Electronic Supplementary Information for Dalton Transactions
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Supporting Information

Solid-state reactions in colloidal nanocrystals: The examples of sulfidation of surfactant-protected iron oxide nanoparticles

Chih-Jung Chen and Ray-Kuang Chiang*

Nanomaterials Laboratory,Far East University, Tainan County 74448, Taiwa, Republic of China. Fax: 886 6 5977766; Tel: 886 6 597776; E-mail: rkc.chem@msa.hinet.net

Synthesis of α-Fe NPs and their Surfidation. The precursor, iron oleate ($Fe(oleate)_3$)1, were used for synthesis of**α-Fe** NPs following the process reported previously.[1] In the typical synthesis process, 3 mmol $Fe(oleate)_3$, 0.2 g sodium oleate were dissolved in 6 ml degassed Oleic acid to give a brown solution. The solution was heated up to 380 ℃ at a rate of 15 ℃ mm^{-1} under vigorous stirring, and was kept at 380 ℃ for 2 hr under N_2 gas. The temperature was controlled using a heating mantel and a thermocouple. During the reaction, the color of the reactant mixture changed from brown to black, suggesting the formation of NPs. An aliquot sample was taken for characterization before the sulfidation. Then, sulfur powder (1.5 equivalents of Fe) was added with vigorous stirring at about 340 ^{o}C. After 10 min the mixture was cooled and the resulting black colloidal suspension was diluted with a mixture of hexane and acetone (1:20) and centrifuged at speed of 5000 rpm. The TEM sample was prepared by dropping the hexane suspension of NPs onto a copper grid.

Synthesis of γ-Fe_2O_3 NPs and their Sulfidation. Iron oleate ($Fe(oleate)_3$) were used for the synthesis of**γ-Fe_2O_3** NPs following the process reported previously.[2] In a typical synthesis process, 3 mmol $Fe(oleate)_3$, 4.5 mmol oleic acid were dissolved into 9 ml degassed 1-Eicosane to give a brown solution. The solution was heated up to 340 ℃ at a rate of 15 ℃ mm^{-1} under vigorous stirring, and was kept at 340 ℃ for 2 hr under flowing N_2 gas, and then the solution was cooled down to 200 ℃ for 2 hr under air atmosphere to be fully oxidized to the phase of γ-Fe_2O_3.. The temperature was controlled using a heating mantel and a thermocouple. During the reaction, the color of the reactant mixture changed from brown to black, suggesting the formation of NPs. An aliquot sample was taken for characterization before the sulfidation. Then, sulfur powder (1.5 equivalents of FeO) was added with vigorous stirring at about 340 ^{o}C. After 10 min the mixture was cooled and the resulting black colloidal suspension was diluted with a mixture of hexane and acetone (1:20) and centrifuged at speed of 5000 rpm. The TEM sample was prepared by dropping the hexane suspension of NPs onto a copper grid.

1. D. Kim, J. Park, K. An, N. K. Yang, J. G. Park and T. Hyeon, *J. Am. Chem. Soc.*, 2007, **129**, 5812.
2. C. J. Chen, H. Y. Lai, C. C. Lin, J. S. Wang and R. K. Chiang, *Nanoscale Res. Lett*,. 2009, **4**, 1343.

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Table S1. Reaction parameters for the sulfidation reactions using NP presursors[a]

Run	NP precursors (mmol)	Sulfur (mmol)	Solvent[b] (mL)	Temperature (℃)	Reaction time (min)
1	3	4.5	10	360	10 min
2	3	4.5	9	340	10 min
3	3	4.5	10	360	10 min
4	6	9	20	250	10 min
5	2	3	20	250	10 min

[a] Precursors used: run 1, FeO; run 2, γ-Fe_2O_3; run 3, α-Fe; run 4, MnO; run 5 CoO.

[b] Solvent used: run 1 and run 3, OA; run 2, 1-eicosane; run 4, OA and OAm; run 5, ODE.

