Electronic Supplementary Information (ESI) for

Metal-semiconductor ternary hybrids for efficient visible-light photocatalytic hydrogen evolution

Dae Han Wi,[‡a] Se Young Park,[‡a] Seunghoon Lee,[a] Jiha Sung,[b] Jong Wook Hong*[ac] and Sang Woo Han*[a]

[a] Center for Nanotectonics, Department of Chemistry and KI for the NanoCentury, KAIST, Daejeon 34141, Korea

[b] Department of Applied Chemistry, Dongduk Women's University, Seoul 02748, Korea

[c] Department of Chemistry, University of Ulsan, Ulsan 44610, Korea

*Corresponding author. *E-mail*: sangwoohan@kaist.ac.kr (S.W.H.), jwhong@ulsan.ac.kr (J.W.H.)

[‡]These authors contributed equally to this work.

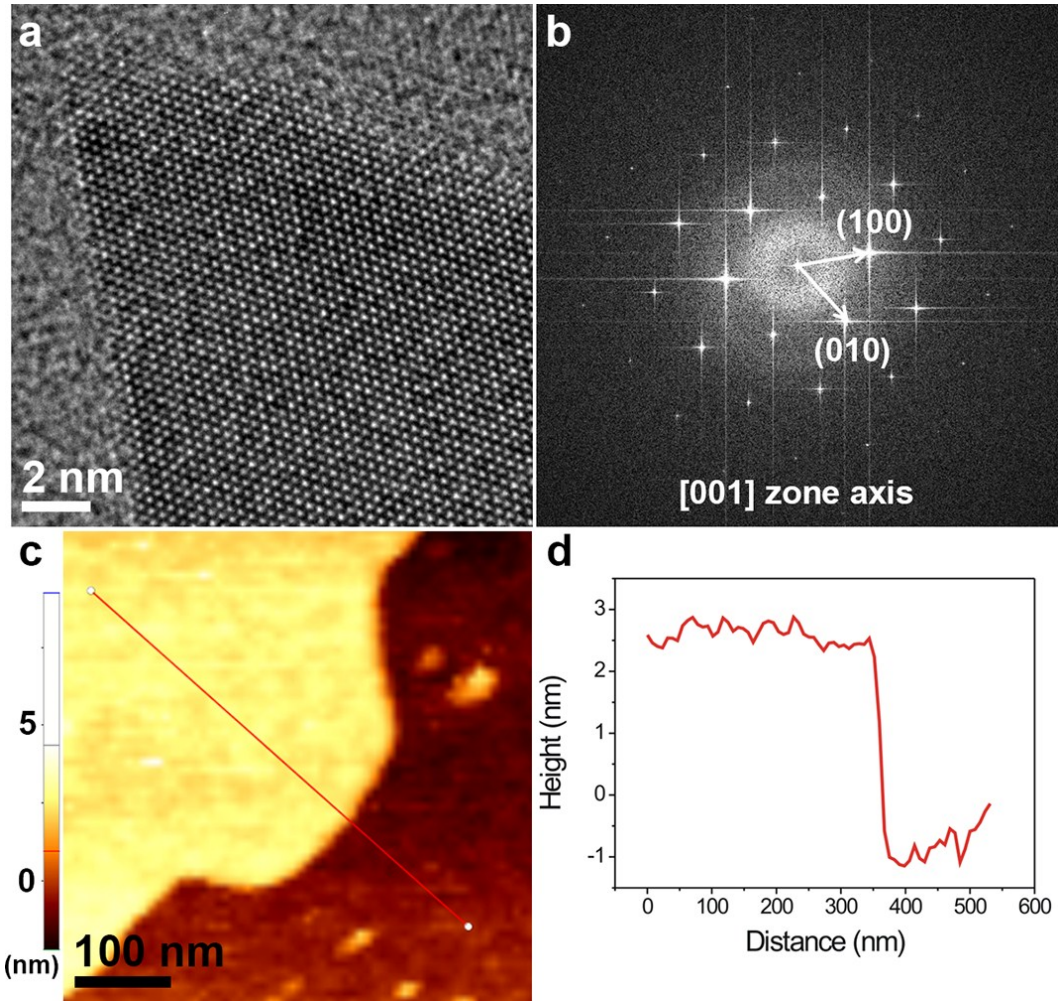

Fig. S1 (a) HRTEM image and (b) corresponding FFT pattern of e-MoS_2. (c) AFM image and (d) corresponding height profile of e-MoS_2.

