Supplementary Information

Carbon quantum dots decorated Cu_2S nanowire arrays for enhanced photoelectrochemical performance

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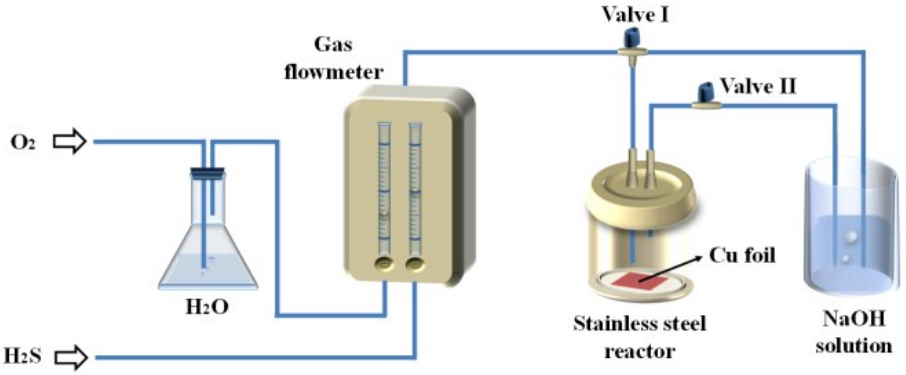

Scheme S1 Schematic illustration of the home-made setup for the growth of Cu_2S NWAs on Cu foil.

Synthesis and Properties of CQDs

CQDs were prepared using arc-synthesized carbon by-products reported by our group. Briefly, 1.0 g single-walled CNT products were adequately dispersed in 1000ml sodium dodecylsulfate (SDS, 1.0wt%) solution under ultrasonic vibrations, followed by centrifugation at 6000 rpm to remove large carbon particles and catalysts. The stable dispersions were further centrifuged at 9000 rpm, and the residual carbon particles were collected after SDS removal and freeze drying. Fluorescent CQDs with narrow size distribution can be obtained sequentially by strong acid reflux, dialyzing and rotary evaporation.

It can be observed that the as-prepared CQDs are well-dispersed spherical nanoparticles with good mono-dispersity and have a narrow particle-size distribution in the range of 3.8-8.8 nm with average diameter of 6.2 nm as shown in **Fig. S1a**. The FTIR spectrum of the CQDs (**Fig. S1b**) demonstrates the characteristic peaks of C-H, C-OH, and C=C at 1118, 1429, and 1622 cm^{-1}, respectively. The absorption spectrum of CQDs (**Fig. S1c**) exhibits a broad peak at about 375 nm, which is assigned to the presence of π orbitals of larger CQDs. Additionally, the CQDs show a strong absorption of sunlight in the short-wavelength region. The insets in **Fig. S1c** depict the solutions of CQDs under lamplight and UV light (365 nm), and obviously, a distinct green luminescence can be observed

under UV light excitation. **Fig. S1d** presents the excitation-independent PL down-conversion spectra of the CQDs. When the excitation wavelength changes from 270 to 480 nm, the corresponding PL spectrum remains almost invariable and shows a strong peak at ~502 nm.

