

Supporting information

Highly Efficient and Noble Metal-Free NiS/CdS Photocatalysts for H₂ Evolution from Water under Visible Light

Wei Zhang,^a Yabo Wang,^a Zhan Wang,^b Ziyi Zhong^b and Rong Xu^{*a}

^a*School of Chemical & Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459*

^b*Institute of Chemical & Engineering Sciences, Agency for Science, Technology and Research, No. 1, Pesek Road, Jurong Island, Singapore 627833.*

* To whom correspondence should be address. Email: rxu@ntu.edu.sg

Experimental details

Synthesis of NiS/CdS photocatalysts. CdS was synthesized according to the literature method¹ except without undergoing the final drying step before the loading of NiS. In a typical synthesis of NiS/CdS photocatalyst, around 0.5 g of CdS (in a wet state, weight estimated on a dry basis), 30 mmol of thiourea (99%, Alfa Aesar) and 75 μ mol of nickel acetate (>99%, Alfa Aesar) were dispersed in 100 mL of deionized water in a Teflon-lined autoclave with 120 mL in capacity. The mixture was subjected to ultrasonication for 2 h followed by hydrothermal treatment at various temperatures for 4 h. The dark green solids were collected by centrifugation and washed with deionized water for several times, followed by drying overnight at 60 °C. Different loading concentrations of NiS were achieved by using different amounts (75-380 μ mol) of nickel acetate precursor during the hydrothermal treatment at 140 °C, while keeping other conditions the same. The loading of CoS, CuS and Ag₂S was performed with the same procedure using cobalt nitrate (>99%, cobalt nitrate hexahydrate, Fluka Chemika), copper acetate (99.999%, Alfa Aesar) and silver acetate (99%, Alfa Aesar) precursors, respectively.

Photocatalytic activity measurement. Visible light driven H₂ evolution reactions were conducted in a closed gas circulation and evacuation system fitted with a top window Pyrex cell. In each run, 0.3 g of the as-prepared photocatalyst was well dispersed with constant stirring in a 100 mL of aqueous solution containing 30 vol% of L-(+)-lactic acid (85-90% aqueous solution, Alfa Aesar). Deposition of 1 wt% of Pt co-catalyst for the generation of Pt/CdS photocatalyst was carried out using an in-situ reduction method according to the literature method.¹ The photocatalytic water splitting was carried out using a 300 W Xenon lamp equipped with a cut-off filter ($\lambda > 420$ nm). The reaction cell was kept at room temperature with cooling water. The produced H₂ was detected using an online gas chromatography. The activities were calculated based on the H₂ evolution in the first 5 h reaction. The quantum efficiency (QE) was measured under the same reaction conditions except a band pass interference filter (Newport, centre wavelength 420 nm, band width 10 nm) was equipped to provide photons with wavelength between 415 and 425 nm. The number of photons from irradiation was measured using a photodiode. The following equation was used to calculate the QE.

$$\text{QE} = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\%$$

Materials characterization. The powder X-ray diffraction (XRD) pattern was recorded in a Bruker AXS D8 X-ray diffractometer with Cu K α ($\lambda = 1.5406$ Å) radiation at 40 kV and 20 mA. The UV-visible diffuse reflectance spectra (DRS) were obtained from an UV-visible spectrophotometer (UV-2450, Shimadzu). The morphology, particle size, lattice fringes and Energy-filtered TEM analysis was performed on a TEM (JEOL 2010) equipped with a Gatan imaging filter. The High-Angle Annular Dark Field Scanning-TEM (HAADF-STEM) studies, energy dispersive X-ray spectroscopy (EDX) scan and line scan were carried out on a FEI Titan 80-300 electron microscope operated at 300 kV, which is equipped with an electron beam monochromator, an EDX and a Gatan electron

energy loss spectrometer. The probing electron beam size of EDX measurement was around 0.3 nm with the dwell time of 20 seconds. Elemental profile was obtained by recording EDX spectrum at 2 nm steps along 50 nm line on one particle. The metal compositions in the photocatalysts were measured using inductively coupled plasma (ICP) optical emission spectroscopy in a Perkin Elmer ICP Optima 2000DV. Energy-filtered TEM analysis was performed on a TEM (JEOL 3010) equipped with a Gatan imaging filter to obtain elemental maps.