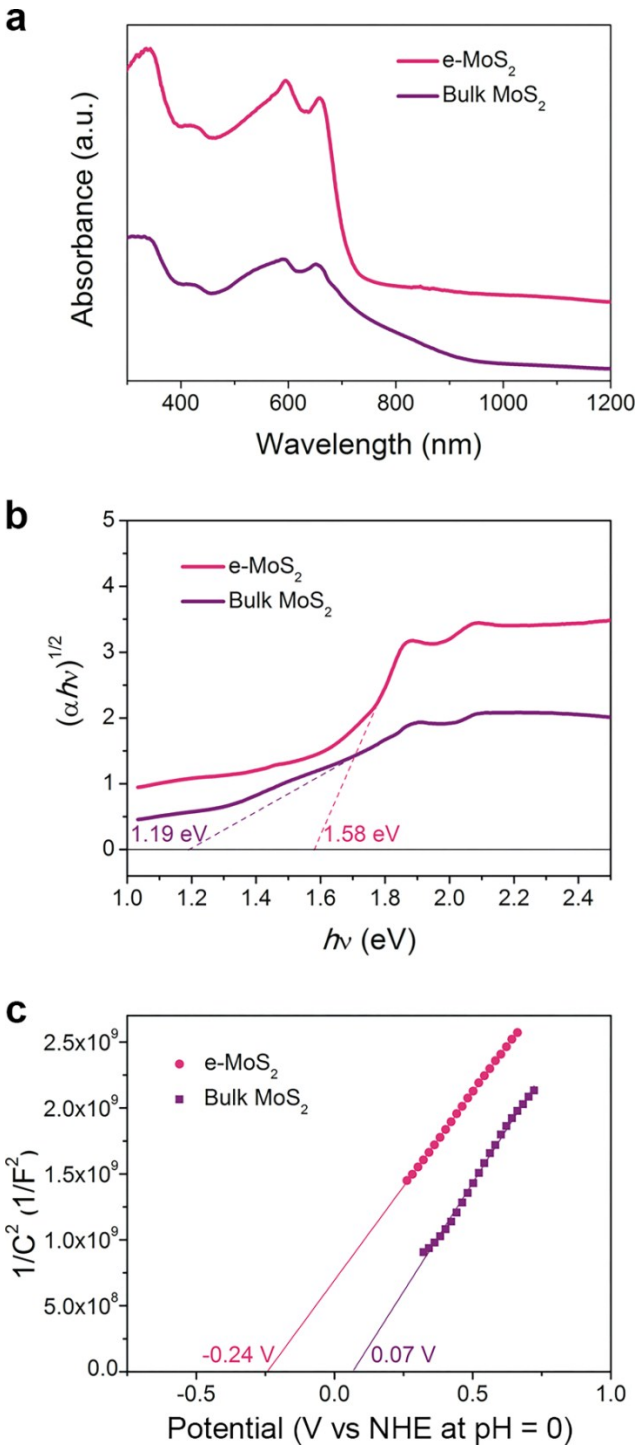

Fig. S2 (a) Diffuse reflectance spectra and (b) corresponding Tauc plots of e-MoS_2 and bulk MoS_2. (c) Mott-Schottky plots of e-MoS_2 and bulk MoS_2.

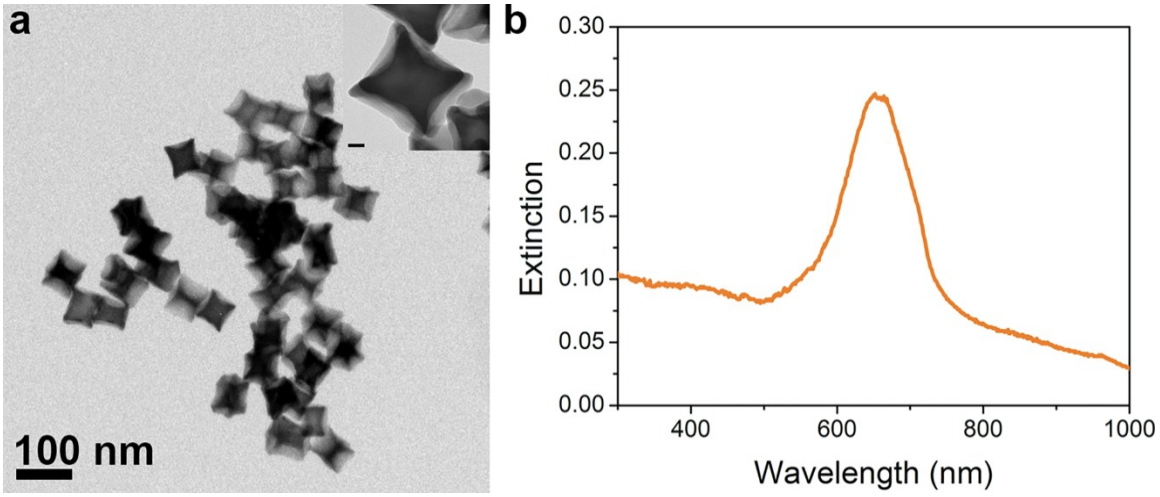

Fig. S3 (a) TEM image of Au CNCs. Inset shows a magnified TEM image of Au CNCs (scale bar = 10 nm). (b) Extinction spectrum of Au CNCs in water.

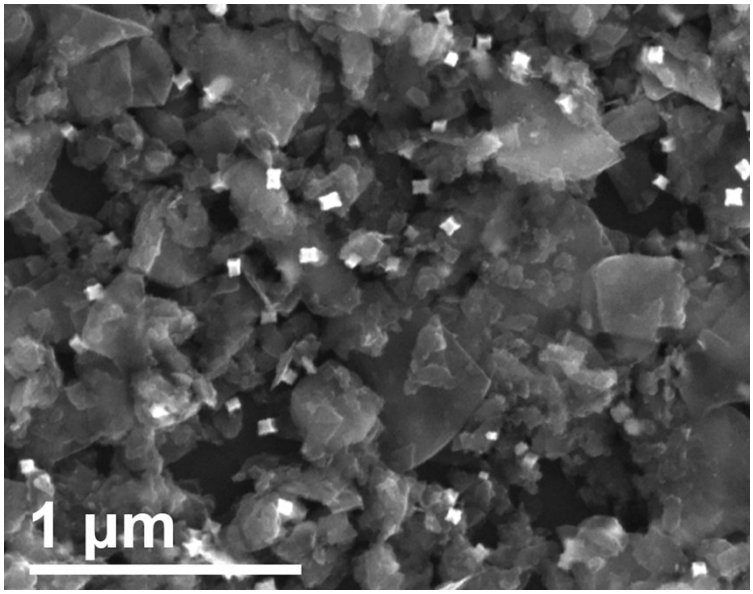

Fig. S4 SEM image of e-MoS_2-Au_{CNC} hybrids.

