Supporting information

Synthesis of Amino functionalized Ti-MOF derived Yolk-Shell and Hollow heterostructures for enhanced Photocatalytic Hydrogen Production under visible light.

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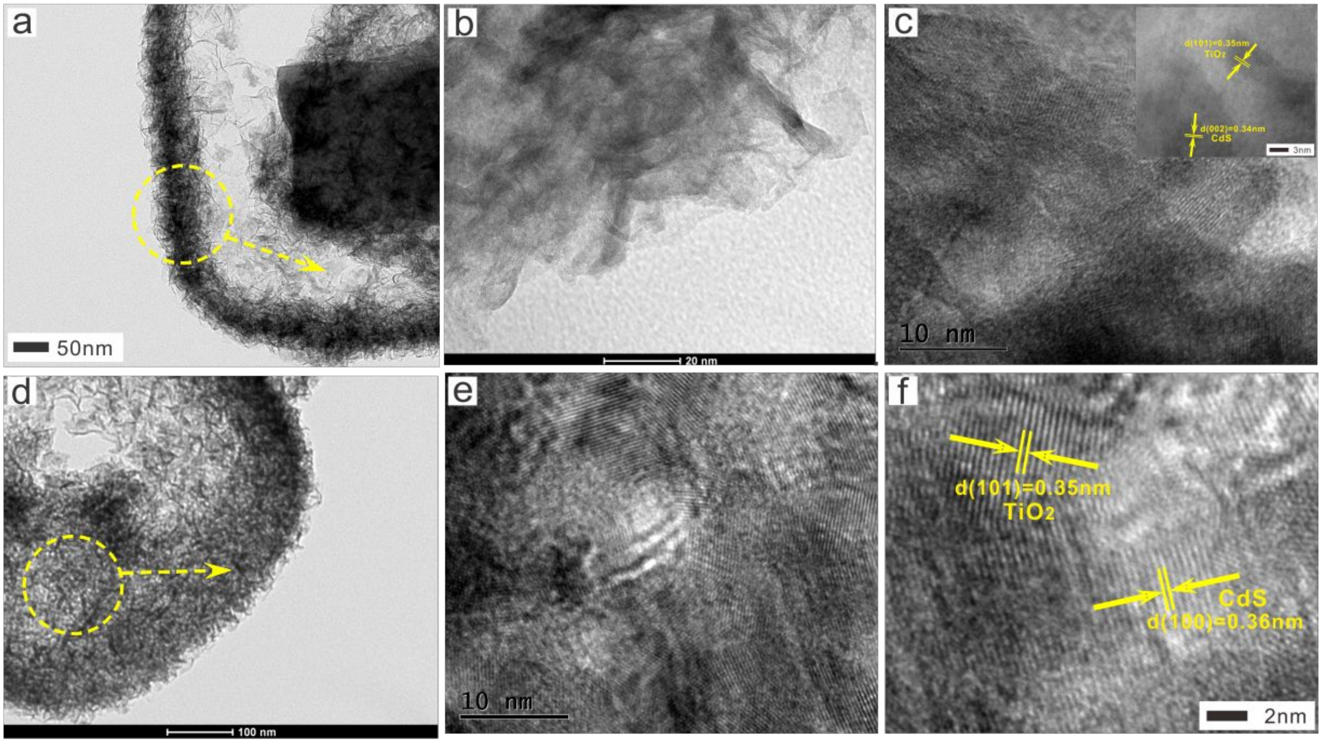

Fig. S.1. HRTEM image of (a-c) NH_2-MIL-125/TiO_2/CdS (30) (d-f) H-TiO_2/CdS (30).

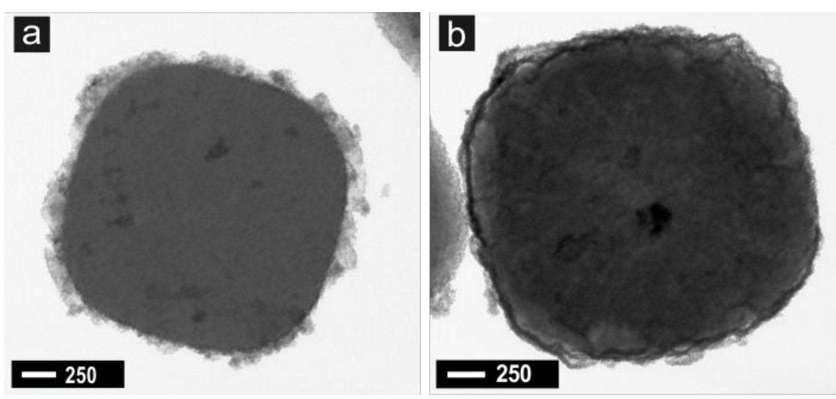

Fig.S.2. (a) MOF stability in ethanol at 70 ℃ (2) MOF stability in methanol at 70℃.