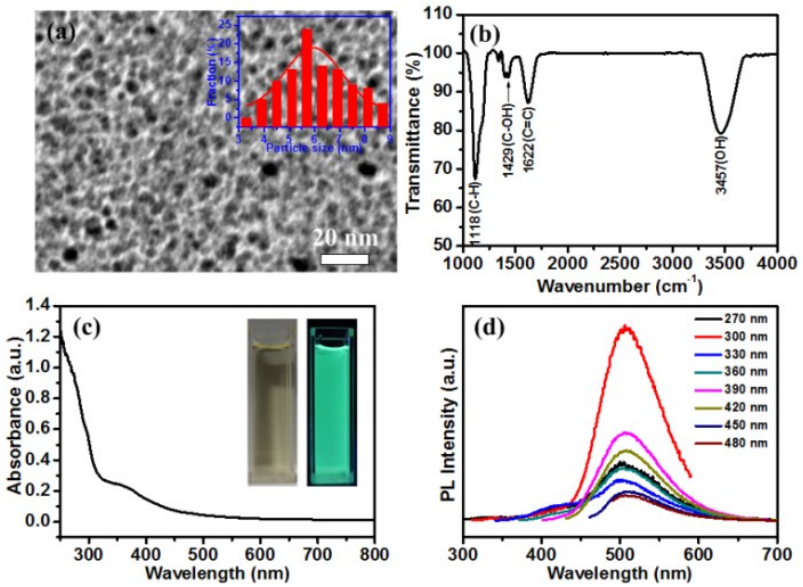

Fig. S1 (a) TEM image of the synthesized CQDs. Inset: particle size distribution of CQDs. (b) FTIR spectrum of the CQDs. (c) UV-vis absorption spectrum of the CQDs. Inset: optical image of the CQDs aqueous solution under lamplight (left) and UV light (right, 365 nm) illumination. (d) PL spectra of the CQDs with different excitation wavelengths.

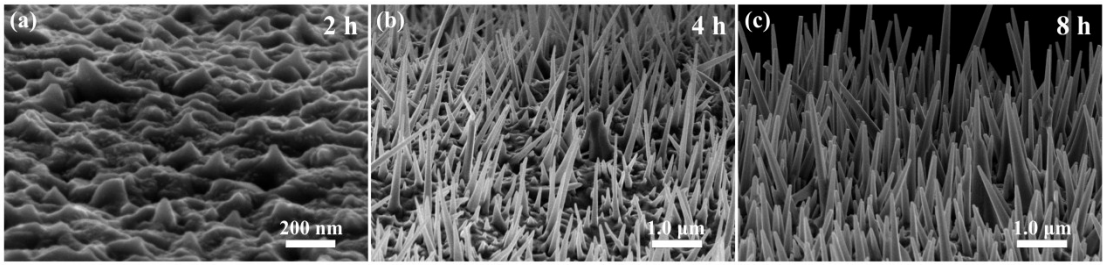

Fig. S2 SEM images of Cu_2S NWAs grown for different reaction times.

Table S1 Relationship between preparation conditions and the diameter, length and density of Cu_2S NWAs.

Sample	Synthesis temperature (°C)	Reaction time (h)	Average diameter (nm)	Average length (μm)	Spacing density (p μm^{-2})
Cu_2S-1	20	12	88	28	64
Cu_2S-2	25	12	155	4.5	46
Cu_2S-3	30	12	200	4.3	31
Cu_2S-4	25	2	52	0.06	/
Cu_2S-5	25	4	115	1.1	16
Cu_2S-6	25	8	135	1.8	23

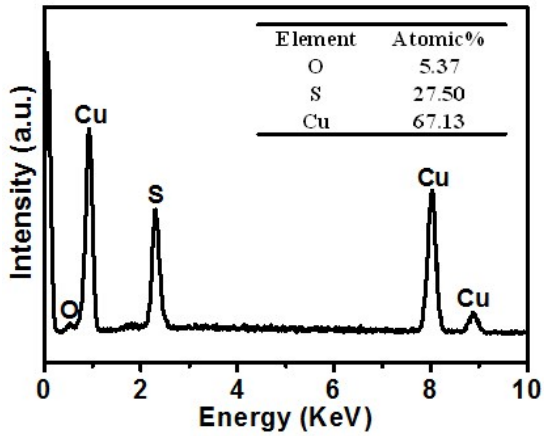

Fig. S3 EDS of Cu_2S NWAs.

