

Supporting Information (SI)

Application of Composition Controlled Nickel-alloyed Iron Sulfide Pyrite Nanocrystal Thin Films as the Hole Transport Layer in Cadmium Telluride Solar Cells

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Thin Film Preparation

Nanocrystalline thin films were prepared using layer by layer drop-casting onto a sodalime glass substrate. For this, Ni-alloyed iron pyrite NCs were dispersed in chloroform at a concentration of ~ 6 mg/mL. It was sonicated for ~30 secs to disperse the NCs properly in the solvent using a Digital Ultrasonic Cleaner Model PS-10A, at an ultrasonic power of 70 W.

Characterization

The X-ray diffraction (XRD) pattern of the synthesized NCs films were taken using a Rigaku Ultima III X-ray Diffractometer fitted with small angle X-ray Scattering (SAXS) at 40 KV accelerating voltage, and 44 mA current. The SEM images were obtained using an Hitachi S-4800 UHR microscope to investigate the surface morphology and confirm the size of the grains. Energy dispersive X-ray spectroscopy (EDS) analysis was carried out at an accelerating voltage of 20 kV and 20 μ A current to estimate each sample's composition. To understand the crystal structure and the bonds present in the material, Raman spectroscopy measurement was employed using a Jobin Yvon Horiba confocal Raman spectrometer fitted with a HeNe laser source of wavelength 632.8 nm. The UV-Vis-NIR spectra of these Ni-alloyed NCs were taken using PerkinElmer Lambda 1050 UV/VIS/NIR spectrophotometer by dispersing the NCs in chloroform taken in a cuvette of optical path length of 2 mm. The majority charge carriers in the NC thin films were determined by using the lab-constructed thermal-probe measurement, and the Hall-effect measurement were carried using the van der Pauw geometry at an applied magnetic field of 2000 Gauss.

Device Fabrication

CdS/CdTe devices prepared by vapor transport method on the top of TECTM 15 (Fluorine doped tin oxide) glass were used to test the hole transport properties of these Ni-alloyed iron pyrite ($\text{Ni}_x\text{Fe}_{1-x}\text{S}_2$) NCs. For the control device, 3 nm Cu and 40 nm Au were deposited on the top of cadmium chloride (CdCl_2) treated CdTe absorbing layer, and annealed at 150 °C for about 30 minutes to diffuse the Cu atoms into the CdTe. To study the effect of these alloyed NCs in the CdTe devices, $\text{Ni}_x\text{Fe}_{1-x}\text{S}_2$ NC layers were fabricated after 3 nm Cu deposition and diffusion into CdTe, and 40 nm Au was finally thermally evaporated on top of $\text{Ni}_x\text{Fe}_{1-x}\text{S}_2$ layer to complete the back contact. During the deposition of the NCs, the device were submerged in 1 M hydrazine solution in methanol for about 2 mins. to remove the ligands (TOPO) from the NC surface.¹ The performance of these CdS/CdTe devices with $\text{Ni}_x\text{Fe}_{1-x}\text{S}_2$ NC thin film as the interface layer was tested by illuminating devices with simulated AM1.5G solar irradiance and measuring the

current density and voltage (J - V). Additionally, the external quantum efficiencies ($EQEs$) were also measured to verify the current density in the J - V measurement.

Energy-dispersive X-ray spectroscopy (EDS) of the alloyed NCs

Here, the EDS spectra of the alloyed nanocrystals (NCs) are presented below in Figure S1. The average atomic percentage of the elements are shown in the corresponding spectrum. The value of the Ni concentration (x) in the alloyed NCs was obtained by taking the ratio of Ni concentration to the sum of the Ni concentration and Fe concentration. The EDS spectrum of the pure FeS_2 was similar to the previous report.¹ The X-axis in the EDS spectrum is in the unit of KeV.

