

*Supporting Information*

**Integration of Aminopyridine Derived Cobalt based Homogenous  
Cocatalyst with a Composite Photocatalyst to the Promote the H<sub>2</sub>  
Evolution from Water**

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## Experimental details

### Materials

All the reagents and chemicals used in this study such as 2-aminopyridine, 2-amino-6-methylpyridine, cobalt acetate ( $\text{Co}(\text{C}_4\text{H}_6\text{O}_4, 98\%)$ ), nickel acetylacetonate ( $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2, 98\%$ ), cadmium chloride hemipentahydrate ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}, 99.0\%$ ), oleylamine ( $\text{C}_{18}\text{H}_{37}\text{N}, 98\%$ ), Thiourea ( $\text{CH}_4\text{N}_2\text{S}, 99.0\%$ ), cobalt (II) acetate tetrahydrate ( $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}, 99.0\%$ ), sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}, 99.0\%$ ) and anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_3, 99.0\%$ ), were directly purchased from the Adamas or Aldrich with analytical grade purity and used without any further purification.

### Synthesis of cocatalysts and photocatalysts

Cobalt-based molecular cocatalysts were prepared according to previous studies.<sup>1,2</sup> Initially, ligands **P1** {2-((pyridin-2-ylimino)methyl)phenol} and **P2** {2-(((6-methylpyridin-2-yl)imino)methyl)phenol} were synthesized in two 50 mL flasks. Amino compounds (10 mmol) were dissolved in 10 mL ethanol, separately. The solutions were heated to 50 °C and 10 mL ethanolic solution of salicylaldehyde (10 mmol) was added dropwise to each flask. The temperature was increased to 70 °C and the final solutions were refluxed for 2 hours. The products were filtered, washed with ethanol and dried under vacuum at 60 °C. **P1** yield: 85%. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  13.05 (s, 1H), 9.48 (s, 1H), 8.53 (d,  $J = 5.6$  Hz, 1H), 7.95 – 7.90 (m, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.46 (t,  $J = 6.5$  Hz, 2H), 7.38 – 7.34 (m, 1H), 7.02 – 6.97 (m, 2H) (Figure S1). **P2** yield: 87%. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  13.15 (s, 1H), 9.46 (s, 1H), 7.80 (d,  $J = 24.5$  Hz, 2H), 7.46 (d,  $J = 17.3$  Hz, 1H), 7.25 (d,  $J = 14.7$  Hz, 2H), 7.00 (d,  $J = 14.7$  Hz, 2H) (Figure S2).

To prepare cobalt complex **PX1**, ligand **P1** (5 mmol) was dissolved in 10 mL ethanol and heated to 70 °C under inert atmosphere. Cobalt acetate (5 mmol) solution was added to hot solution of ligand and refluxed for 2 hours. The dark brown precipitates were separated through filtration and washed with ethanol. Solid mass was dried under vacuum at 60 °C overnight. Yield: 77%.  $\text{CoC}_{24}\text{H}_{18}\text{N}_4\text{O}_2$ : calculated C 63.58, H 4.00, N 12.36; found C 63.69, H 4.07, N 12.42. ESI-MS: 453.21 (Figure S3a). Moreover, **PX2** complex was synthesized using aforementioned procedure for **PX1**. Yield: 72%.  $\text{CoC}_{26}\text{H}_{22}\text{N}_4\text{O}_2$ : calculated C 64.87, H 4.61, N 11.64; found C 65.09, H 4.46, N 11.22. ESI-MS: 481.12 (Figure S3b).

A reported method was followed for CdS NRs synthesis.<sup>3</sup> Thermolysis of the  $\text{Ni}(\text{acac})_2$  in oleylamine and tetraethyleneglycol was done to prepare highly pure  $\text{Ni}_3\text{C}$ .<sup>4</sup> Approximately, 0.5 g of the  $\text{Ni}(\text{acac})_2$  was placed in round bottom flask (100 mL) under inert environment. Then, 40 mL mixed solvent of tetraethyleneglycol and oleylamine (1:1) was added to the flask and heated at 60 °C. A highly transparent and sky-blue colored solution was resulted after 30 min. Furthermore, final solution was heated at 320 °C for 90 min. Centrifugation was performed to collect precipitates and were thoroughly washed with 1-butanol and ethanol solvents, respectively. Finally, the product was kept to dry under vacuum at ambient temperature.