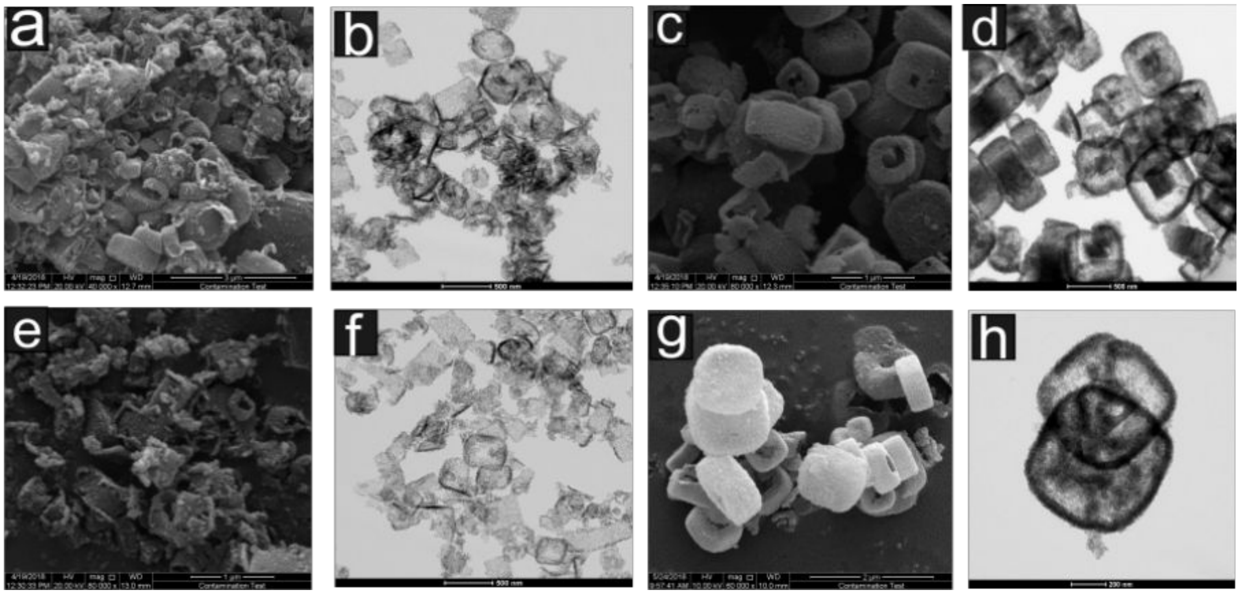

Fig.S.3. (a-b) SEM and TEM images of NH_2-MIL-125-thioacetamide (TAA) for one-hour (c-d) NH_2-MIL-125 +TAA+(Cd $(CH_3COO)_2.2H_2O$) (e-f) NH_2-MIL-125 +TAA for two-hours. (g-h) NH_2-MIL-125 +TAA+(Cd $(CH_3COO)_2.2H_2O$) for two-hours.

Table S1. CdS amount of heterostructures by ICP-MS analysis.

Samples	**Wt % (ICP-MS)**	
	Cd	**S**
NH_2-MIL-125/TiO_2/CdS (30)	18.575	3.601
H-TiO_2/CdS (30)	27.257	5.933