To investigate the oxidation products in the reaction solution, electrospray ionization-mass spectrometry (ESI-MS) and attenuated total reflectance (ATR) techniques were used to analyze the reaction solutions. The solution after 24 h reaction was subjected to the ESI-MS analysis, and standard solution containing lactic acid and pyruvic acid at a mole ratio of 13.6:1 (based on theoretical conversion of lactic acid to pyruvic acid) was also examined for comparison. Mass spectra were recorded on a Thermo Finnigan LCQ Deca XP Max (San Jose, CA) ultra high sensitivity quadrupole ion trap mass spectrometer fitted with Surveyor LC Auto Sampler and MS Pump. Acquisition mass range was typically with m/z 15-200. Data were recorded and processed using X-Calibur software (Thermo Scientific, MA, USA). ATR-IR was conducted on a Perkin-Elmer Spectrum One FTIR Spectrometer from using the reaction solutions before and after reaction of 24 h. The ATR crystal was fully covered by the solution during the analysis.

Ref 1: H. J. Yan, J. H. Yang, G. J. Ma, G. P. Wu, X. Zong, Z. B. Lei, J. Y. Shi and C. Li, *J. Catal.* 2009, **266**, 165.

Table S1. Photocatalytic activities of NiS(1.2mol%)/CdS with the reaction conducted using cut-off filters at different wavelengths

Cut-off wavelength (nm)	Hydrogen evolution rate (mmol/h)
400	2.56
420	2.18
455	1.97
475	1.28

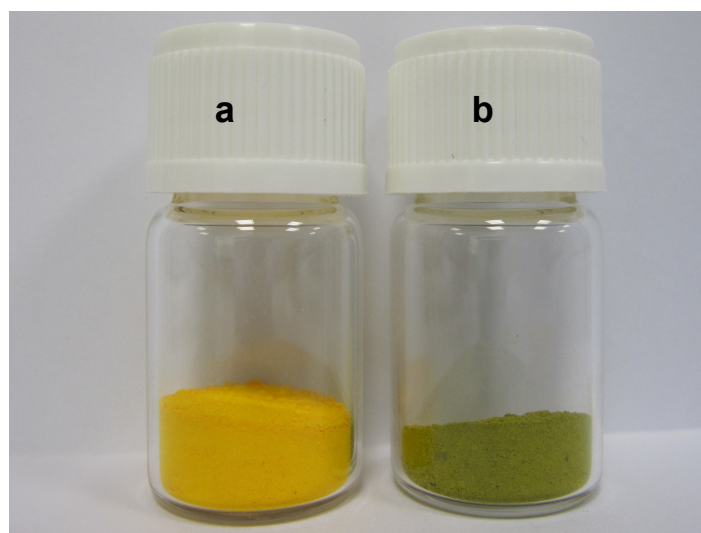


Fig S1. Picture of samples before and after loading of NiS. (a) CdS and (b) NiS(1.2mol%)/CdS.