101 mg of the CdS NRs and a calculated amount of  $\text{Ni}_3\text{C}$  was dispersed in 10 mL ethanol to prepare different ratios of CdS/ $\text{Ni}_3\text{C}$  NRs. The flask was purged with Nitrogen ( $\text{N}_2$ ) to remove the absorbed air. While, ultrasonication for 30 min was performed to disperse suspension homogeneously. Meanwhile, sample was dried at 80 °C under high vacuum. The obtained sample was fully grounded in an agate mortar for the 15 min. While, prepared samples having different amounts of  $\text{Ni}_3\text{C}$  were labeled as NC1, NC2, NC3 and NC4. Moreover, similar process was repeated with pure CdS NRs to make comparison. Finally, 1 wt% was loaded on Pt pristine

CdS NRs for CdS/Pt NRs sample preparation using a reported method to compare with present composite photocatalysts.<sup>5</sup>

### **Photocatalytic H<sub>2</sub> production**

The Photocatalytic activities of the CdS/Ni<sub>3</sub>C NRs photocatalysts for production of H<sub>2</sub> were explored in round bottom flask (50 mL) under visible light. For the visible light irradiation, a 300 W Xe lamp equipped with 420 nm cut-off filter was used. The photocatalytic samples were further prepared in 20 mL Millipore water containing 1.0 mg photocatalyst, Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagent. Air was completely removed by swapping pure N<sub>2</sub> gas from flask while, 5 mL methane was added as internal standard reference. Gas chromatography (GC, SP-6890, N<sub>2</sub> as carrier gas) equipped with thermal conductivity detector (TCD) for quantitative analysis of generated H<sub>2</sub>. A 420 nm monochromatic light was used for apparent quantum yields (AQYs) and following equations were used for calculations:

$$\begin{aligned} AQY (\%) &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \quad (1) \end{aligned}$$

### **Photoelectrochemical studies**

Photocurrent performance of the resulted samples was examined using a CHI602E work station (Shanghai Chenhua Instrument Co., Ltd, Shanghai, China). A photocatalyst-coated FTO as a working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode were used to establish a standard three-electrode system. Visible light irradiation was achieved with a 300 W Xe lamp equipped with 420 nm cut-off filter. 15 μL suspensions of CdS and CdS/Ni<sub>3</sub>C NRs (20 mg/mL) were added onto surface of FTO to prepare working electrodes and dried at

ambient temperature. For further measurements, an applied potential of 0 V vs Ag/AgCl was set up by 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as electrolyte.

### **Characterization**

Scanning electron microscopy (SEM) using a JSM-6700F microscope used to study morphologies of resulted samples. Transmission electron microscopy (TEM) and energy-dispersive X-ray analysis (EDX) analysis were achieved on the transmission electron microscope JEM-2010 equipped with a Rontec EDX system and electron diffraction (ED) attached with an acceleration voltage of 200 kV. MS analysis of the metal complexes was carried out on a MALDI-TOF (LTQ-Orbitrap XL) mass spectrometer. XPS studies were performed on an ESCALAB 250 X-ray photoelectron spectrometer. Nickel contents in photocatalysts were determined using ICP-AES (Optima 7300 DV). Powder X-ray diffraction analysis of the synthesized samples was performed on (XRD, D/max-TTR III) using graphite monochromatized Cu K $\alpha$  radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was kept 5° min<sup>-1</sup> from 20° to 80° in 2 $\theta$ . UV-vis diffuse reflectance was measured on a Solid Spec-3700 UV-vis spectrometer. A Perkin-Elmer LS 55 fluorescence spectrometer was used for steady-state photoluminescence (PL) spectra.