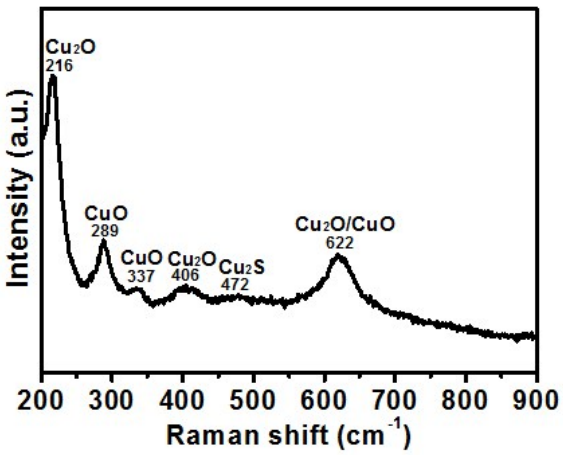

Fig. S4 Raman spectrum of Cu_2S NWAs.

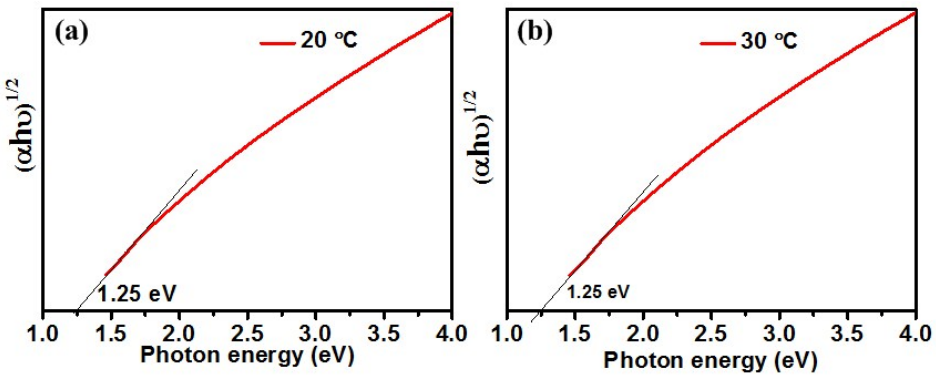

Fig. S5 Energy band gap determination of Cu_2S NWAs.

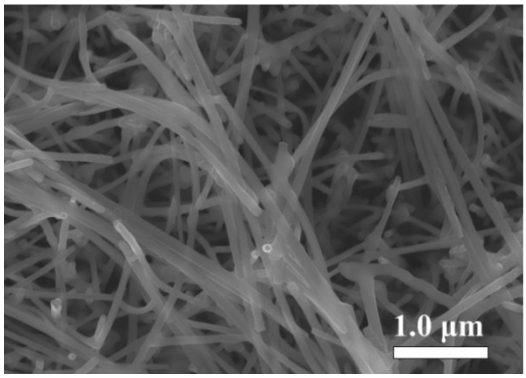

Fig. S6 SEM image of Cu_2S NWAs (prepare at 20℃) after deposition of CQDs.

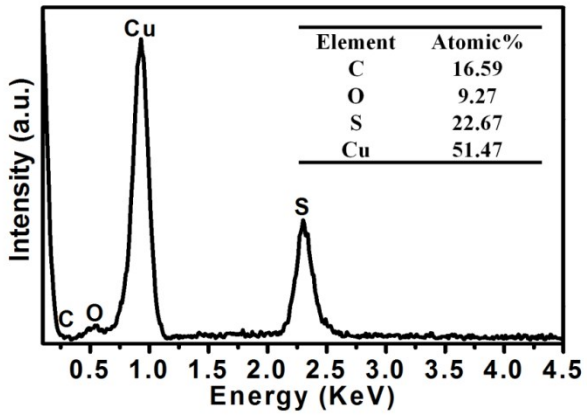

Fig. S7 EDS result of the Cu_2S/CQD-4 NWAs.

