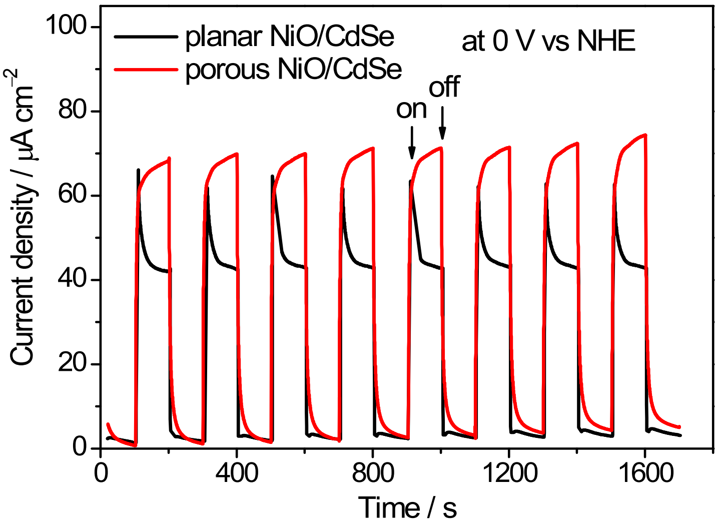


Fig. S4 Transient current responses of the planar and porous NiO/CdSe electrodes to on-off cycles of illumination on photocathodes at 0 V versus NHE in the PEC of 0.1 M Na_2SO_4 solution at pH 6.8, using a three-electrode cell witha Pt wire as counter electrode and Ag/AgCl as reference electrode. The planar NiO/CdSe photocathode was made by doctor-blading a NiO paste on a FTO glass plate and followed by grafting CdSe QDs with the OPAR method.

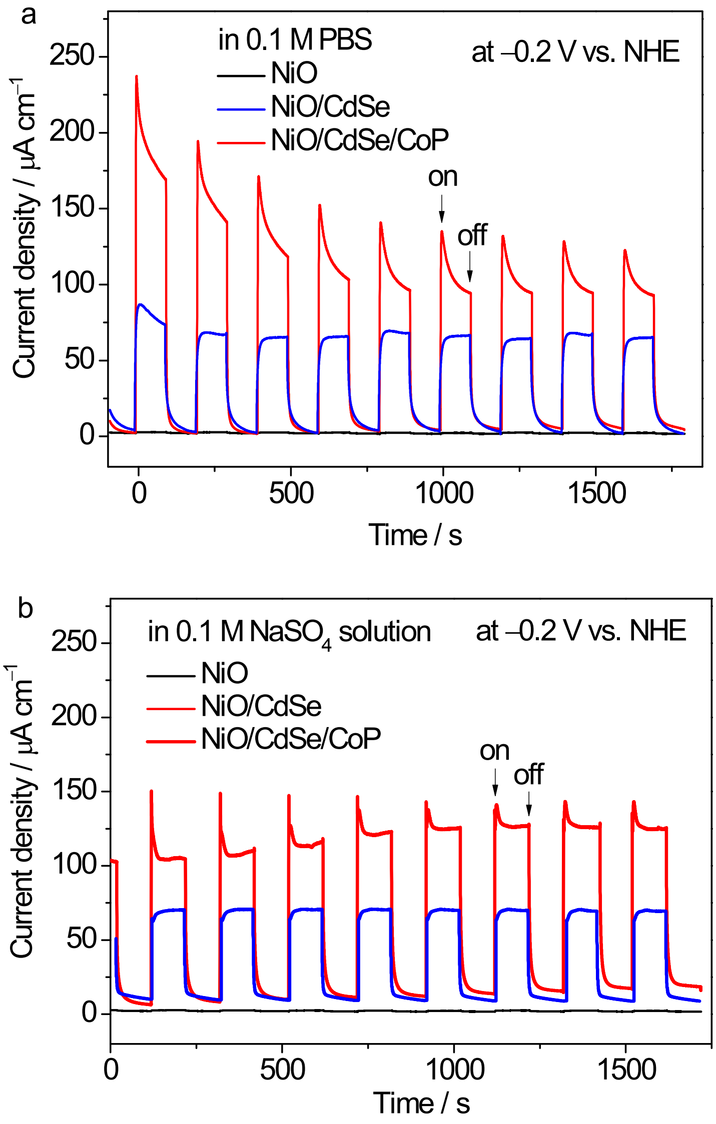


Fig. S5 Transient current responses of porous NiO, NiO/CdSe, and NiO/CdSe/CoP electrodes to on-off cycles of illumination on photocathodes at −0.2 V versus NHE,(a) in 0.1 MPBS and (b) in 0.1 M Na_2SO_4 solution at pH 6.8, using a three-electrode cell with a Pt wire as counter electrode and Ag/AgCl as reference electrode.

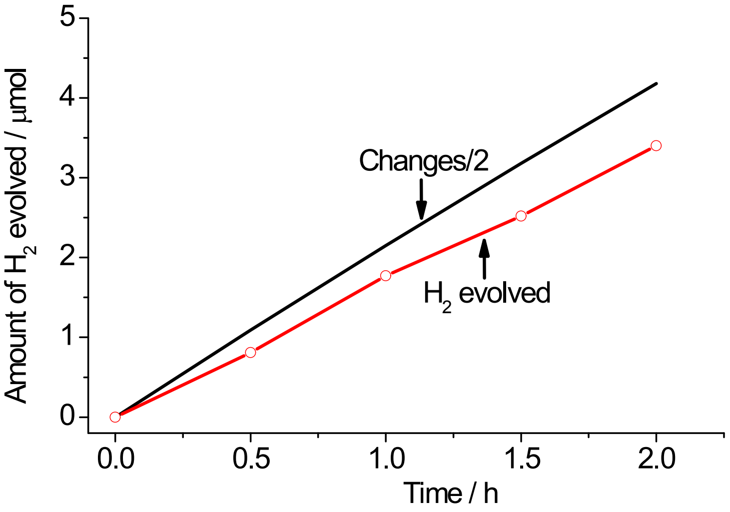


Fig. S6 The amount of hydrogen is calculated from passed charge (black solid); the content of H_2 is determined by gas chromatography (red circle); conditions: electrolysis of 0.1 M Na_2SO_4 solution at pH 6.8 in a gas-tight cell under illumination (λ > 400 nm) at an applied potential of −0.2 V vs. NHE for 2 h with NiO/CdSe/CoP as a working electrode.