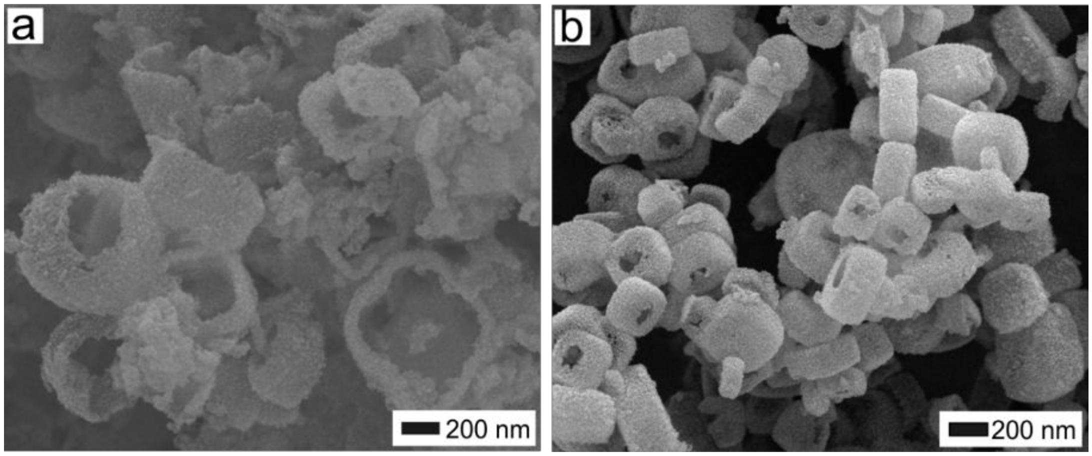

Fig.S.4. (a) SEM image of MOF +$CdCl_2.5H_2O$ + TAA (b) SEM image of MOF + $CH_3COO)_2.2H_2O)$ +TAA.

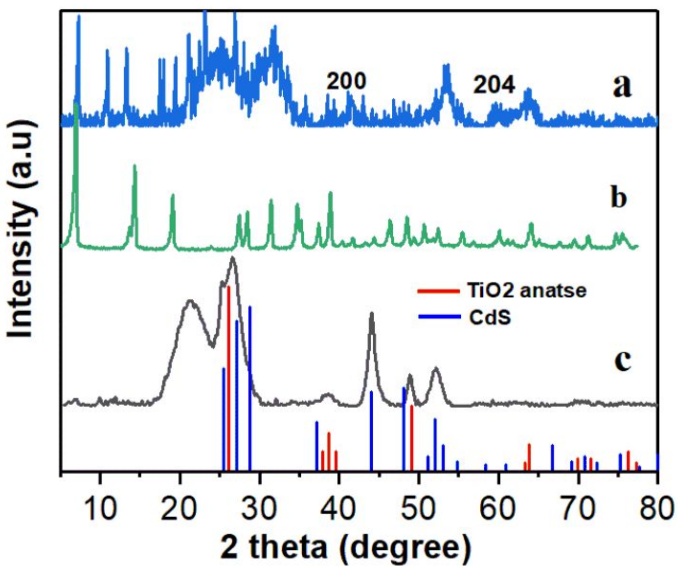

Fig.S. 5. XRD spectra of (a) NH_2-MIL-125/TiO_2/CdS (30) (b) NH_2-MIL-125 (c) H-TiO_2/CdS (30).

XPS spectral annalysis of H-TiO_2/CdS(30).

In the XPS spectrum of H-TiO_2/CdS, the high-resolution Ti 2p spectrum shows two distinct peaks at 464.6 eV and 458.8 eV binding energy values, respectively, indicating that titanium binded with oxygen remained in the oxidation state of IV for the titanium oxo cluster[1]. The Cd 3d spectrum consists of two distinct peaks at 411.61 eV ($3d_{3/2}$) and 404.86 eV (Cd $3d_{5/2}$) with a splitting energy of 6.7 eV, indiacting the successful formation of CdS nanoparticles in the heterostructure.[2] Moreover the binding energies correspond to $S2p_{3/2}$ and S $2p_{1/2}$ are at 161.2eV and 162.36 eV indicating the presence of -2 S in CdS nanoparticles[3].