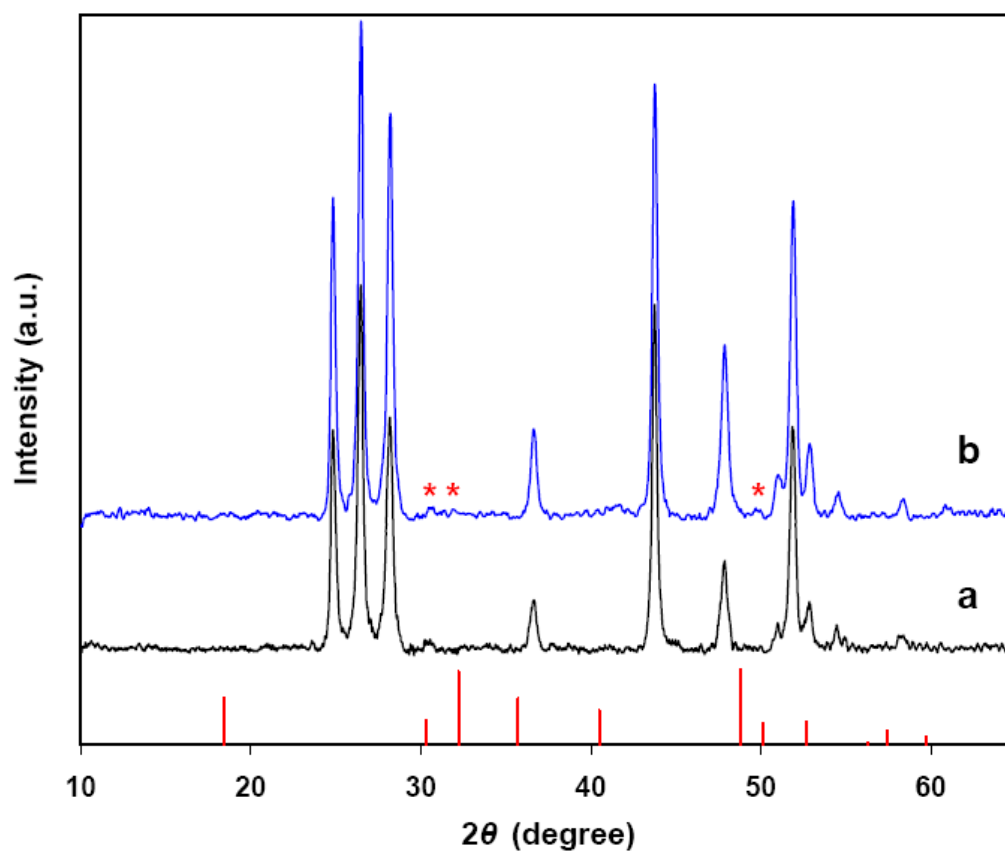


Fig. S2 XRD patterns of (a) CdS, (b) NiS(1.2mol%)/CdS, and the line pattern of rhombohedral NiS (PDF #86-2281).

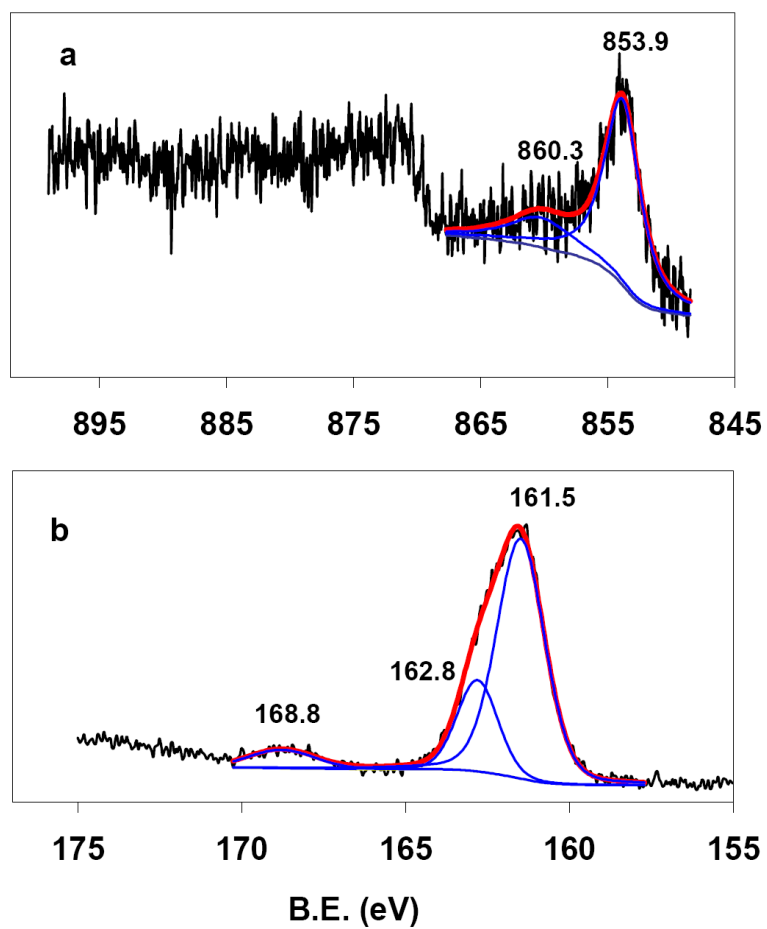


Fig. S3 XPS results of the sample NiS(1.2 mol%)/CdS. (a) Ni 2p, and (b) S 2p.