**Table S1.** ICP-AES data of CdS/Ni<sub>3</sub>C samples.

Sample	Ni (wt%)/ ICP-AES data
NC1	2.09
NC2	5.20
NC3	11.15
NC4	23.44

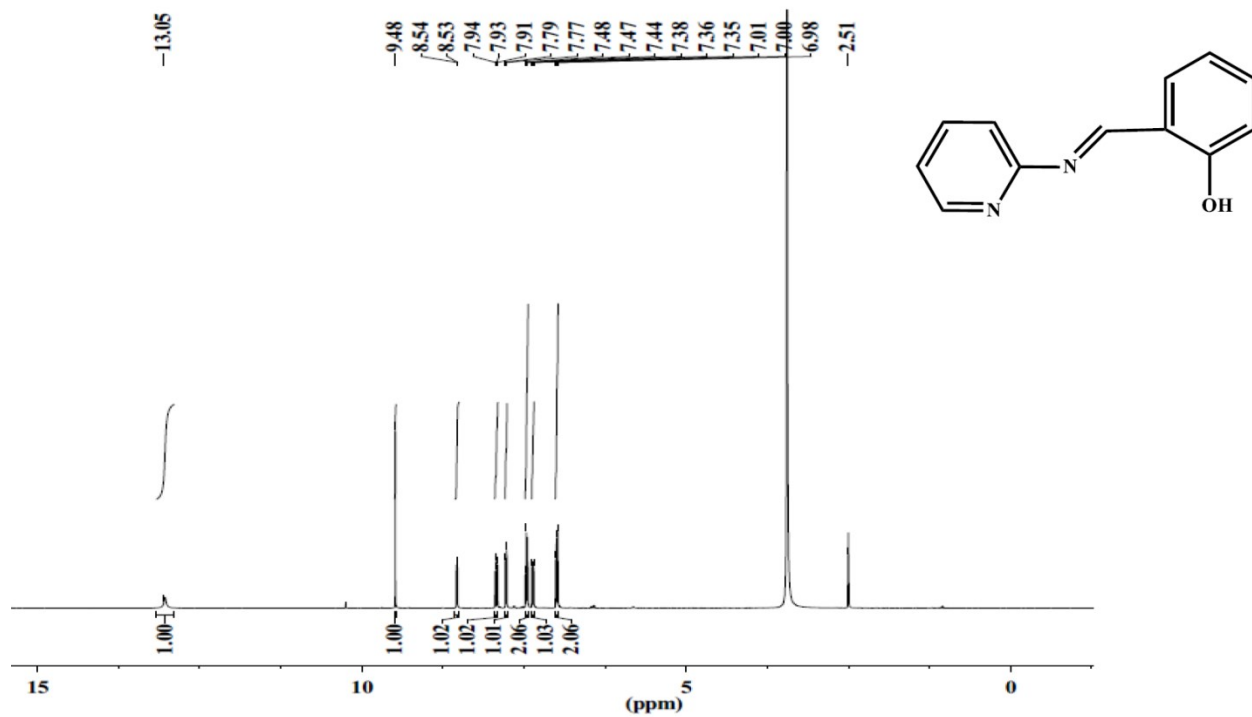


Figure S1. NMR of ligand P1.