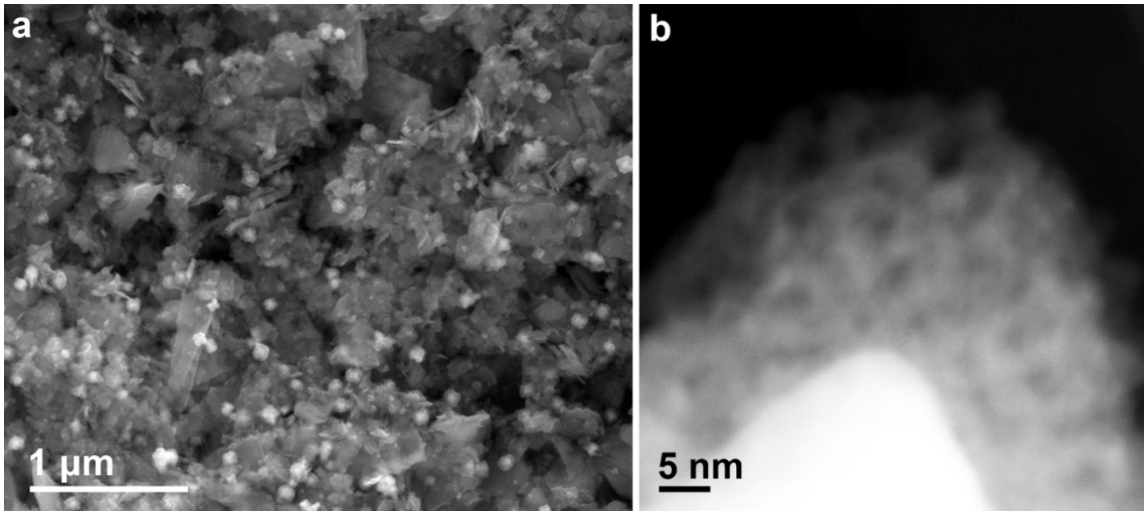

Fig. S5 (a) SEM image and (b) high-magnification HAADF-STEM image of e-MoS_2-Au_{CNC}-CdS hybrids.

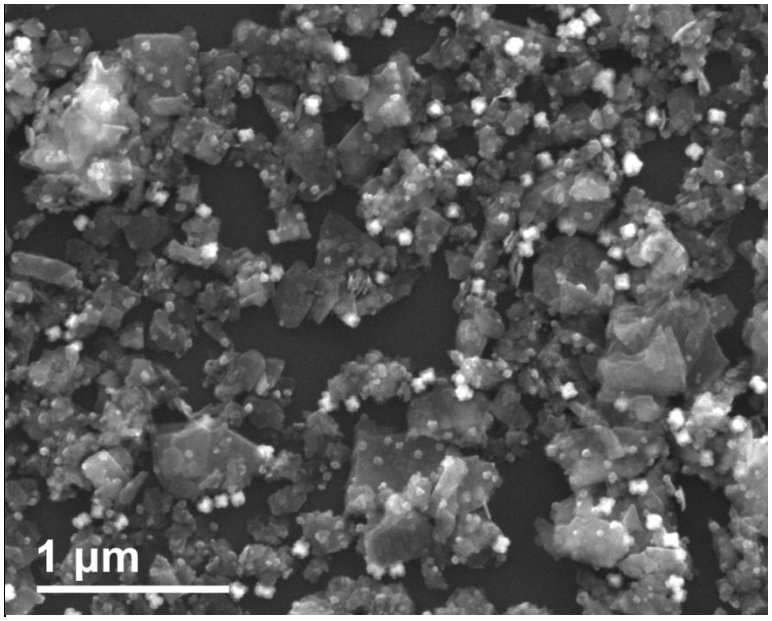

Fig. S6 SEM image of hybrids prepared with 100 mM of CTAB solution. In the standard synthesis, 400 mM of CTAB solution was used.

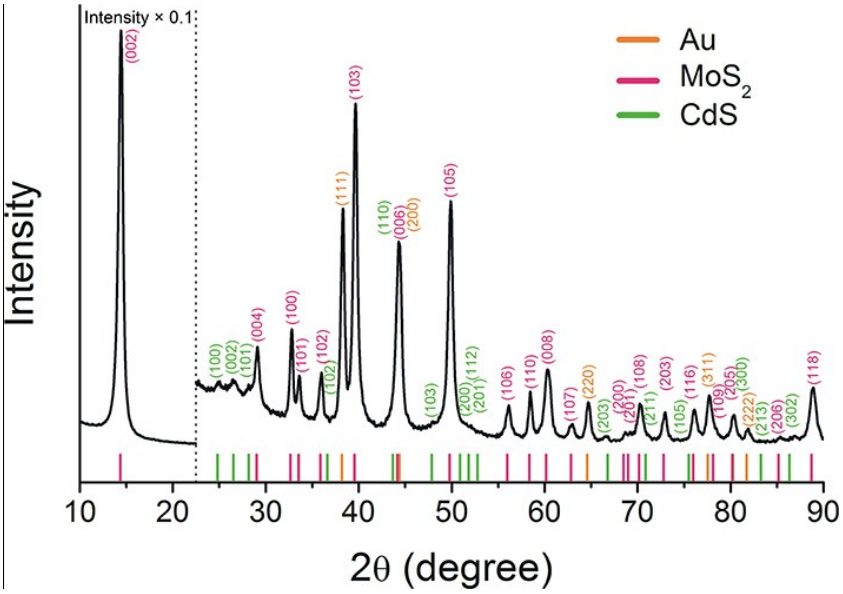

Fig. S7 XRD pattern of e-MoS_2-Au_{CNC}-CdS hybrids. The positions of Au, MoS_2, and CdS references were taken from the JCPDS database (Au: 04-0784, MoS_2: 37-1492, CdS: 41-1049).