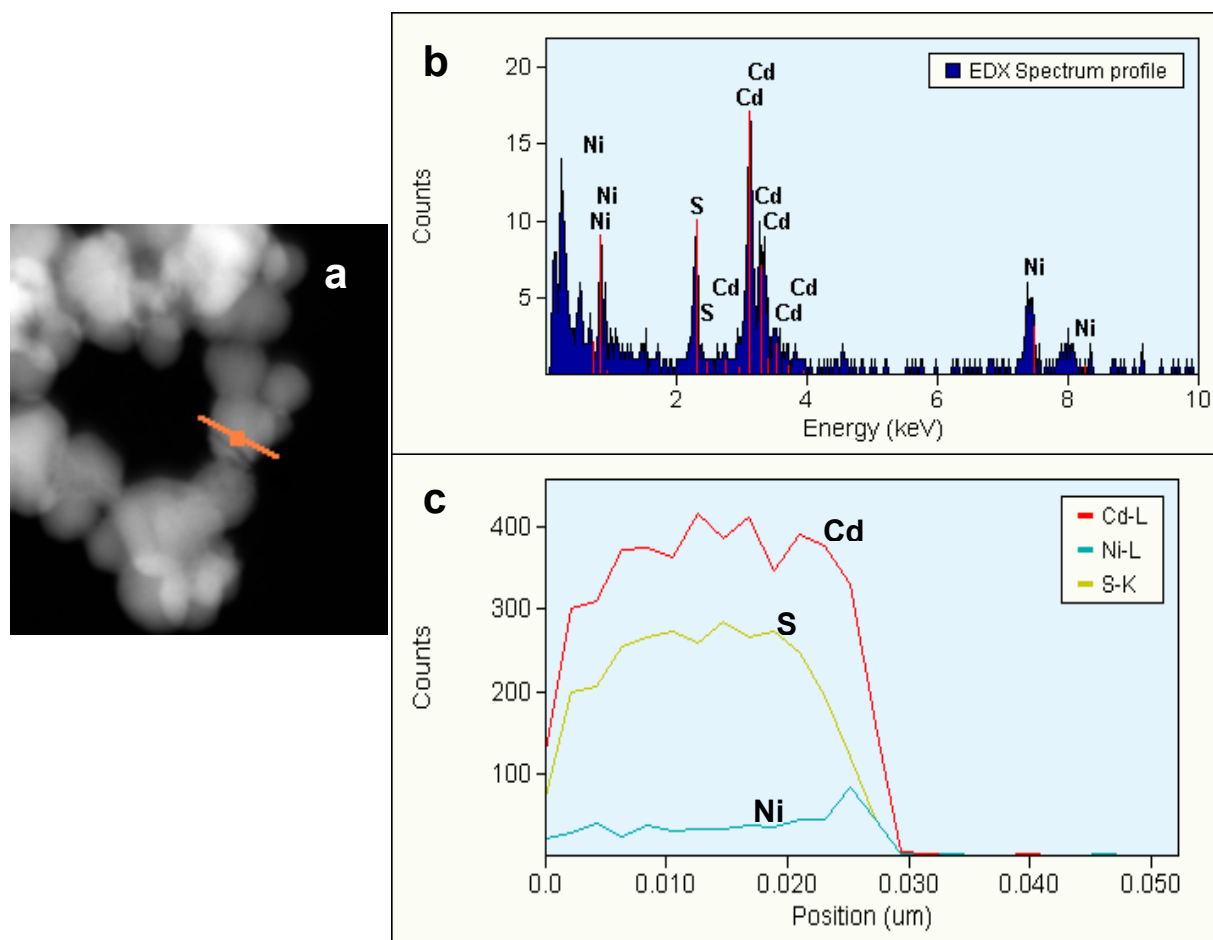


Fig. S4 (a) HAADF-STEM image of NiS(1.2mol%)/CdS, (b) the corresponding EDX results of the sample area shown in (a), and (c) EDX scan results of Cd, Ni and S along the line indicated in (a).