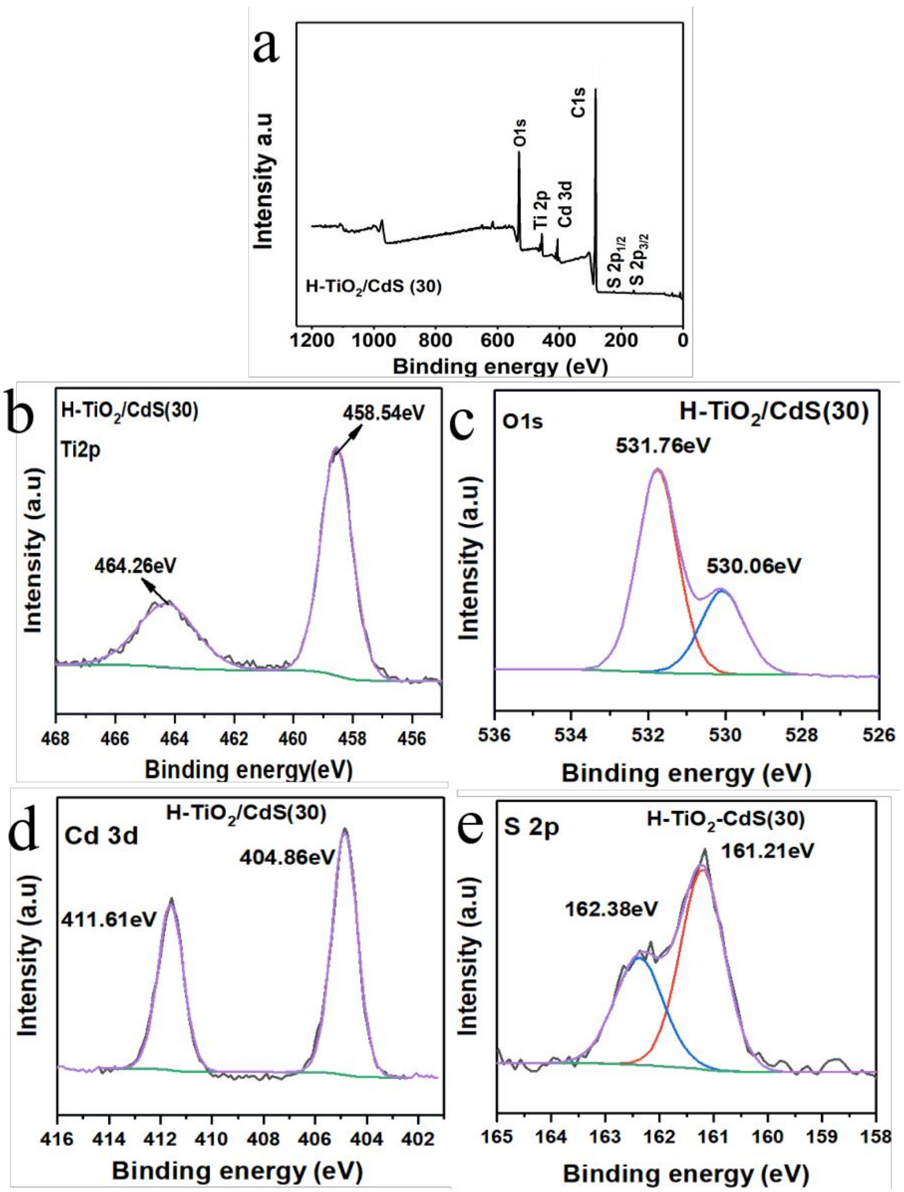

Fig. S.6. XPS spectra of H-TiO_2/CdS (30).

Electrochemical impedance spectroscopy.

The photoinduced charge separation and transfer were further evaluated by electrochemical impedance spectroscopy (EIS). For comparison purposes, NH_2-MIL-125 derived heterostructures (NH_2-MIL-125/TiO_2 and hollow TiO_2 without CdS nanoparticles were prepared by the Bingxing Zhang method [4], followed by measuring their EIS spectra. The experimental results shown in Figure S.7, revealed that with the addition of CdS nanoparticles, the photocatalytic activity MOF derived heterostructures increases.

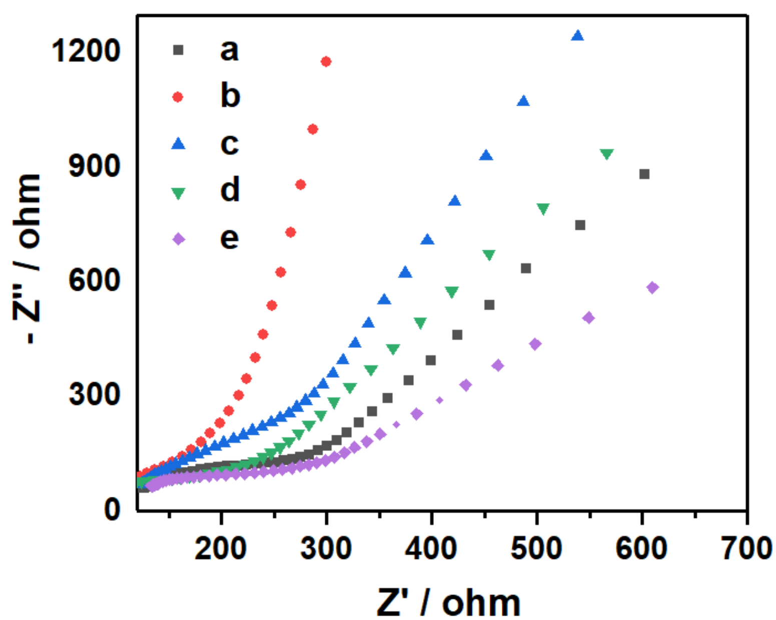

Fig. S.7. Nyquist plots of (a)H-TiO_2/CdS (30) (b) MOF derived hollow TiO_2 (no CdS) (c) NH_2-MIL-125 (d) NH_2-MIL-125@TiO_2 (e) NH_2-MIL-125/TiO_2/CdS (30).