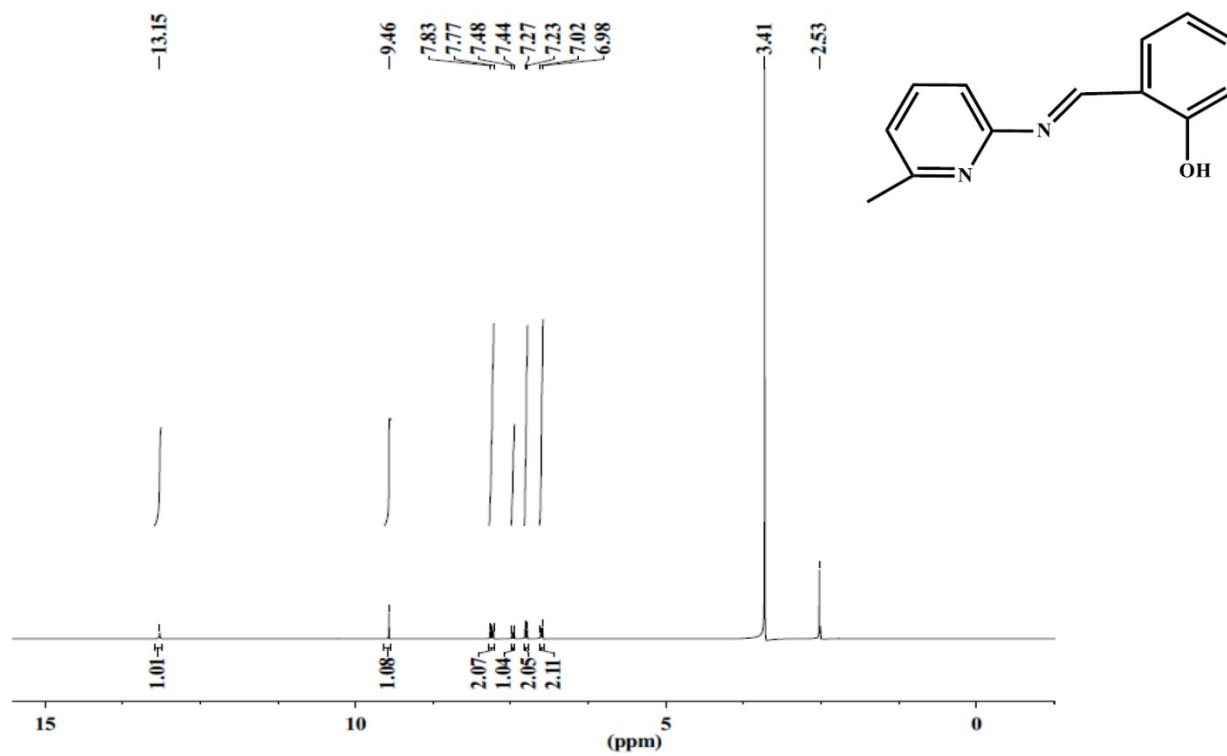
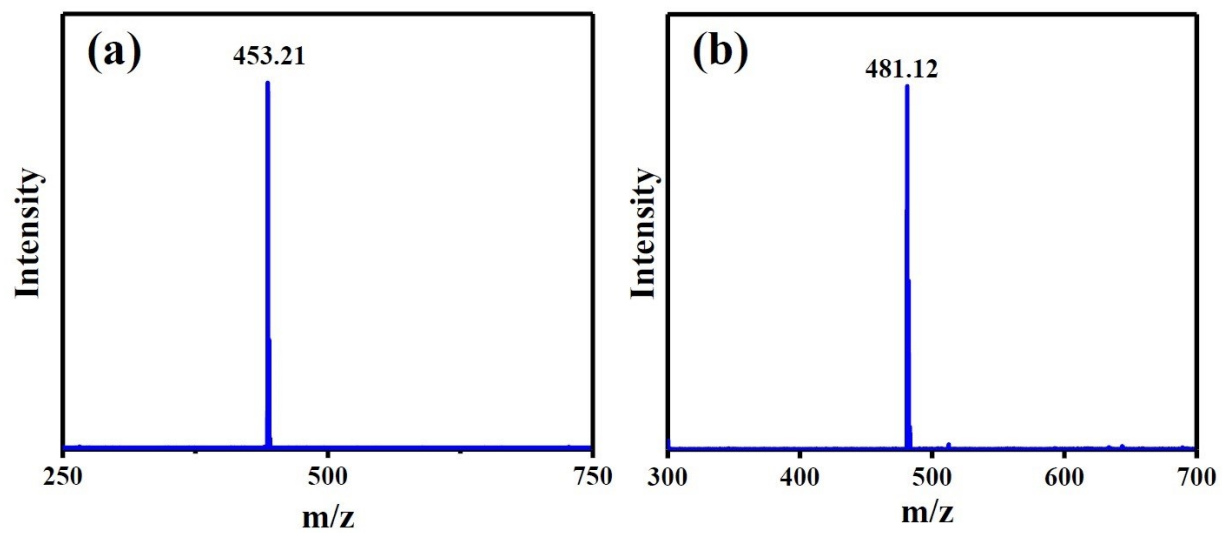
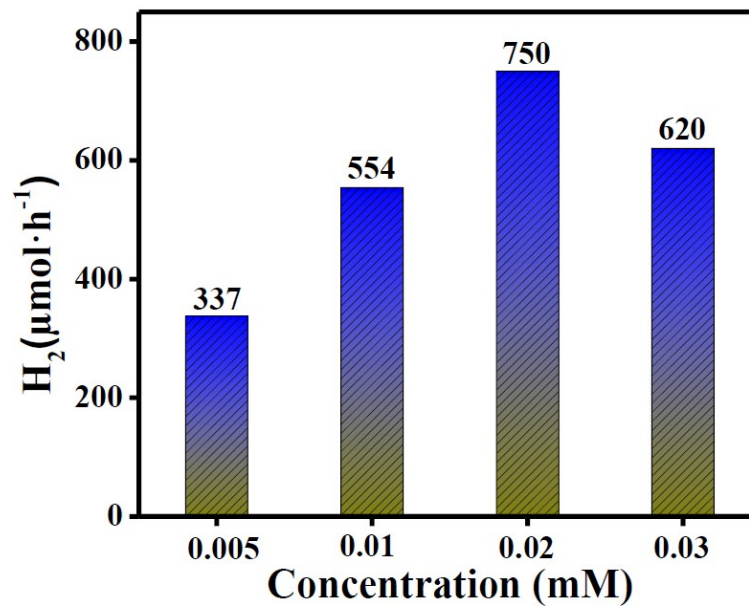