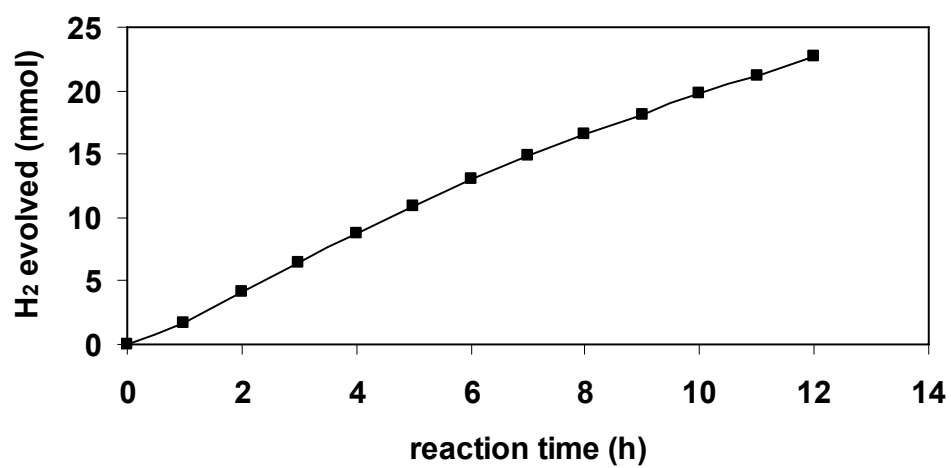


Fig. S5 The amount H₂ evolved on NiS(1.2mol%)/CdS in 12 h of continuous reaction.