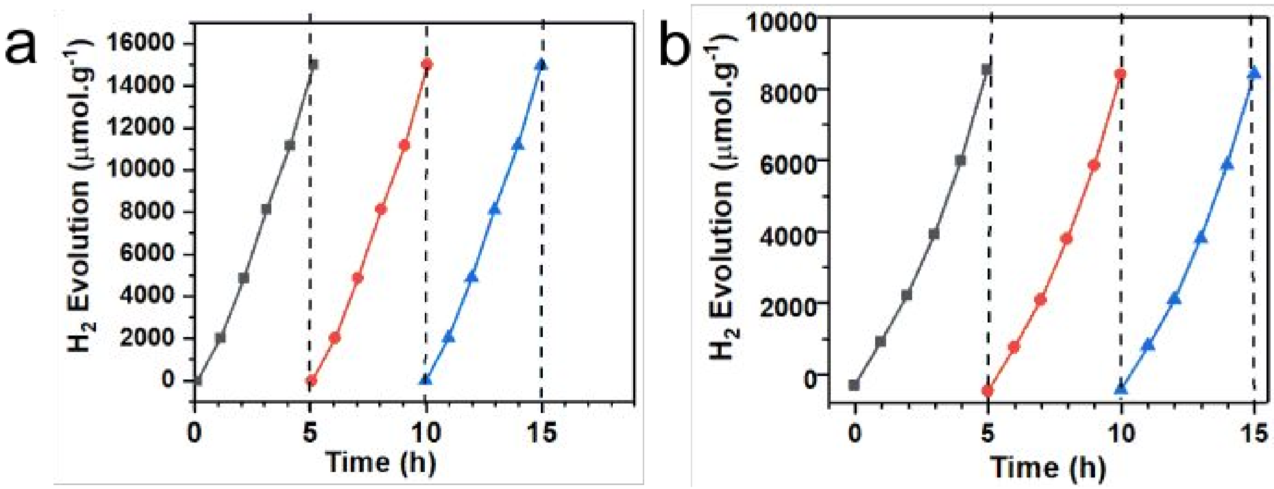

Fig. S.8. recycling test for H_2 production of (a) NH_2-MIL-125/TiO_2/CdS (30), (b) H-TiO_2/CdS(30)

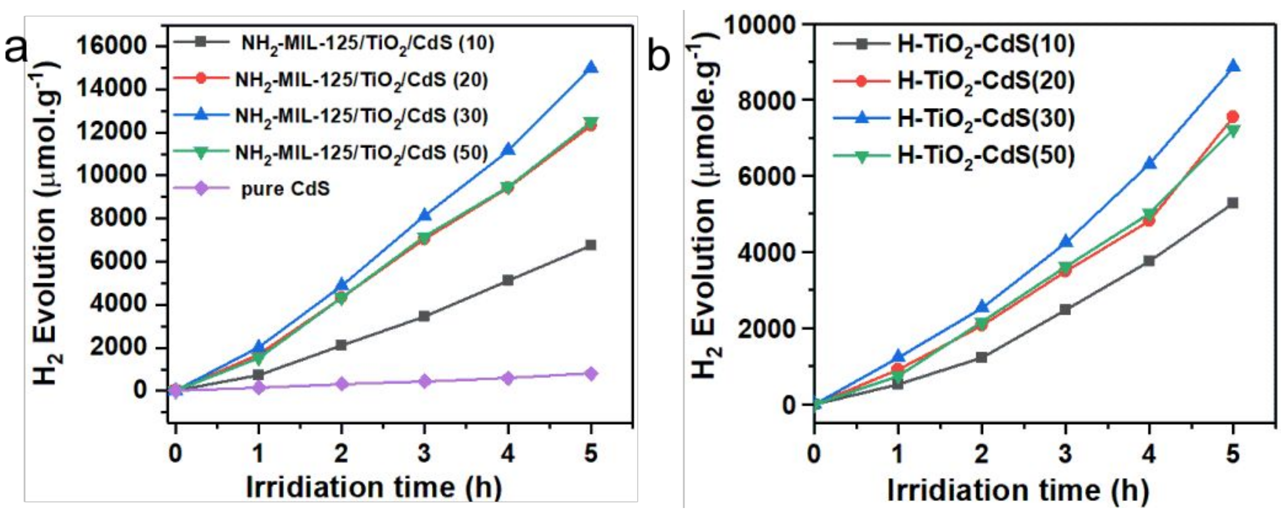

Fig. S.9. Photocatalytic H_2 evolution of various yolk-shell and hollow heterostructures with respect to time (a) NH_2-MIL-125/TiO_2/CdS (x) (b) H-TiO_2/CdS(x).

