

Supplementary Information for

Matching and adjusting energy band structures of Pd-modified sulphides (ZnS, In₂S₃ and CuS) and improving the photocatalytic activity of CO₂ photoreduction

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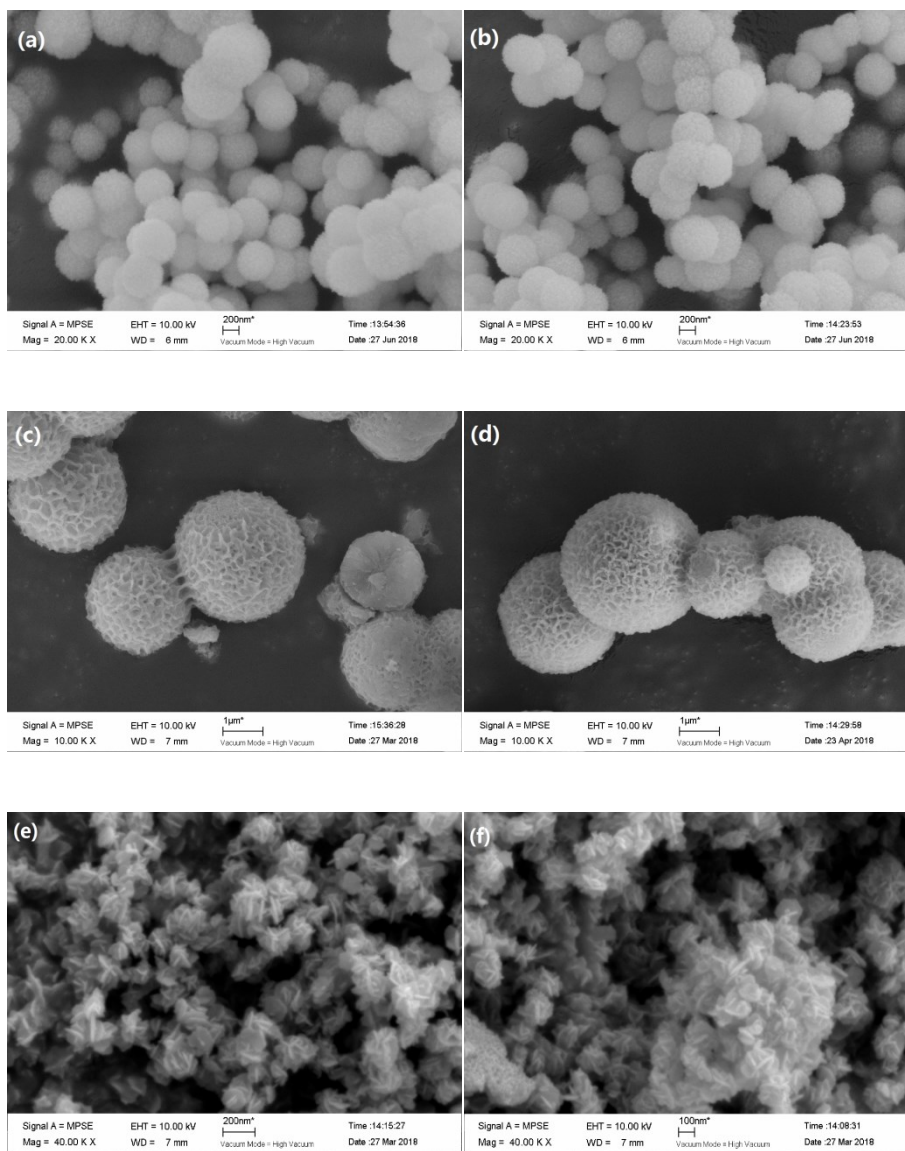


Fig. S1. SEM images of (a) ZnS, (b) ZnS-Pd1.5%, (c) In₂S₃, (d) In₂S₃-Pd1.5%, (e) CuS and (f) CuS-Pd1.5% samples.

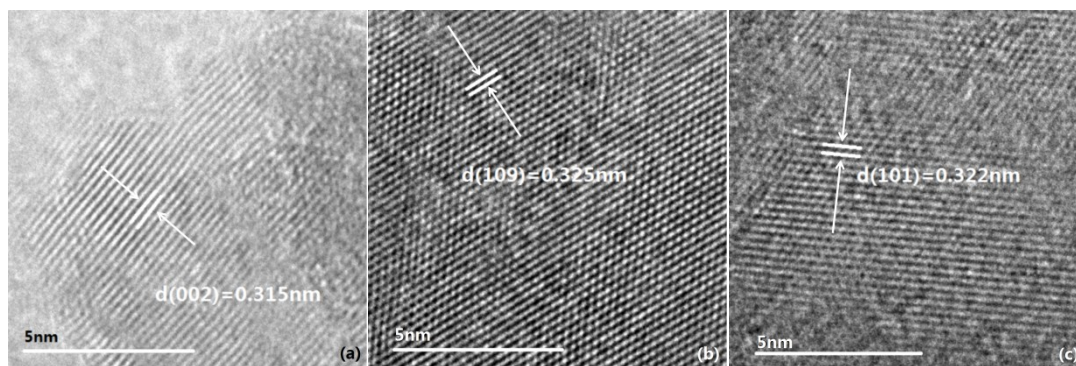


Fig. S2. TEM images of (a) ZnS, (b) In_2S_3 and (c) CuS samples.