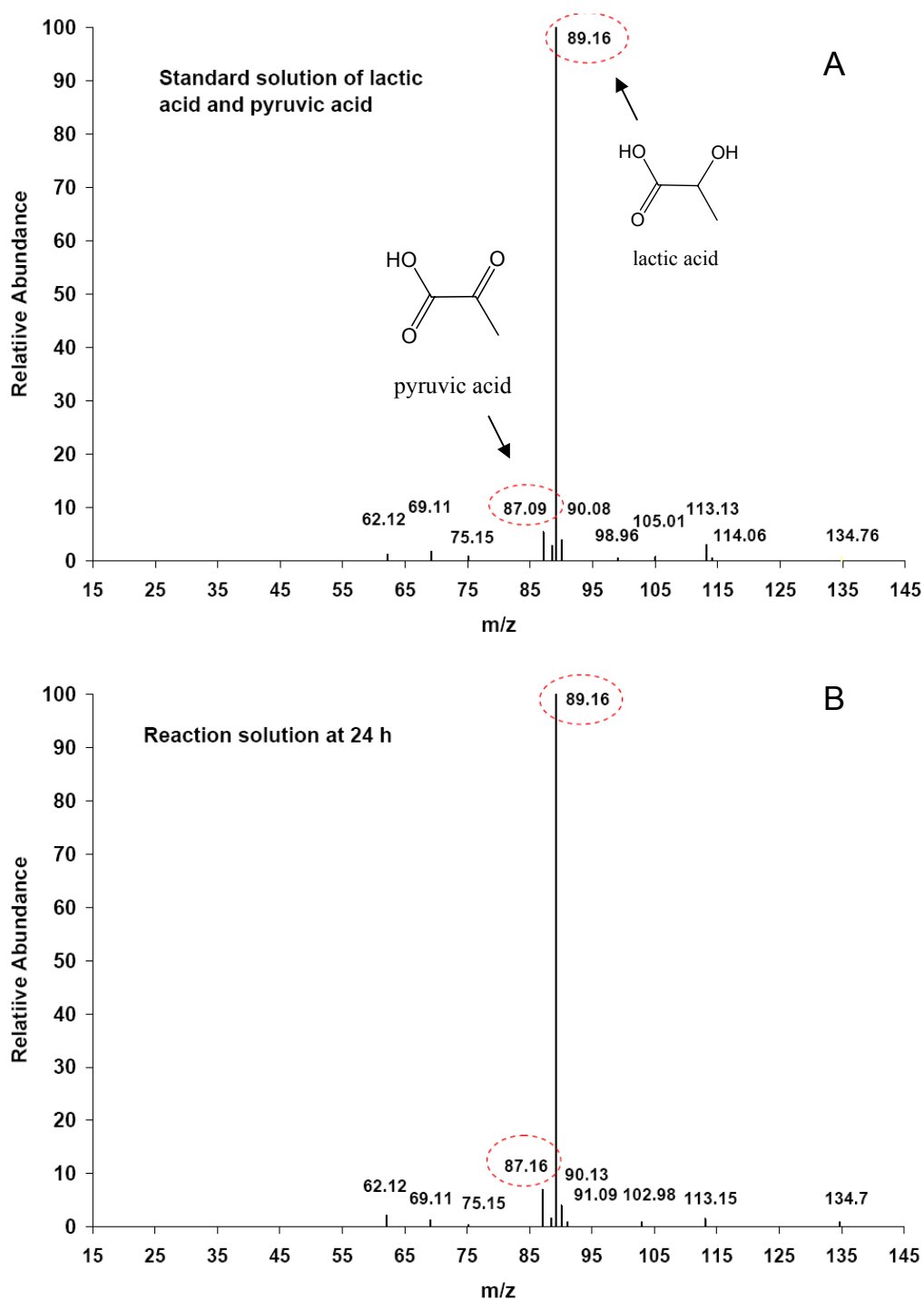


Fig. S6 ESI-MS spectra of (A) the standard solution prepared from lactic acid and pyruvic acid with a mole ratio of 13.6:1 (this ratio was calculated based on the amount of hydrogen produced at 24 h and assuming that all photogenerated holes reacted with lactic acid to pyruvic acid), (B) the reaction solution at 24 h of photocatalytic reaction. The signals with m/z at 89 and 87 are assigned to lactic acid and pyruvic acid, respectively.