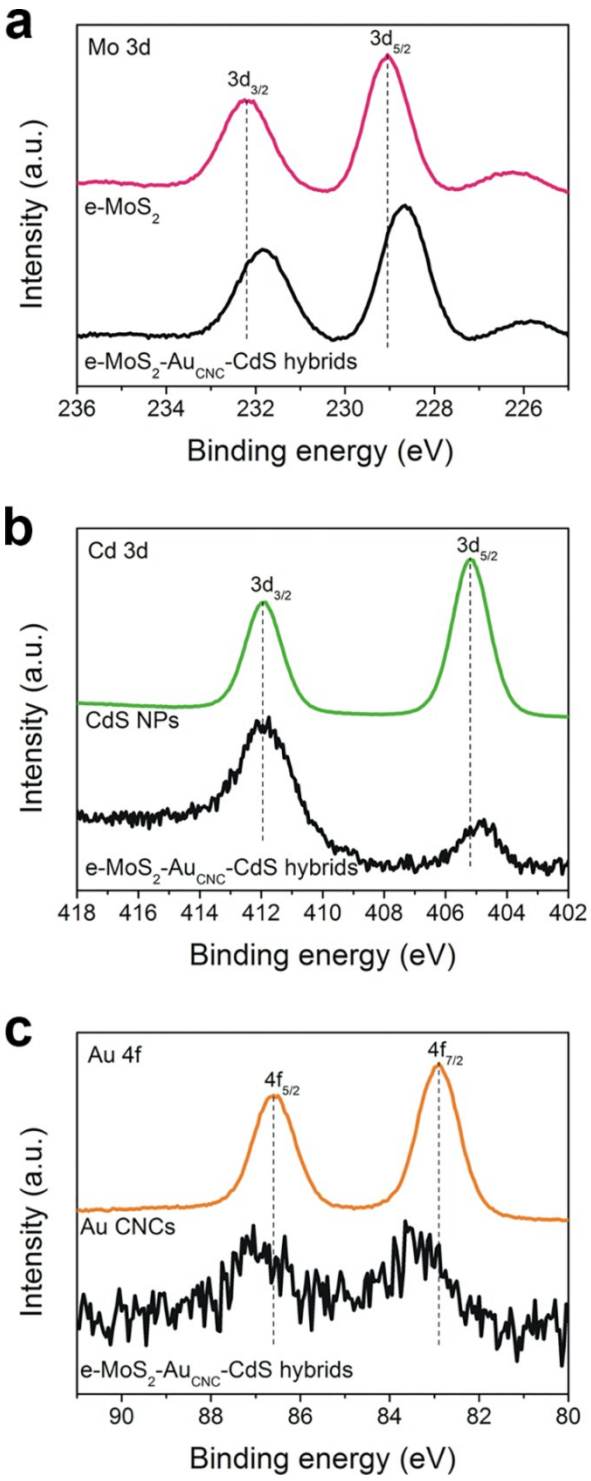

Fig. S8 XPS spectra of e-MoS_2-Au_{CNC}-CdS hybrids, e-MoS_2, CdS NPs, and Au CNCs in (a) Mo 3d, (b) Cd 3d, and (c) Au 4f regions.

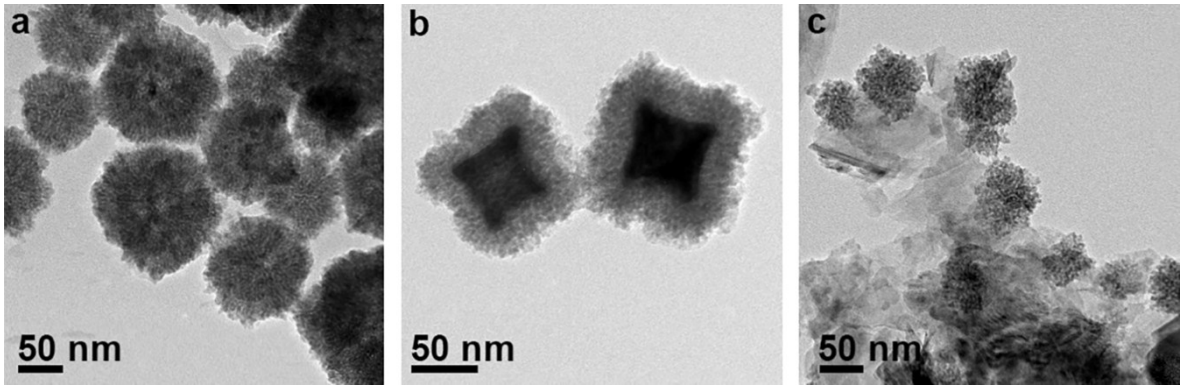

Fig. S9 TEM images of (a) CdS NPs, (b) Au_{CNC}-CdS hybrids, and (c) e-MoS_2-CdS hybrids.