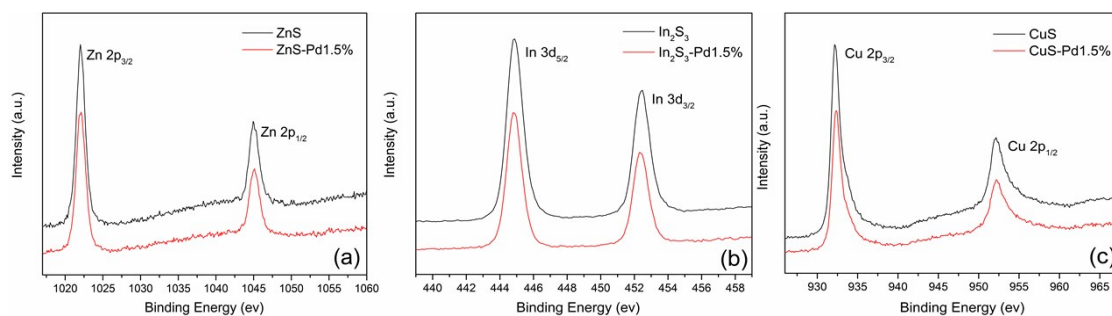


Fig. S3. (a) Zn2p XPS spectra of ZnS and ZnS-Pd1.5% samples. (b) In3d XPS spectra of In_2S_3 and In_2S_3 -Pd1.5% samples. (c) Cu2p XPS spectra of CuS and CuS-Pd1.5% samples.

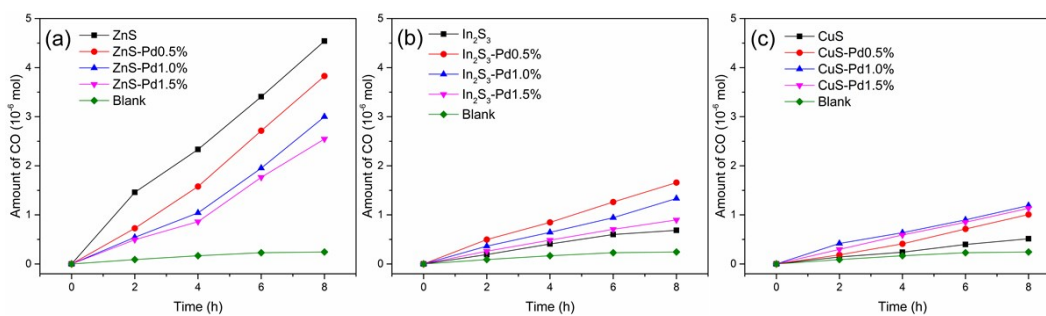


Fig. S4. Photocatalytic activity of (a) ZnS, ZnS-PdX%, (b) In_2S_3 , In_2S_3 -PdX% and (c) CuS, CuS-PdX% on the reduction of CO_2 into CO under UV light irradiation for 8 h.

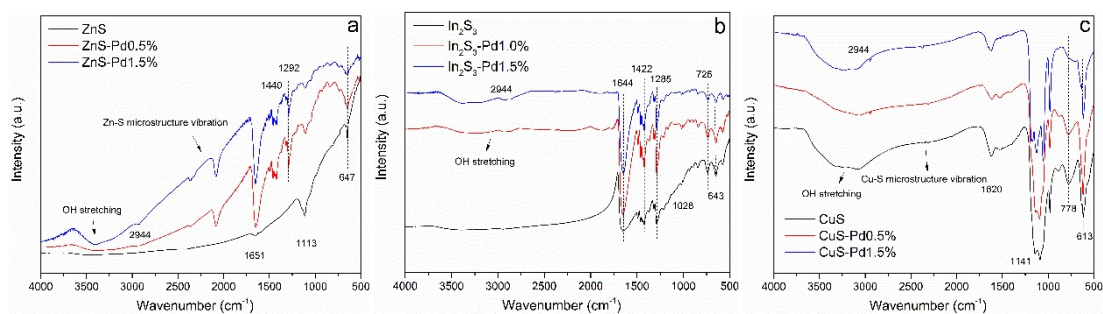


Fig. S5. FTIR spectra of (a) pure ZnS, ZnS–Pd0.5% and ZnS–Pd1.5% samples; (b) pure In_2S_3 , In_2S_3 –Pd0.5% and In_2S_3 –Pd1.5% samples; (c) pure CuS, CuS–Pd0.5% and CuS–Pd1.5% samples.