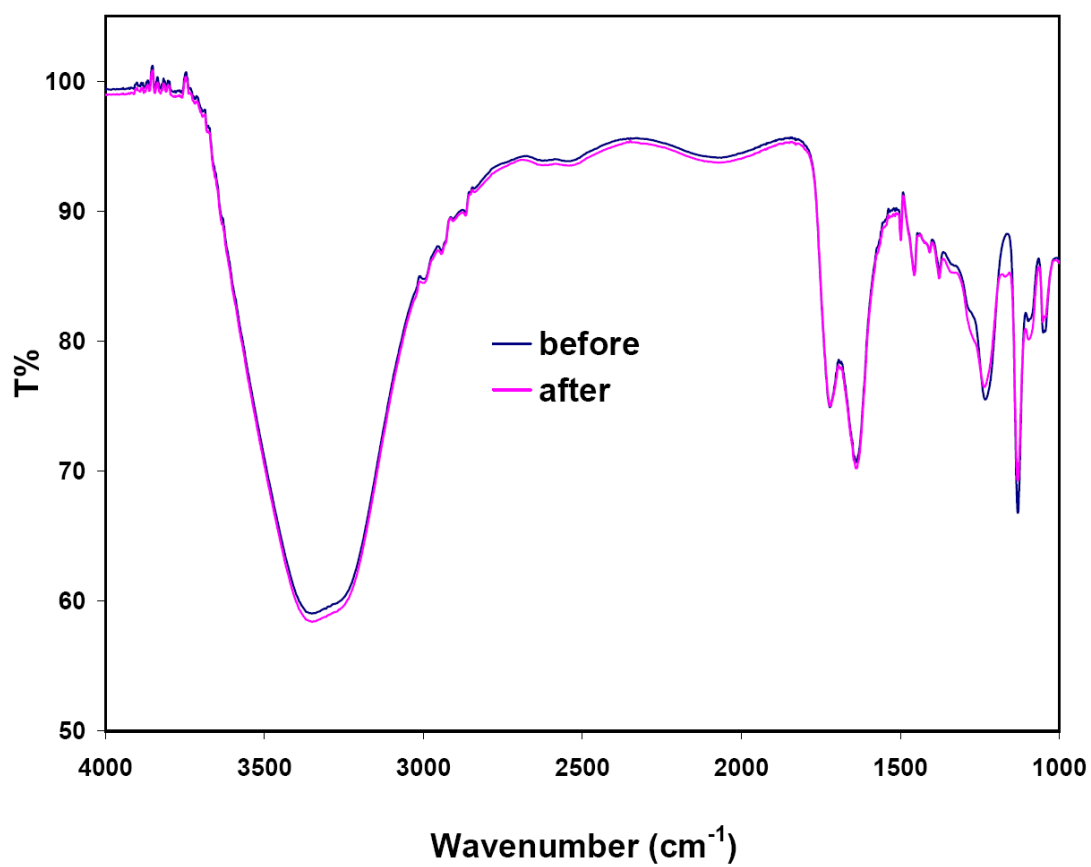


Fig. S7 The ATR spectra of solutions before and after 24 h of photocatalytic reaction.

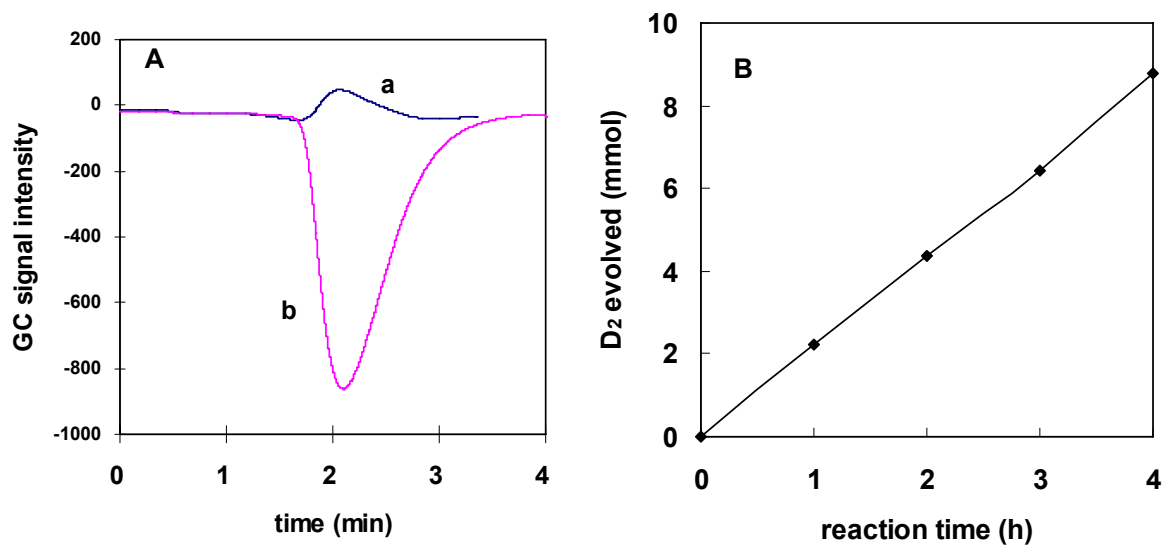


Fig. S8 (A) GC signals obtained using He (instead of Ar) as the carrier gas. (a) H₂ peak when reaction was carried out in H₂O, and (b) D₂ peak when the reaction was carried out in D₂O dissolved with lactic acid anhydrous solids. Catalyst: NiS(1.2mol%)/CdS, other reaction conditions were kept the same as that described in Experimental details. (B) D₂ evolution rate on NiS(1.2mol%)/CdS photocatalyt. The calibration was done using D₂ gas and a linear equation was obtained with R² close to 1.0.

