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RSC Advances

Electronic Supplementary Information

Local structural studies on Co doped ZnS nanowires by synchrotron X-ray atomic pair distribution function and Micro-Raman shift†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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XPS measurement and analysis

The XPS data has been recorded using X-ray with Al K_α (1486.61 eV) X-rays at 13 KV, 300 W. The data lists Intensity (counts/s) vs kinetic energy. The KE values can be converted to BE values (BE = 1486.61 - KE). There can be charging in the samples; which can be corrected by referring Carbon C1s at 284.6 eV. The peaks of carbon: C1s ref1 is recorded in the beginning of the scans, and C1s ref2 at the end of the scans. A checked peak position of these two peaks is same ($\pm$ 0.2 eV). By taking average of these two peaks positions C1s ref1 and C1s ref2 and subtract 284.6 eV from the average value to calculate the difference. This difference gives the peak shift due to charging. The difference value was obtained by subtraction from the BE values of the entire elements data. After subtraction the peaks will move towards lower BE side. With further detailed examinations, the compositions of pure and Co doped ZnS nanowires (NWs) are consistent with stoichiometric Co:ZnS free of other impurities such as carbon. The Co doping level in the Co:ZnS NWs is further quantified from the integrated peak area of Co 2p, Zn 2p, Zn3d, Zn3p, S2s and S2p core level XPS spectra. The binding energy values of Co 2p, Zn 2p, Zn3d, Zn3p, S2s and S2p peaks shifted toward lower BE value are due to doping effect of Co content.

The XPS was employed for the confirmation of chemical species. The XPS analysis of Co doped ZnS NWs scanned in the range of 0–1400 eV is shown in Figure S1. The survey spectrum of Figure 9a shows that Co as well as Zn and S were present in the as synthesized NWs. No contaminant species were observed within the sensitivity range of the technique. The binding-energy (BE) data have been standardized to an energy scale that assumes adventitious carbon C1s 284.6 eV and recorded C1s around 290 eV then the charge correction factor is 5.4 eV. The peaks corresponding to Zn, S and Co binding energies can be identified. The corrected peak positions at 1020.09, 1020.26, 1020.45, 1020.39, 1020.77 and 1043.15, 1043.51, 1043.31, 1043.88, 1043.38 eV for pure Co doped ZnS NWs were observed due to the binding energy of $Zn2p_{3/2}$ and $Zn2p_{1/2}$ respectively.[1-3] From the high-resolution spectra of Zn 2p in figure S1 (b), the spin–orbit splitting of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ was found to be about 23.06, 23.06, 23.05, 23.11, 22.99 eV for pure and Co doped ZnS NWs which can be assigned Zn(II). For S $2p_{1/2}$ the binding energy was observed at 160.03, 160.34, 160.25, 160.54, 160.37 eV and the appearance of all the binding energy values for Zn 2p and S 2p were in accordance with previously reported work.[1-7] With further detailed examinations, the compositions of pure and Co doped ZnS NWs were consistent with stoichiometric Co:ZnS free of other impurities such as carbon. The Co doping level in the Co:ZnS NWs was further quantified from the integrated peak area of Co 2p, Zn 2p, Zn3d, Zn3p, S2s and S2p core level XPS spectra. The binding energy values of Co 2p, Zn 2p, Zn3d, Zn3p, S2s and S2p peaks shifted toward lower BE value was due to doping effect of Co contents.[4-6] With increasing the amount of cobalt nitrate during the synthesis, the binding energy for the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks of the ZnS NWs shifted gradually to a lower energy. This indicates that, to a certain degree, the concentration of S vacancies can be controlled by varying the amount of cobalt content in the samples.[7] The binding energy was calculated using equation (1)

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† *Electronic Supplementary Information (ESI) available:* [XPS and EDAX spectra were provided in figure S1 and figure S2 for details information. Also the full scan SCXRPD was provided in figure S3 with tabulated values in table S1 and S2 for pure and Co doped ZnS NWs. The first peak fitted with Gaussian, first PDF peaks width and strain in Zn-S bond given in figure S4. *See DOI: 10.1039/x0xx00000x*

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$
(1)

where E_{binding} is the BE of the electron, E_{photon} is the energy of the X-ray photons is being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument and ϕ is the work function is dependent on both the spectrometer and the material.