In order to better study the surface species, structure and chemical bond of samples, the FTIR spectra of the samples in the frequency range 500–4000 cm^{-1} were shown in Fig. S5. It was obvious that the FTIR spectra of Pd modified sulphide samples showed peaks similar to that of the pure sulphide samples. In Figure S5(a), the characteristic ZnS vibration peaks can be noticed around the bands of 1113 cm^{-1} and 647 cm^{-1} . And the broad band of about 2500–3300 cm^{-1} corresponded to the stretching vibration of O-H, indicating the presence of water molecules adsorbed on the surface of photocatalysts. With the increase of Pd modification, the adsorption capacity of the photocatalysts to water molecules increases gradually. The band around 1700–2500 cm^{-1} may be due to the microstructure formation of the sample. For Pd modified ZnS samples, the splitting into two new bands at 2944 cm^{-1} was due to the surface species of Pd. The bands around 1292 cm^{-1} , 1440 cm^{-1} , and 1651 cm^{-1} can be attributed to C=O symmetric and asymmetric stretching modes, which were caused by the absorption of atmospheric carbon dioxide by the photocatalyst surface. In Figure S5(b), the characteristic In_2S_3 vibration peaks can be noticed around the bands of 643 cm^{-1} , 726 cm^{-1} and 1028 cm^{-1} . And the peaks from 3500 to 2600 cm^{-1} are corresponding to the O-H stretch vibration of H_2O , and the peaks at 1644 cm^{-1} , 1422 cm^{-1} and 1285 cm^{-1} are corresponding to the C=O stretch vibration of CO_2 absorbed in the sample. For Pd modified In_2S_3 samples, the splitting into two new bands at 2944 cm^{-1} was due to the surface species of Pd. In Figure S5(c), three peaks at 613, 778 and 1141 cm^{-1} were observed. The weak transmittance peaks are attributed at 613 and 778 cm^{-1} due to metal sulfide stretching vibration corresponding to CuS. The other one IR peak appeared at 1141 cm^{-1} is owing to stretching frequency of C=C and C=S. The broad peak at 3050 to 3650 cm^{-1} is attributed to the stretching vibration of OH bond. The narrow peak observed at 1620 cm^{-1} is attributed to asymmetric and symmetric stretching vibrations of O–C–O bonds. The band around 2334 cm^{-1} may be due to the microstructure formation of the sample. For Pd

modified CuS samples, the new peak at 2944 cm^{-1} was due to the surface species of Pd.

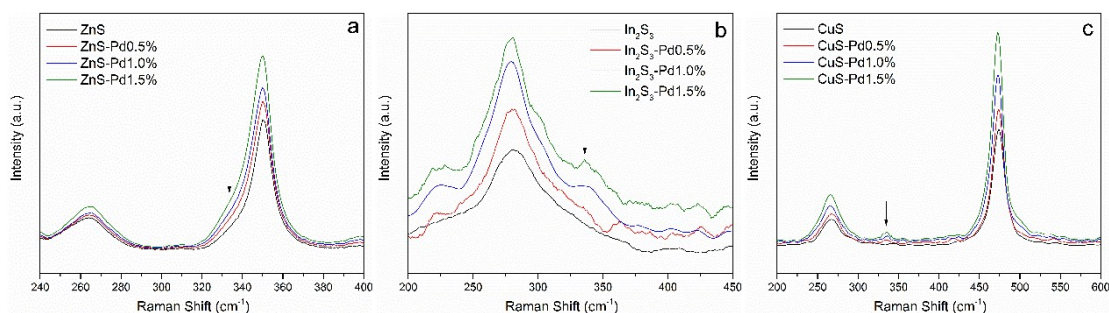


Fig. S6. Raman spectra of (a) pure ZnS, ZnS–Pd0.5%, ZnS–Pd1.0%, and ZnS–Pd1.5% samples; (b) pure In_2S_3 , In_2S_3 –Pd0.5%, In_2S_3 –Pd1.0%, and In_2S_3 –Pd1.5% samples; (c) pure CuS, CuS–Pd0.5%, CuS–Pd1.0%, and CuS–Pd1.5% samples.

The existence of surface active species S-Pd-S was further confirmed by Raman spectra. Raman spectra were taken on a Horiba Scientific LabRAM HR Evolution by using the 532 nm line of 532 semiconductor laser. Raman spectra of pure sulphide and Pd modified sulphide are plotted in Figure S6, to further investigate the structure of the obtained samples. In Figure S6(a), The LO and TO phonon modes from these ZnS-Pd samples were observed at 350, and 265 cm^{-1} , respectively, consistent with observations for pure ZnS. In Figure S6(b), The high-energy polarized Raman peak at 280 cm^{-1} can be clearly ascribed to the A_{1g} mode, and the peaks occurring at 225 cm^{-1} corresponds to E_g mode of In_2S_3 . In Figure S6(c), a primary sharp and intense peak at the frequency of 473 cm^{-1} , and a relatively wide peak at the frequency of 264 cm^{-1} were observed. The former sharp band in the high frequency region is ascribed to the S-S stretching vibrational mode, while the latter broader band corresponds to the lattice vibrational A_{1g} TO mode.

Compared with pure sulphide, no shift of Raman peaks is detected for Pd modified sulphide samples, implying that the Pd ions are not weaved into ZnS, In_2S_3 and CuS lattice and might exist on the surface as some kind of species. In addition, a new Raman peaks at about 334 cm^{-1} in Pd modified sulphide samples is observed, ascribed to stretching modes of S–Pd bonds on surface.