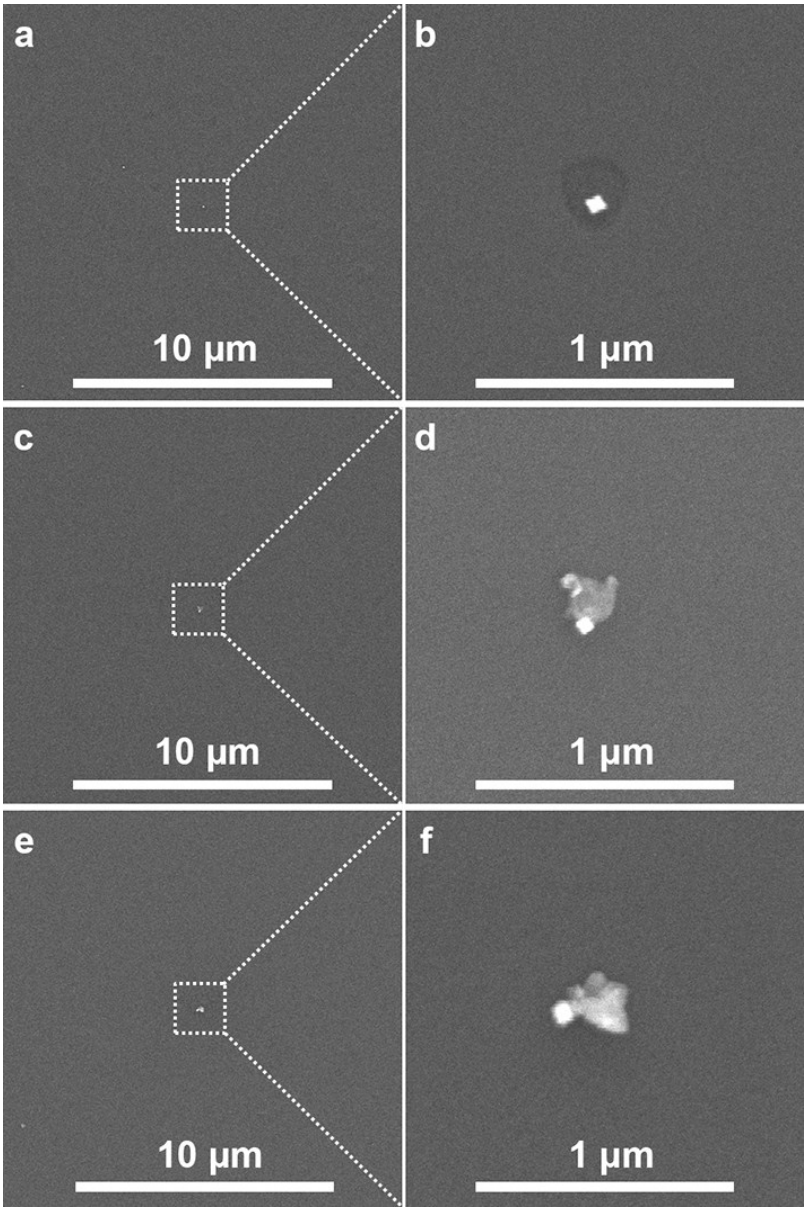

Fig. S10 (a,c,e) Low- and (b,d,f) high-magnification SEM images of (a,b) Au CNCs, (c,d) e-MoS_2-Au_{CNC} hybrids, and (e,f) e-MoS_2-Au_{CNC}-CdS hybrids loaded on cover glass substrates.

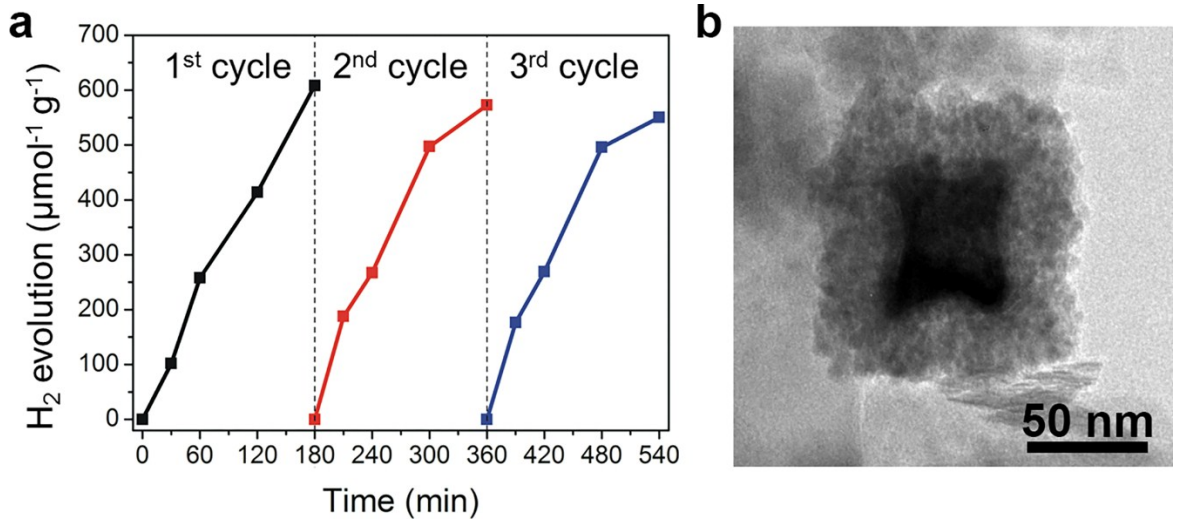

Fig. S11 (a) Recyclability of e-MoS_2-Au_{CNC}-CdS hybrids for photocatalytic hydrogen evolution. After each photocatalysis run, a quartz reaction cell was purged with Ar gas to remove remaining hydrogen, and then subjected to the next photocatalytic reaction. The e-MoS_2-Au_{CNC}-CdS hybrids exhibited 90% photocatalytic activity in the third cycle relative to that in the first cycle. (b) TEM image of the e-MoS_2-Au_{CNC}-CdS hybrids after the third cycle of photocatalysis, revealing that their original morphology was maintained after the reaction.