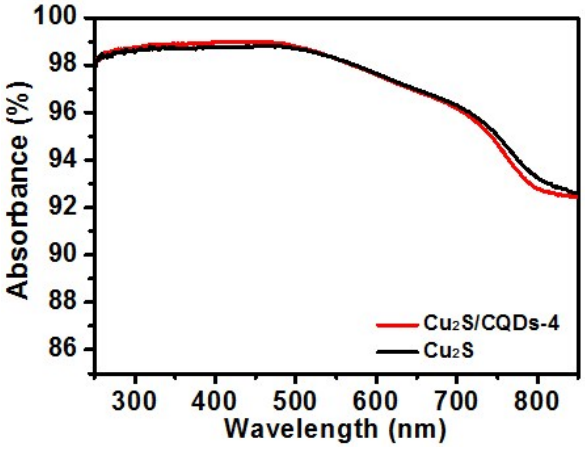

Fig. S8 Absorbance of Cu_2S NWAs before and after decorating with 4 cycles of CQDs.

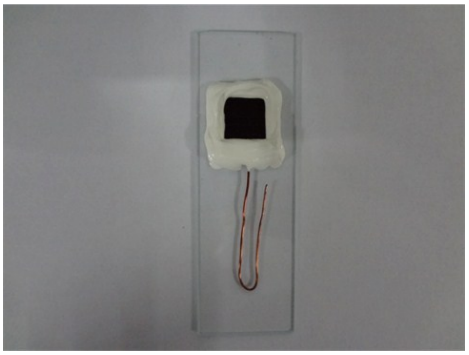

Fig. S9 Optical image of a home-made photocathode.

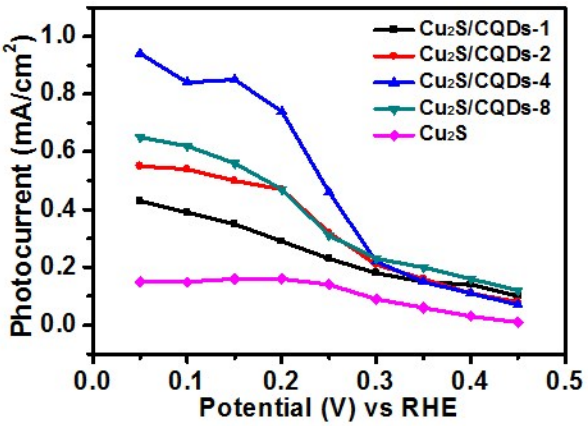

Fig. S10 Photocurrent densities *vs* applied bias potential for the Cu_2S/CQDs-x NWAs.

