Supplementary Data

Nanoparticle transformation from ZnO to ZnS through anion exchange reaction with di-tert butyl disulphide

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Table S1. The calculated crystalline size (a) and particle and void size (b) via XRD pattern and TEM images.

(a)

Crystalline size (nm)	(100)	(002)	(101)	Average crystalline size
Q-ZnO	14.84	16.32	14.55	15.23
Anion exchanged NPs for 30 min	15.25	15.76	14.84	15.28
Anion exchanged NPs for 1 hour	16.23	15.7	14.87	15.6

(b)

	Q-ZnO	Anion exchanged NPs for 30 min	Anion exchanged NPs for 1 hour	Anion exchanged NPs for 2 hours
Particle size (nm)	14.9 ± 1.78	20.25 ± 2.8	19.26 ± 2.9	20.52 ± 3.2
Void size (nm)	X	4.22 ± 0.98	5.75 ± 1.23	8.17 ± 1.89

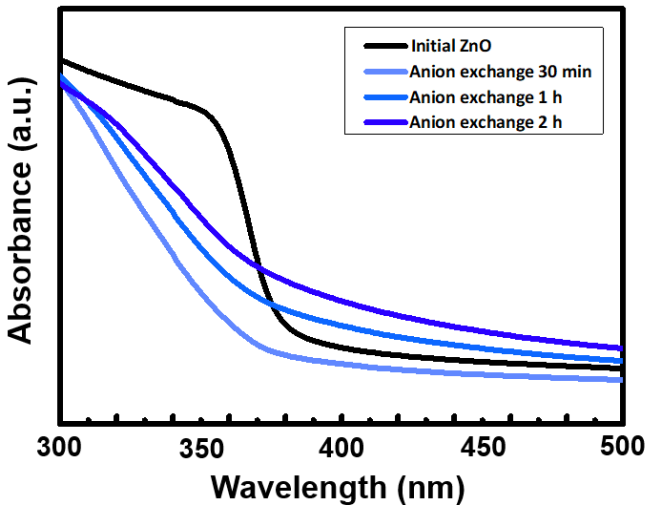

Figure S1. UV-vis spectra of initial ZnO NPs and anion exchanged NPs for 2 h with TBDS as a sulphur source. The strong intrinsic absorption peak of initial ZnO NPs at ~360 nm suggests that the initial ZnO was high crystalline NPs. In ZnO NPs, no significant absorbance for visible light was observed due to their wide energy band gap (3.2 eV). In the anion exchanged NPs for 2 h, absorption band edges were gradually red-shifted, indicating that the electronic structure of NPs was tuned by anion exchange from ZnO to ZnS. Additionally, the absorption of anion exchanged NPs for 1 h and 2 h in the visible region was promoted compared to the initial ZnO NP and anion exchanged NPs for 1 h, which may be attributed by the formation of hybrid bands/orbitals of ZnO and ZnS at interfaces.[1]

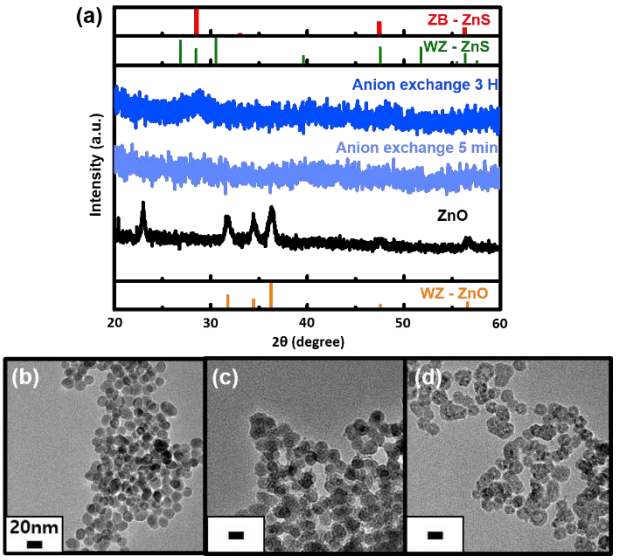

Figure S2. XRD pattern (a) and (b)-(d) TEM images of anion-exchanged NPs synthesized with an elemental sulfur. (b) 5 min, (c) 2 h, (d) 3 h (WZ-ZnO, orange bar, PDF 01-070-8070, WZ-ZnS, green bar, PDF 01-079-2204 and ZB-ZnS, red bar, PDF 03-065-0309, respectively).

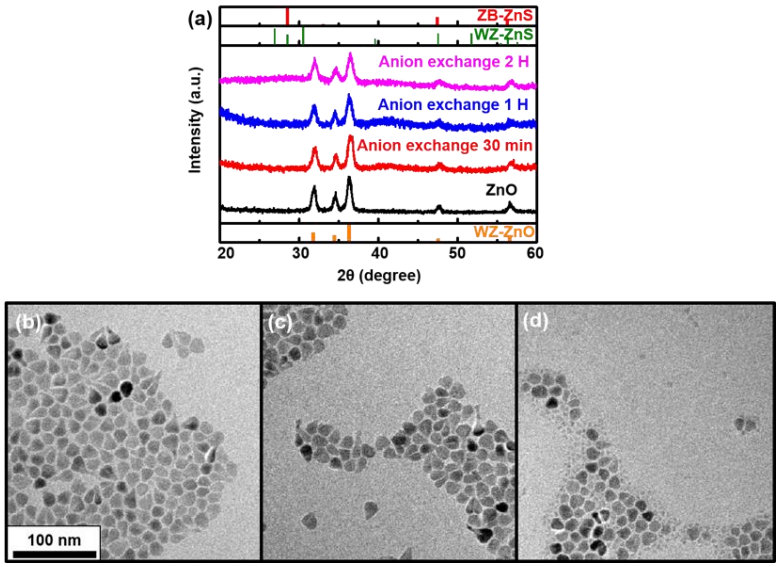

Figure S3. XRD pattern (a) and (b)-(d) TEM images of anion-exchanged NPs synthesized with 1-dodecanethiol (DDT). (b) 30 min, (c) 1 h, (d) 2 h (WZ-ZnO, orange bar, PDF 01-070-8070, WZ-ZnS, green bar, PDF 01-079-2204 and ZB-ZnS, red bar, PDF 03-065-0309, respectively).

Reference

1. P. Devaraji, M. Mapa, H. M. Abdul Hakkeem, V. Sudhakar, K. Krishnamoorthy and C. S. Gopinath, *ACS Omega*, 2017, **2**, 6768-6781.