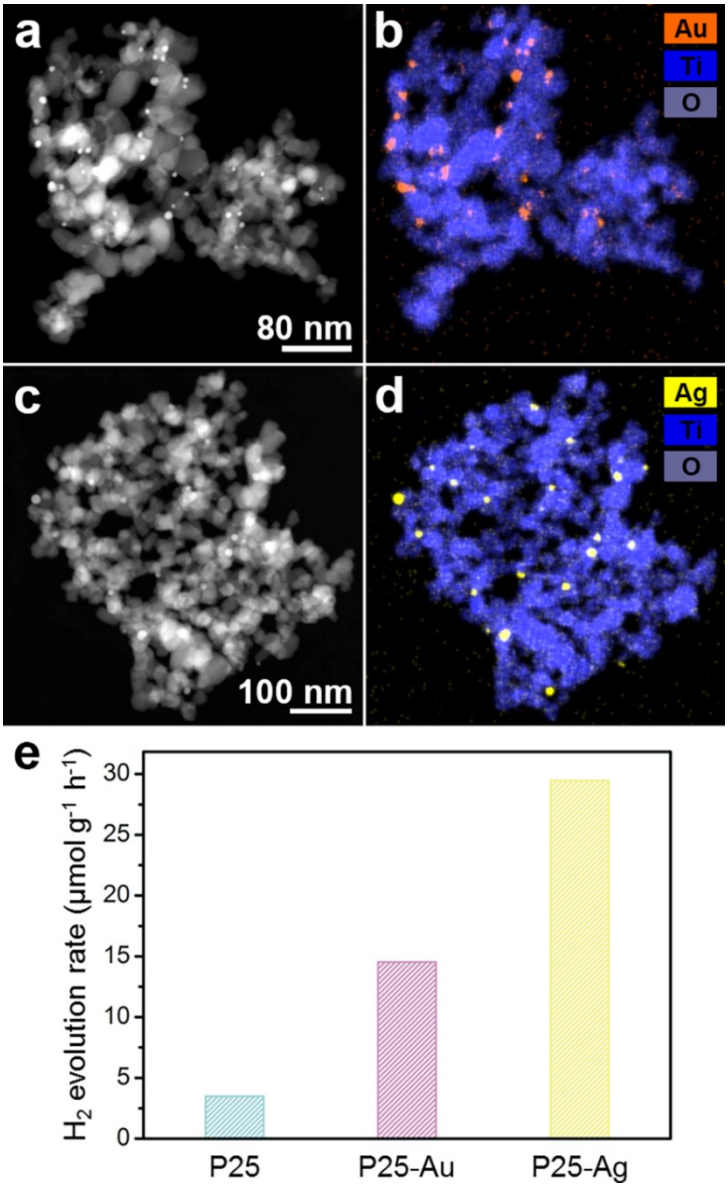

Fig. S12 (a,c) HADDF-STEM and (b,d) corresponding EDS elemental mapping images of (a,b) P25-Au and (c,d) P25-Ag. (e) Hydrogen evolution rates of P25, P25-Au, and P25-Ag.

In a typical synthesis of P25-Au or P25-Ag photocatalyst, 5 mg of P25 powder was injected into a quartz cell containing 45 mL of water and 5 mL of methanol. Then, 1 mL of an aqueous solution of $HAuCl_4$ or $AgNO_3$ (1 mg mL^{-1}) was added to the reaction mixture, and the resultant mixture was bubbled under Ar for 30 min. The mixture was then irradiated using 400 W Hg lamp (Newport 66902) for 30 min. The products were washed with water and ethanol, and dried in an oven at 95 °C. The average Au and Ag particle sizes of P25-Au and P25-Ag were 6 and 9 nm, respectively.

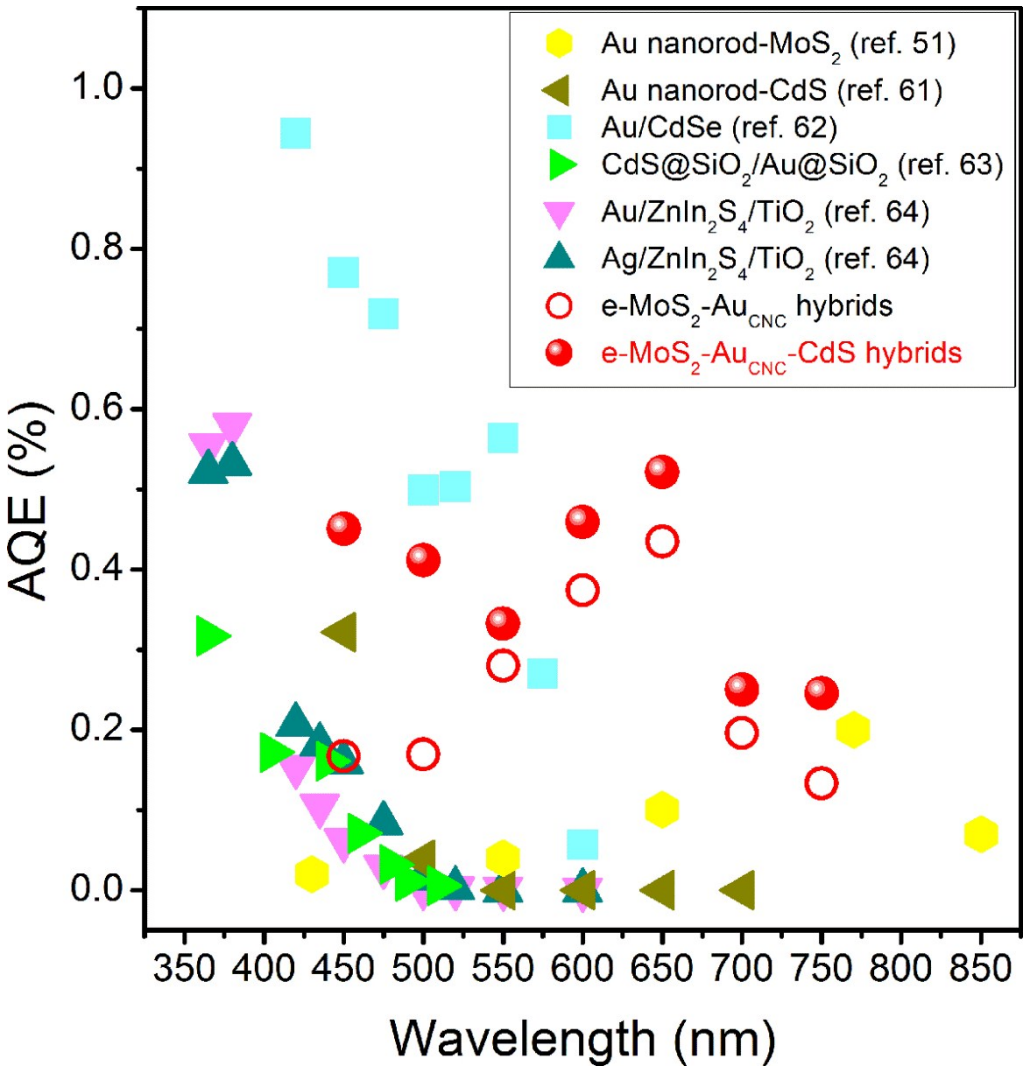

Fig. S13 AQEs of e-MoS_2-Au_{CNC}-CdS hybrids, e-MoS_2-Au_{CNC} hybrids, and other previously reported hybrid photocatalysts as a function of excitation wavelength. The AQE values and excitation wavelengths of other photocatalysts were obtained from literatures: refs. 51, 61-64. The AQE values of e-MoS_2-Au_{CNC}-CdS and e-MoS_2-Au_{CNC} hybrids under 650 nm irradiation were 0.52 and 0.44%, respectively.

