Journal Name

ARTICLE

Supporting Information

Biomolecule-assisted Synthesis of Defect-Mediated $Cd_{1-x}Zn_xS/MoS_2$/Graphene Hollow Spheres for Highly Efficient Hydrogen Evolution

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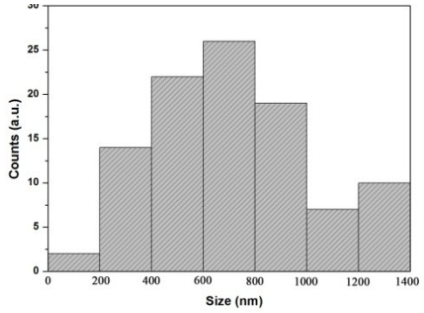

Figure S1. Particle size distribution of $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene hollow spheres.

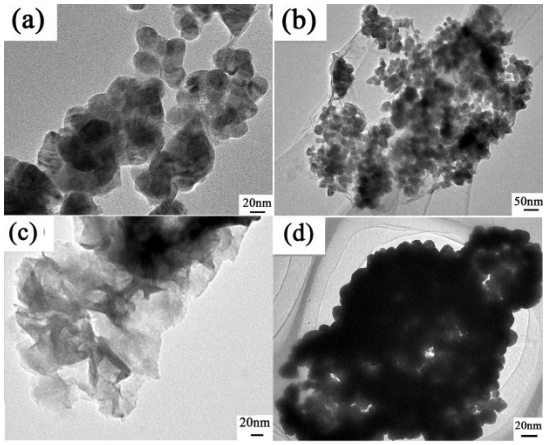

Figure S2. TEM images of (a) blank $Cd_{0.8}Zn_{0.2}S$; (b) $Cd_{0.8}Zn_{0.2}S$/graphene; and (c) MoS_2/graphene composites. (d) $CuInS_2$/ MoS_2/graphene hollow spheres.

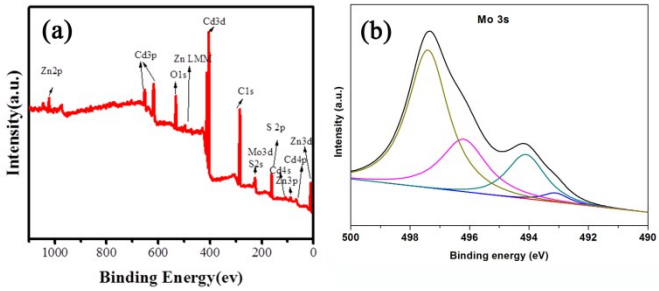

Figure S3. Full XPS spectrum (a) and Mo 3s spectrum (b) of $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene hollow spheres.

Figure S4 shows the high-resolution XPS spectrum and Auger spectrum of $ZnL_3L_{4,5}M_{4,5}$ in $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene hollow spheres. The binding energy of Zn $2p_{3/2}$ and kinetics energy of Auger transition are located at 1022.1 eV and 989 eV, respectively. The Auger parameter, defined as the difference in kinetic energy between an Auger line and a core-level line, is determined to be 2011.1 eV. This value is different from that of metallic Zinc (2013.8 eV), confirming the formation of zinc-based sulfides in the solid solutions.

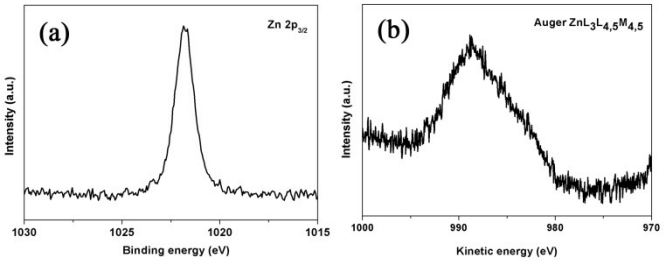

Figure S4. Zn ($L_3M_{45}M_{45}$) Auger spectra of $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene

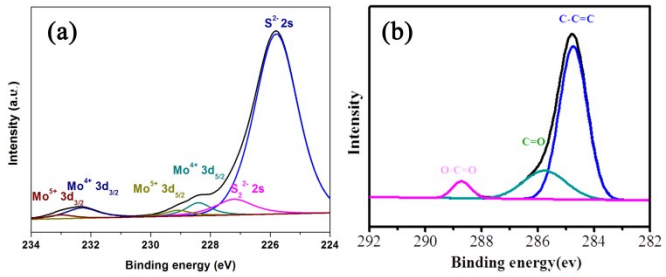

Figure S5. (a) S 2s spectrum and C 1s spectrum (b) of $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene hollow spheres.

To further determine the chemical structures, Raman spectroscopy of $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene was studied in Figure S5. The longitudinal optical (LO) phonon peaks of sulfide are seen at about 304 cm^{-1}, 608 cm^{-1} (second order) and 924 cm^{-1} (third order) for the $Cd_{0.8}Zn_{0.2}S$. The peak at 1338 cm^{-1} (D band) is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The peak at 1588 cm^{-1} (G band) corresponds to the vibration of sp2-bonded carbon atoms in a hexagonal lattce. The small peak intensity ratio of I(D)/I(G) indicates the presence of graphene with restored structures in the composites.

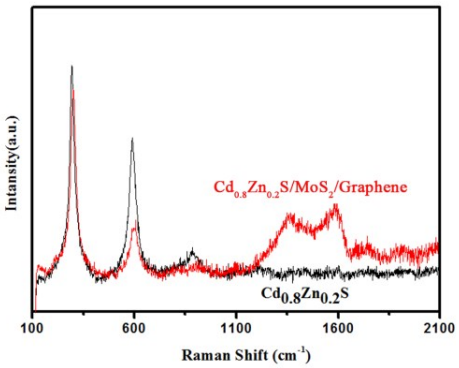

Figure S6. Raman spectra of $Cd_{0.8}Zn_{0.2}S$ nanoparticles and $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene hollow spheres.

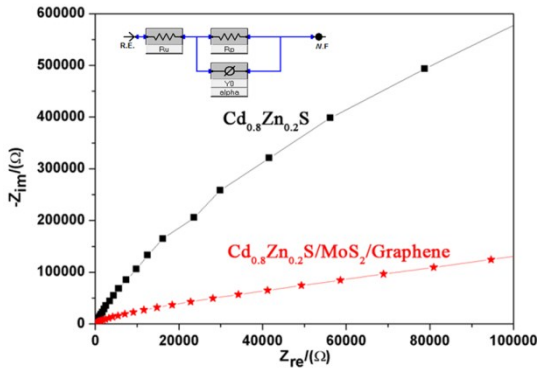

Figure S7. Electrochemical impedance spectra (EIS) of $Cd_{0.8}Zn_{0.2}S$ nanoparticles and $Cd_{0.8}Zn_{0.2}S/MoS_2$/graphene hollow spheres. Inset is the equivalent circuit.