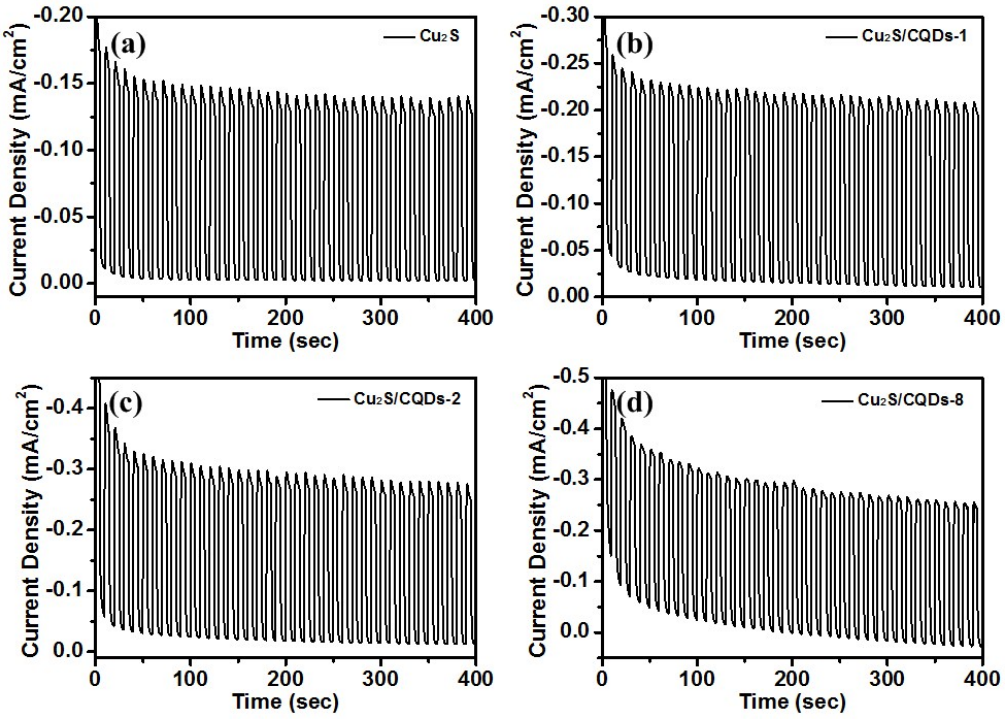

Fig. S11 Amperometric I-t curves of the Cu_2S/CQDs-x NWAs at an applied bias of 0.25 V vs RHE under illumination of chopped AM 1.5G.

Table S2 Summary of photocurrent densities and stability at 0.2 V *vs* RHE, and conversion efficiencies of the Cu_2S/CQDs-x NWAs.

Sample	Cycles of CQDs	Photocurrent density 0.2 V *vs* RHE (mA cm^{-2})	Stability (%)	Conversion efficiency (%)
Cu_2S-2	0	0.16	87.5	0.035
Cu_2S/CQDs-1	1	0.22	90.9	0.058
Cu_2S/CQDs-2	2	0.33	81.8	0.094
Cu_2S/CQDs-4	4	0.39	82.1	0.148
Cu_2S/CQDs-8	8	0.33	87.9	0.094

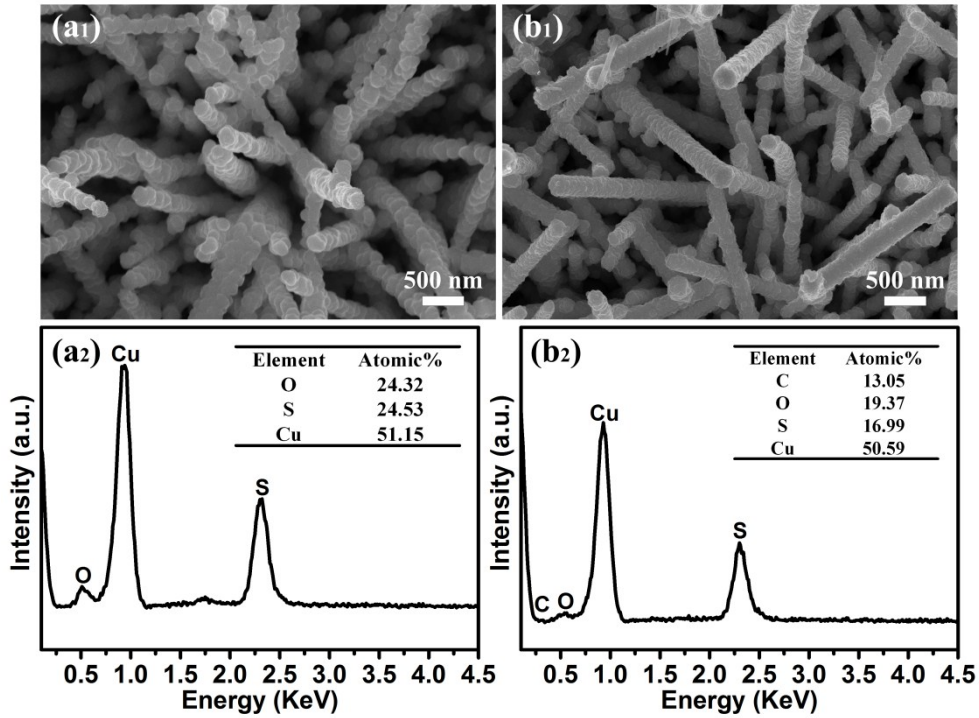

Fig. S12 SEM images of (a_1) Cu_2S-2 NWAs and (b_1) Cu_2S/CQDs-4 NWAs after 30 min PEC water splitting process at 0.2 V *vs* RHE. (a_2) and (b_2) are the corresponding EDS results.