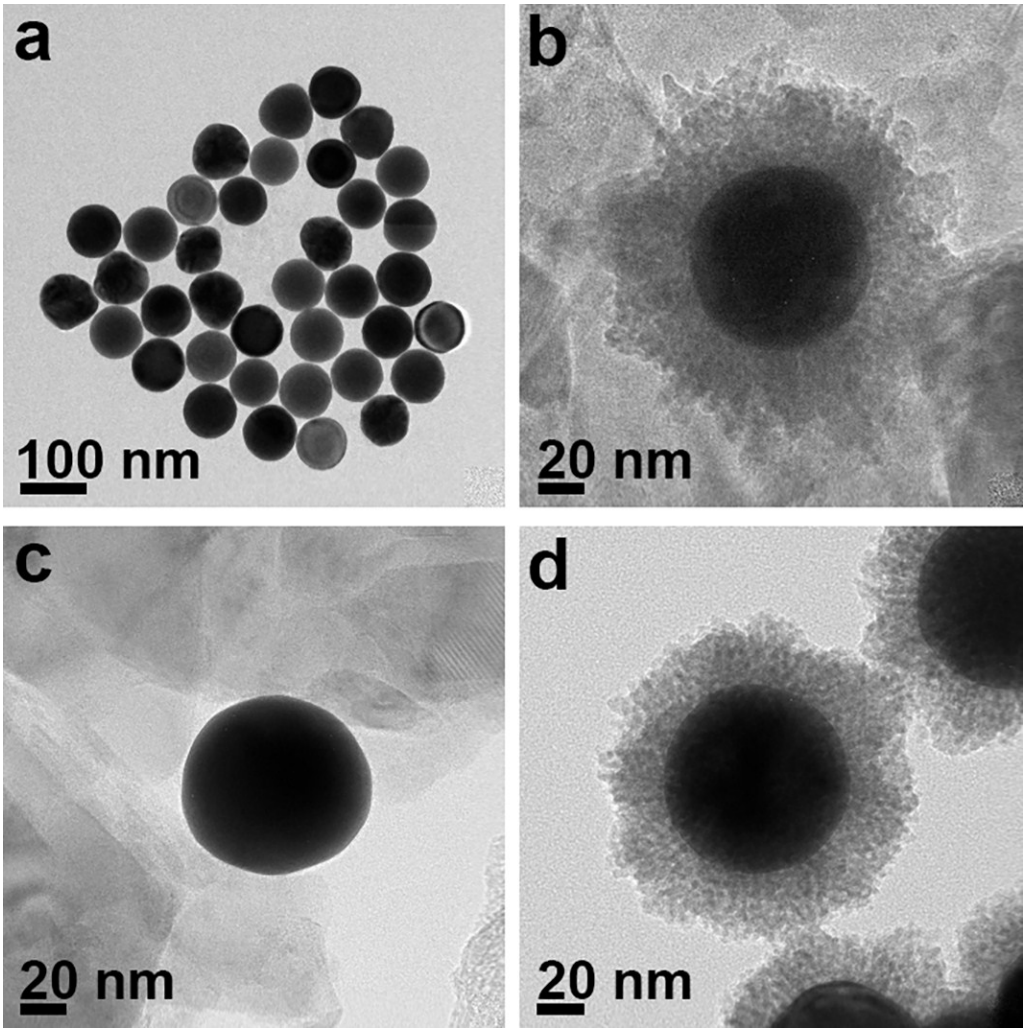

Fig. S14 TEM images of (a) spherical Au NCs, (b) e-MoS_2-Au_{sphere}-CdS, (c) e-MoS_2-Au_{sphere}, and (d) Au_{sphere}-CdS hybrids.