Figure S2. NMR of ligand P2.

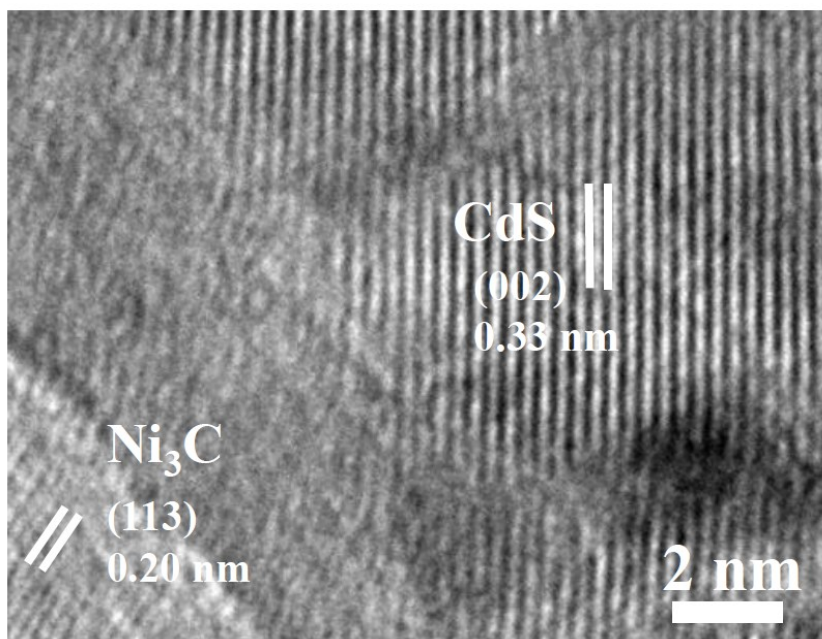




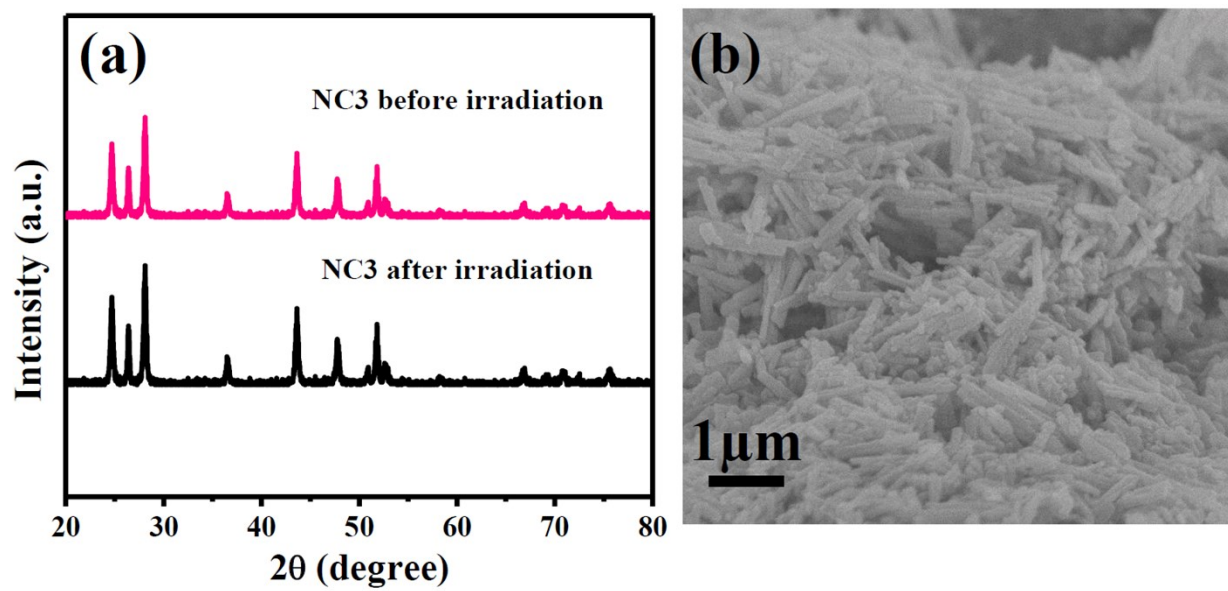
**Figure S3.** MS spectra of **PX1** (a) and **PX2** (b).



**Figure S4.** Effect of concentration of molecular cocatalysts. Photocatalytic samples contained 1.0 mg photocatalyst, 1.0 M Na<sub>2</sub>S and 1.40 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL Millipore water.



**Figure S5.** HRTEM image of NC3.



**Figure S6.** (a) XRD patterns of NC3 before (red plot) and after (black plot) irradiation. (b) SEM image of NC3 after irradiation.