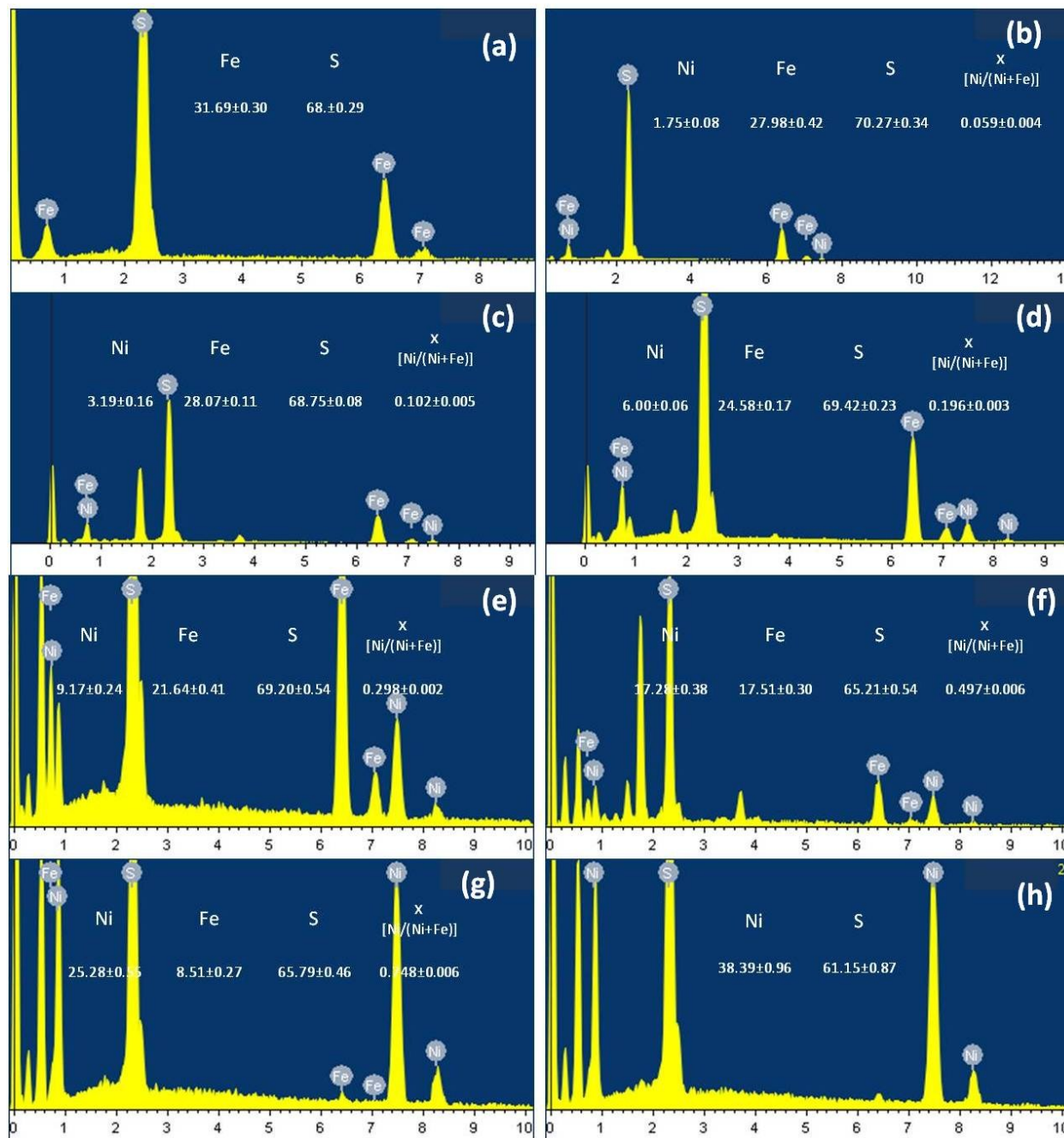


Fig. S1 EDS spectrum of Ni-alloyed iron pyrite NCs synthesized using various molar concentration of NiBr₂ in the metal precursor (a) 10 % (b) 20% (c) 30% (d) 50% (e) 75% and (f) 100%. The atomic percentage of Ni in the synthesized NCs match excellently with the Ni concentration in the precursor taken during the synthesis.

Lattice Parameters Calculation

To calculate the lattice parameters of the synthesized NCs, $a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$, and Bragg's law ($2d_{hkl} \sin\theta = n\lambda$) were used. The diffraction peaks having θ values smaller than $\sim 28^\circ$ have good intensity pattern (see Fig. 1) compared to higher angle diffraction. Though we wanted to use higher diffraction angles for the calculation of lattice parameters, we were not able to do so. Thus, lattice constants were calculated by taking the average of the lattice constants for the diffraction peaks shown below in Table S1.