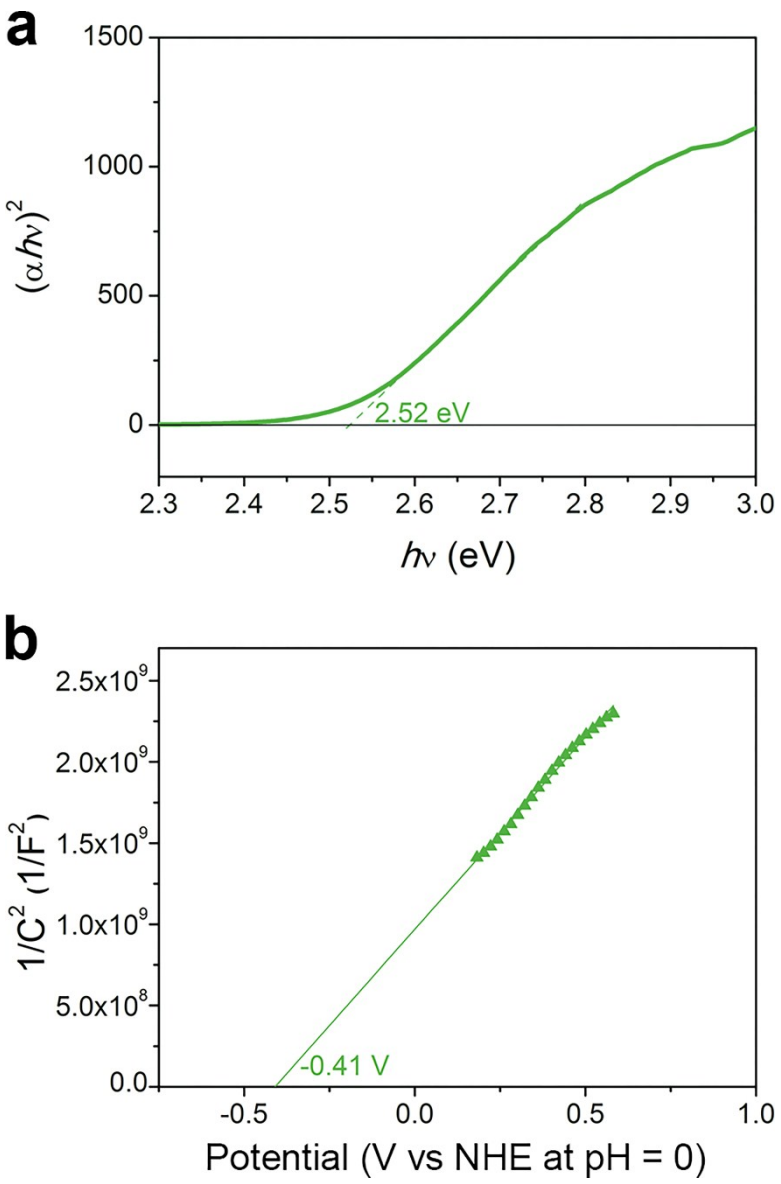

Fig. S15 (a) Tauc and (b) Mott-Schottky plots of CdS NPs.

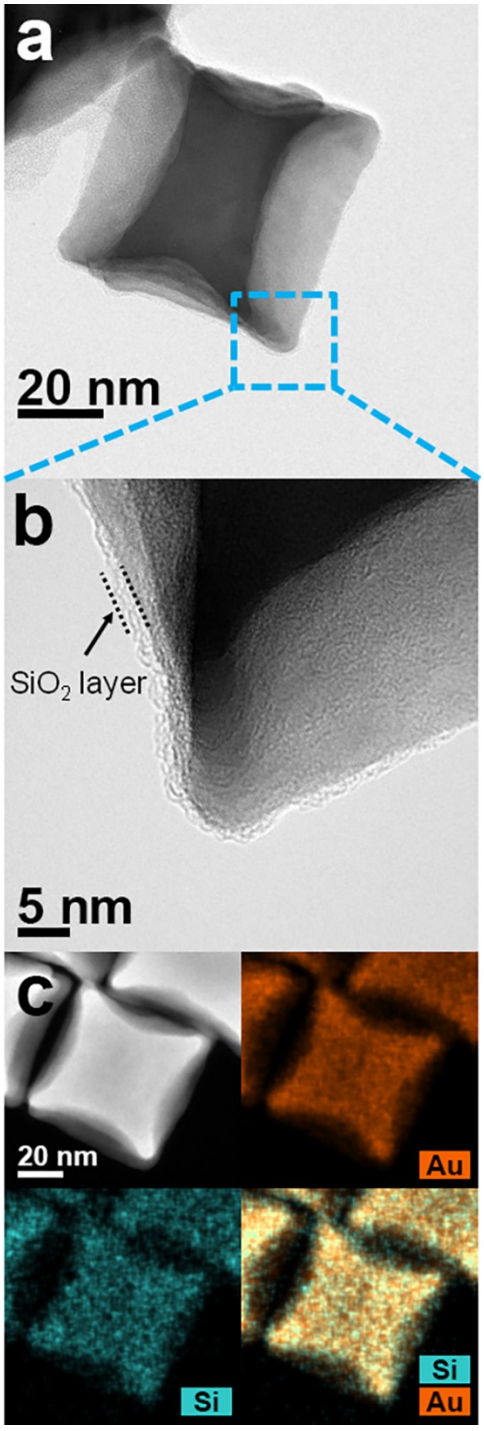

Fig. S16 (a) TEM image of Au_{CNC}@SiO_2 core-shell NCs. (b) HRTEM image of blue square region in part a. (c) HAADF-STEM image and corresponding EDS elemental mapping images of Au_{CNC}@SiO_2 core-shell NCs.

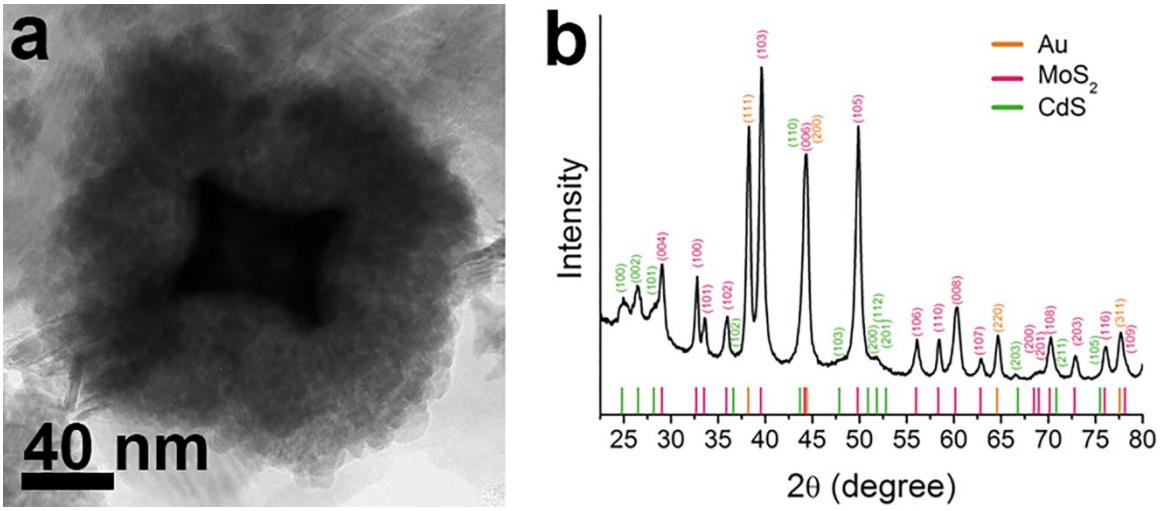

Fig. S17 (a) TEM image and (b) XRD pattern of e-MoS_2-Au_{CNC}-CdS_{thick} hybrids. The positions of Au, MoS_2, and CdS references were taken from the JCPDS database (Au: 04-0784, MoS_2: 37-1492, CdS: 41-1049).