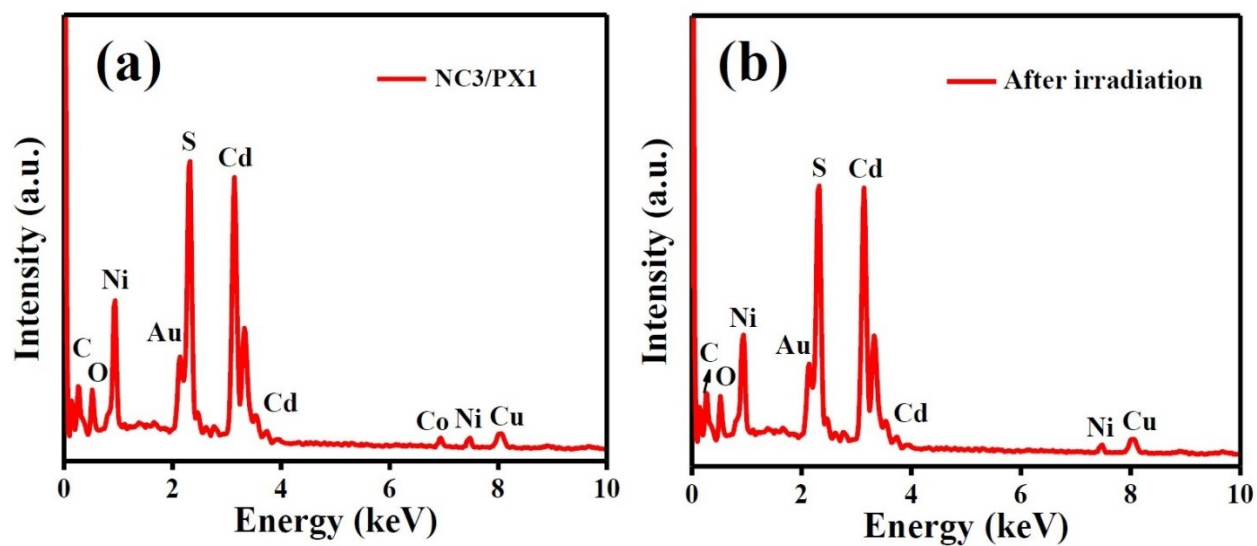
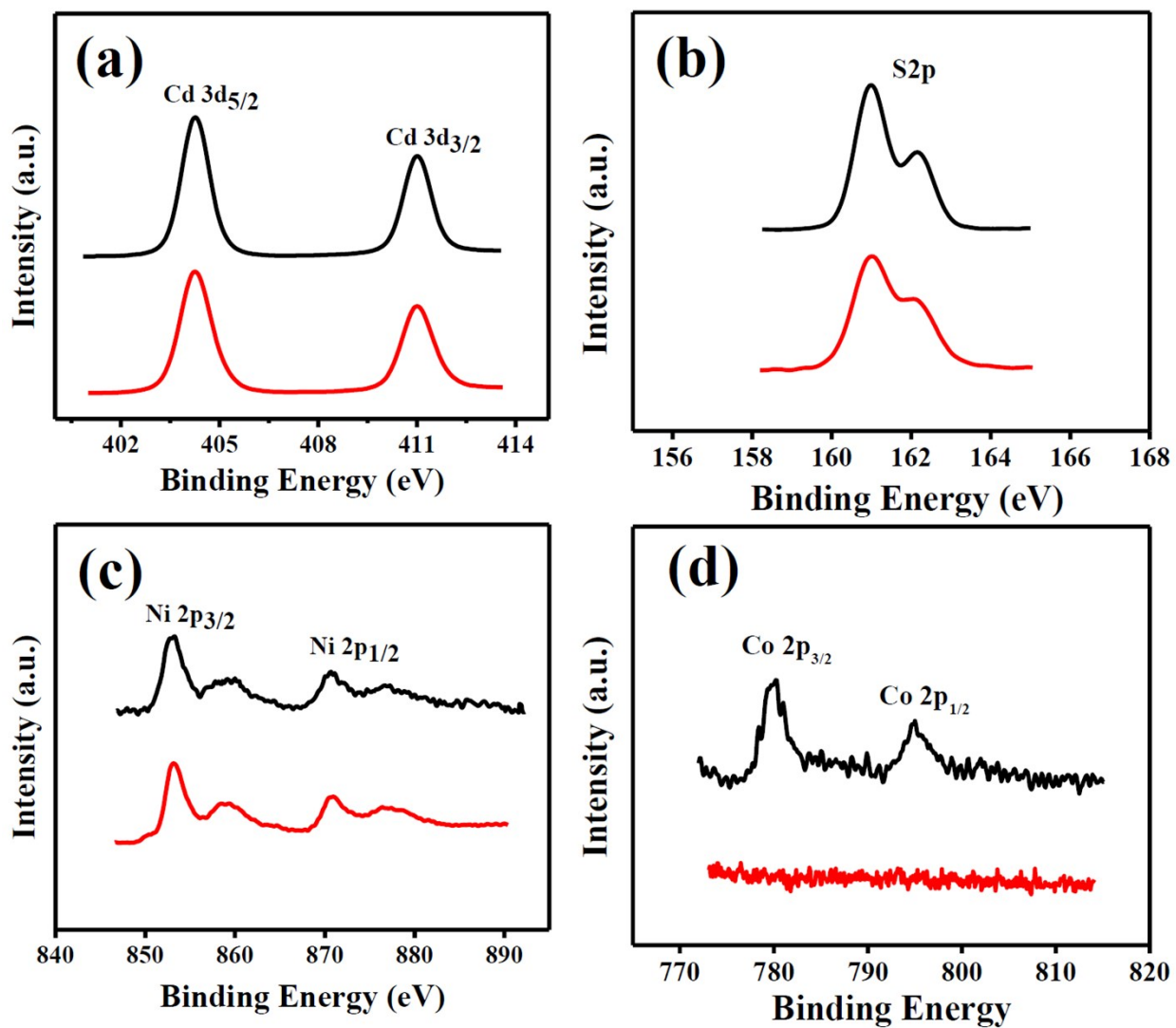