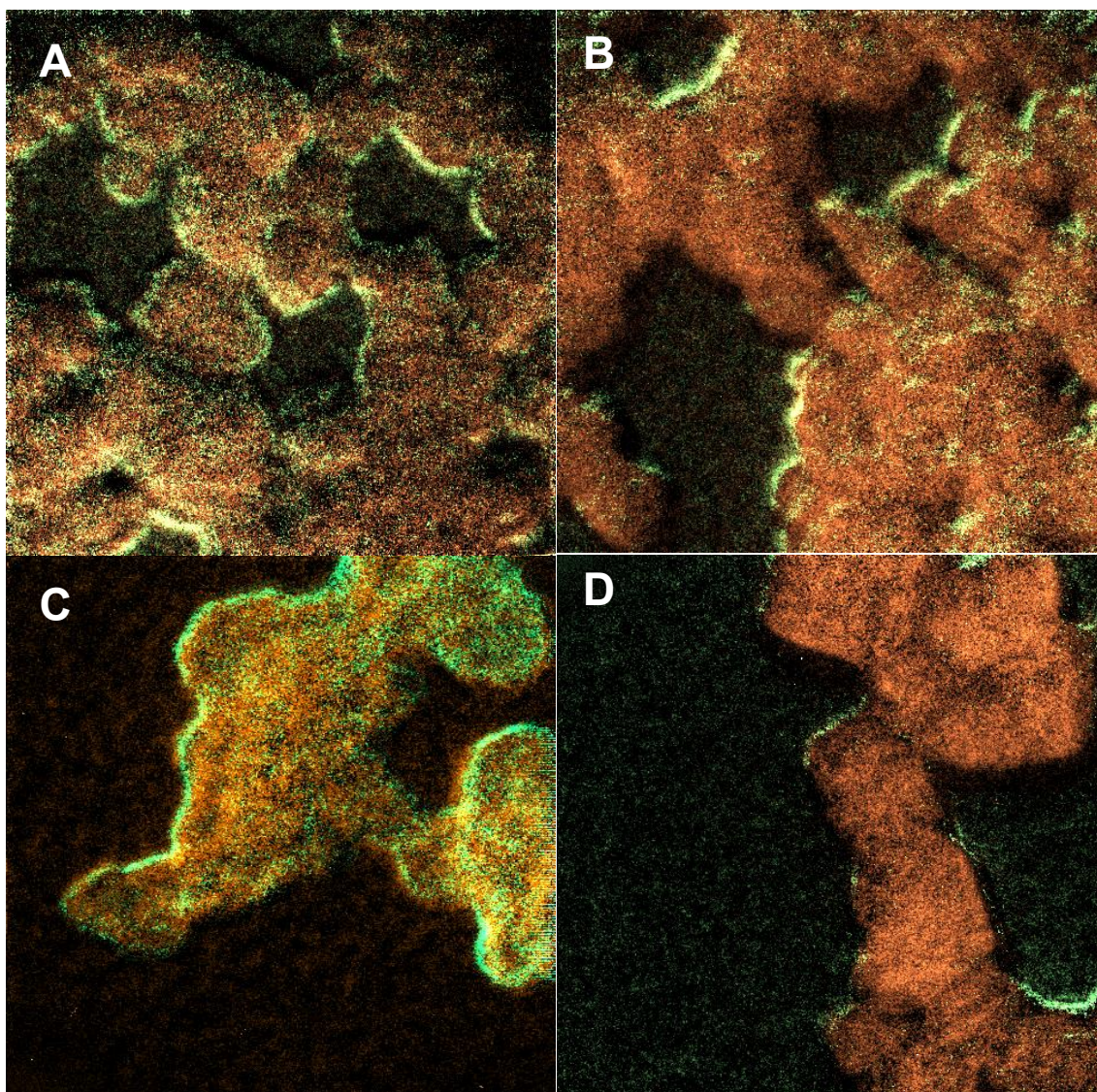


Fig. S9 Energy filtered TEM elemental mapping images of Cd (in orange) and Ni (in green) from samples synthesized hydrothermally at (A) 120 °C, 4h, (B) 120 °C, 24h, (C) 140 °C, 4h, and (D) 200 °C, 4h.