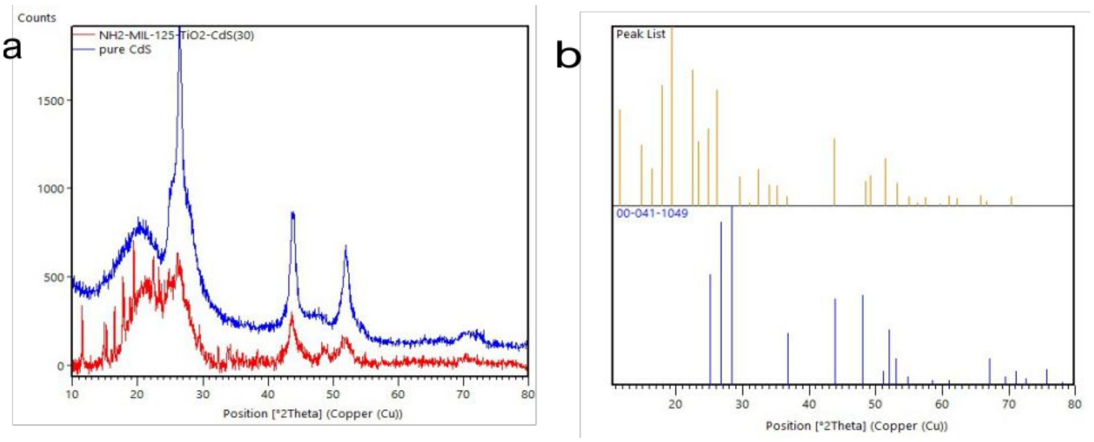

Fig.S.10 (a-b) XRD patterns of NH_2-MIL-125/TiO_2/CdS(30) with reference.

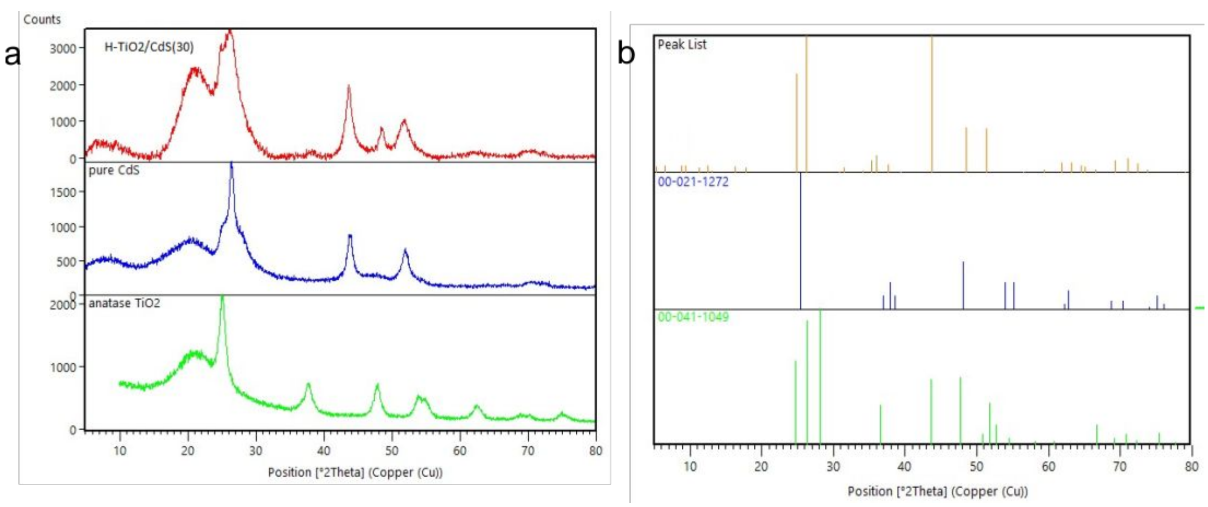

Fig.S.11.(a-b) XRD patterns of H-TiO_2/CdS(30) with reference.

References

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