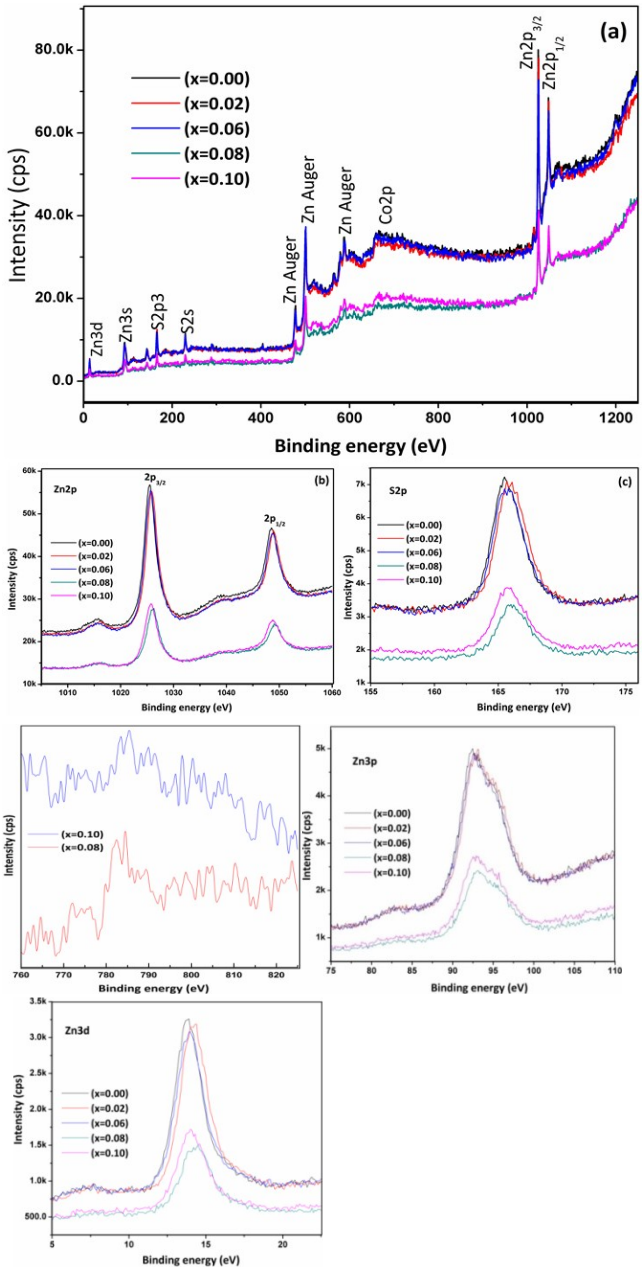

Fig. S1. XPS spectra of cobalt doped ZnS NWs.

Table S1: Weight and atomic percentage of pure and Co doped ZnS NWs obtained from EDAX data.

Samples	Weight %			Atomic %		
(x)	Zn	Co	S	Zn	Co	S
0.00	68.15	0.00	31.85	51.12	0.00	48.79
0.02	67.58	0.62	31.80	50.56	0.63	48.82
0.06	66.95	2.90	30.16	50.87	2.44	46.49
0.10	65.57	4.27	30.16	49.75	3.59	46.66