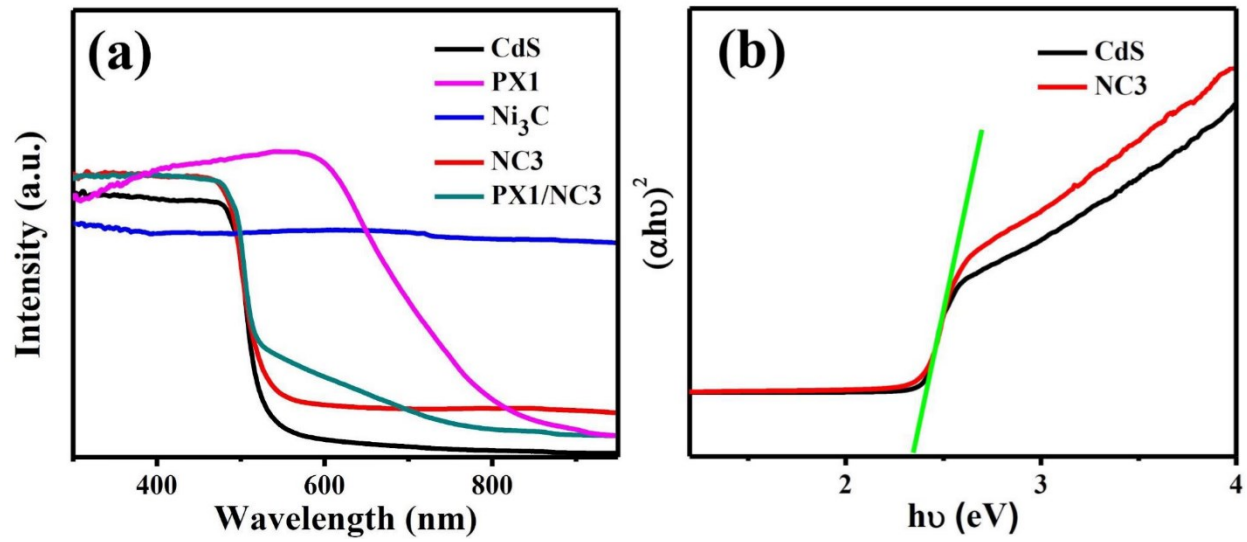