Table S1. The X-ray diffraction peak positions (2θ , in degrees), extracted lattice constants (a) with respect to 2θ values, and calculated lattice constant (a_0) using Vegard's law for Ni_xFe_{1-x}S₂ alloyed Nanocrystals compositions

Ni Fraction (x)	Peak positions (2θ) for different Miller Indices						Lattice Constant, $a(\text{\AA})$	a_0 (\AA) (Vegard's law)
	(111)	(200)	(210)	(211)	(220)	(311)		
0	28.44	33.16	37.02	40.74	47.32	56.20	5.422 ± 0.012	5.430
0.05	28.43	32.91	36.88	40.63	47.18	56.13	5.438 ± 0.006	5.443
0.1	28.08	32.76	36.80	40.40	47.12	55.94	5.463 ± 0.018	5.456
0.2	28.06	32.64	36.68	40.28	47.06	55.76	5.477 ± 0.016	5.481
0.3	27.80	32.66	36.50	40.04	46.94	55.54	5.501 ± 0.030	5.507
0.5	27.55	32.06	35.95	39.75	46.20	54.80	5.569 ± 0.022	5.558
0.75	26.44	31.28	35.26	37.88	45.90	54.74	5.698 ± 0.011	5.622
1	26.42	31.28	35.06	37.82	45.56	54.62	5.714 ± 0.011	5.686

Raman Spectroscopy

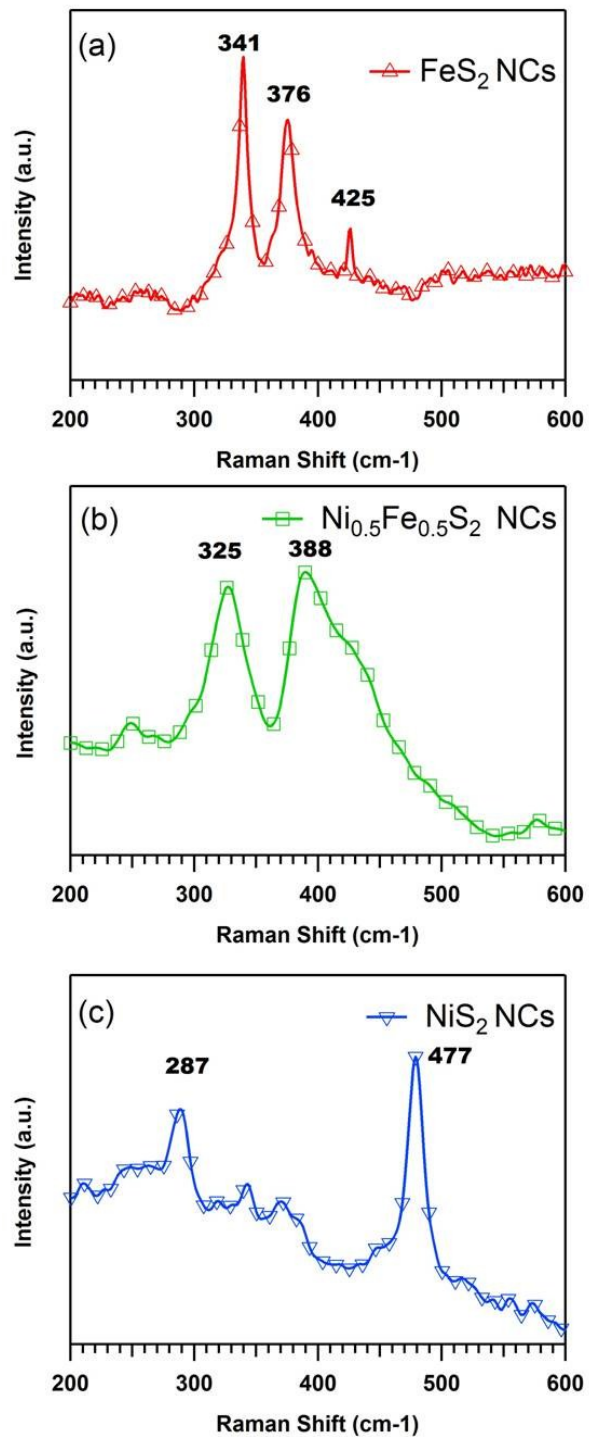


Fig. S2 Raman spectra of as-synthesized Nickel alloyed ($\text{Ni}_x\text{Fe}_{1-x}\text{S}_2$) pyrite nanocrystals with different material composition (a) FeS_2 NCs (b) $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{S}_2$ NCs (c) NiS_2 NCs

References

1. K. P. Bhandari, P. J. Roland, T. Kinner, Y. Cao, H. Choi, S. Jeong and R. J. Ellingson, *Journal of Materials Chemistry A*, 2015, **3**, 6853-6861.