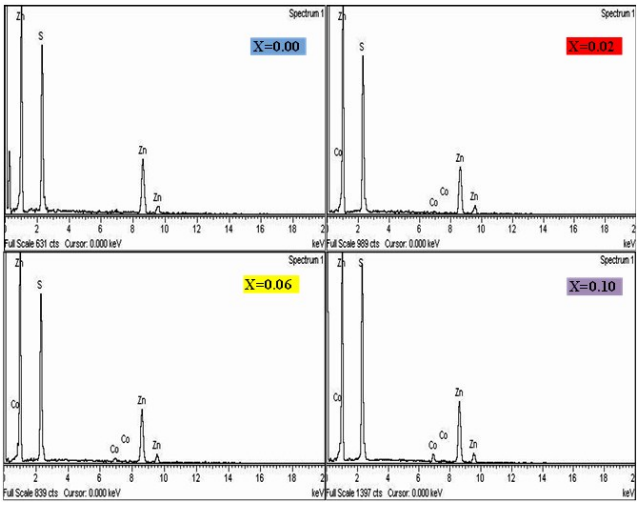

Fig. S2. EDAX patterns of pure and Co doped ZnS nanowires.

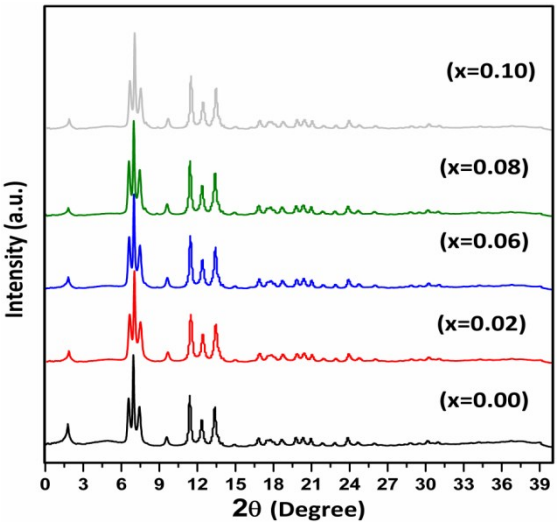

Fig. S3. Full scanned SCXRPD patterns of pure and Co doped ZnS NWs with background.

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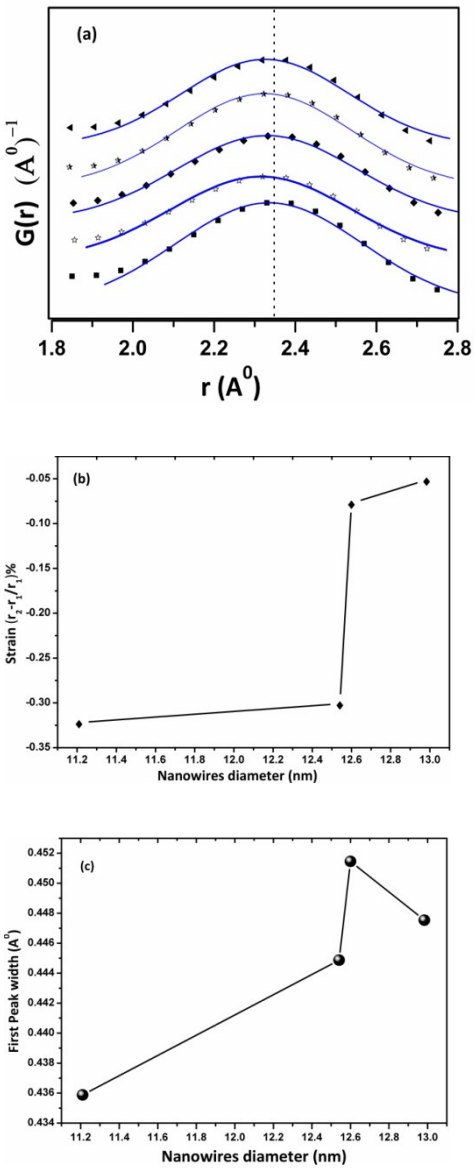

Fig. S4. (a) Gaussian fits to the first PDF peak. Experimental PDFs are indicated by dotted lines and the best fit Gaussian fit shown in blue color (from top to bottom: pure and Co doped ZnS NWs respectively. The vertical dotted line represents the first peak position of the pure ZnS sample as a reference **(b)** inhomogeneous strain, (Δr/r)%, as measured from the first PDF peak coming from the Zn-S bond vs. nanowires diameter **(c)** Width of the first PDF peak vs. nanowire size.

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