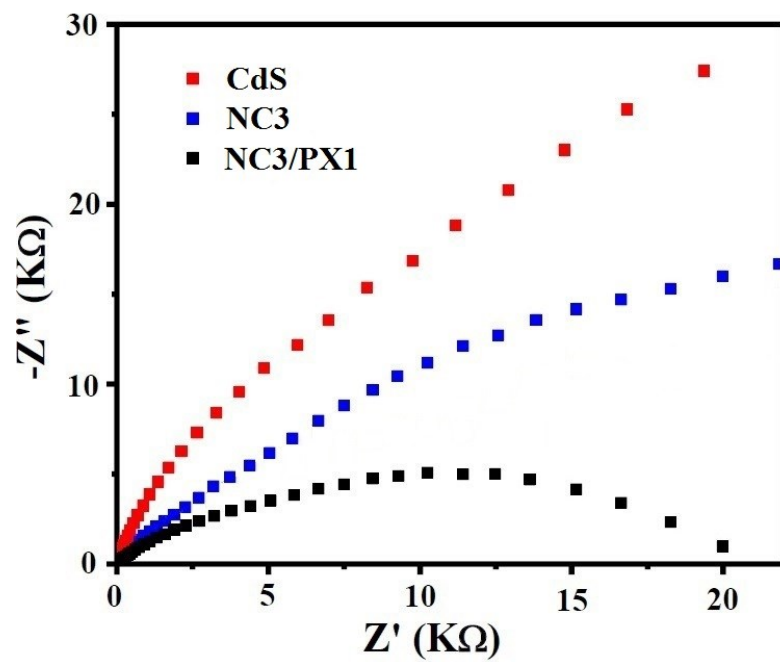
Figure S7. EDX spectrum of NC3 before (a) and (b) after irradiation.



**Figure S8.** (a) High resolution spectra of Cd 3d. (b) High resolution spectra of S 2p. (c) High resolution spectra of Ni 2p. (d) High resolution spectra of Cov 2p Black plot shows before irradiation and red plot shows after irradiation.



**Figure S9.** (a) UV-vis diffuse reflectance absorption spectra of CdS, PX1, Ni<sub>3</sub>C, NC3 and PX1/NC3. (b) Tauc plot of CdS, and NC3.



**Figure S10.** Nyquist plots of CdS, NC3 and NC3/PX1.



## References

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