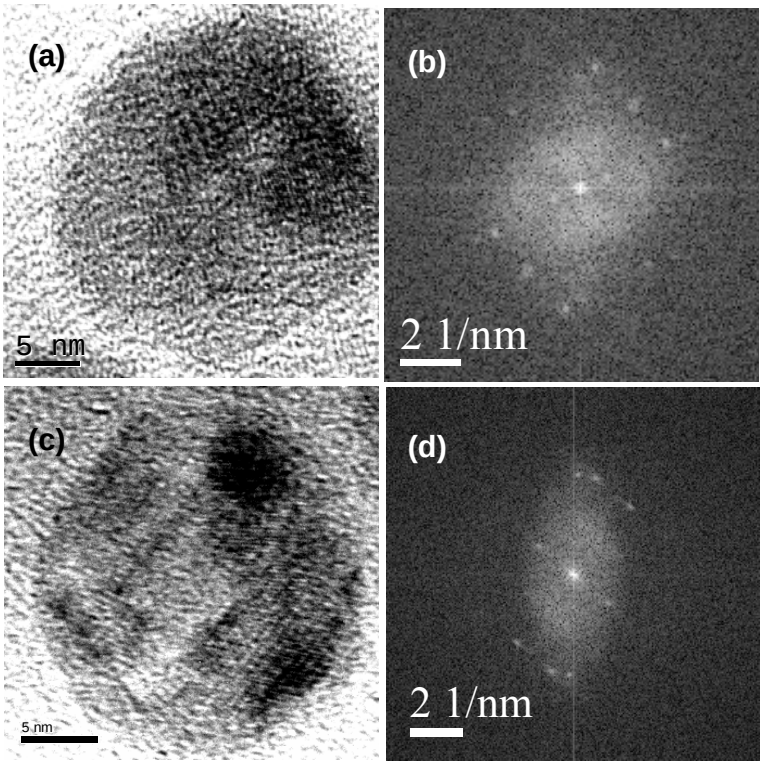

Figure S1. (a, c) HRTEM images of hollow $Fe_{1-x}S$ nanoparticle. (b, d) FFT images obtained form transformation of Figure S1(a) and Figure S1(c), revealing a single-crystal-like structure.

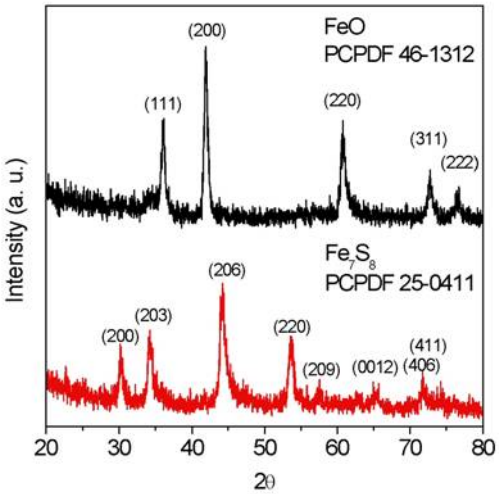

Figure S2. XRD patterns of (a) as-prepared $F_{1-x}O$ NP precursors showing peaks consistent with JCPDS 46-1312 of wustite. (b) hollow $Fe_{1-x}S$ NPs showing peaks consistent with JCPDS 24-0220 of Fe_7S_8.

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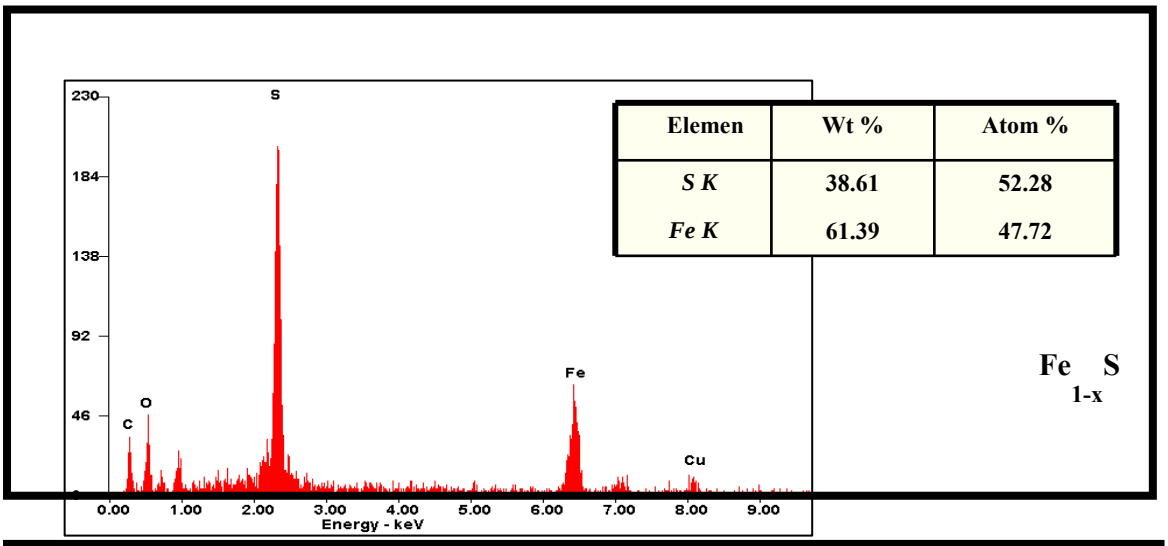
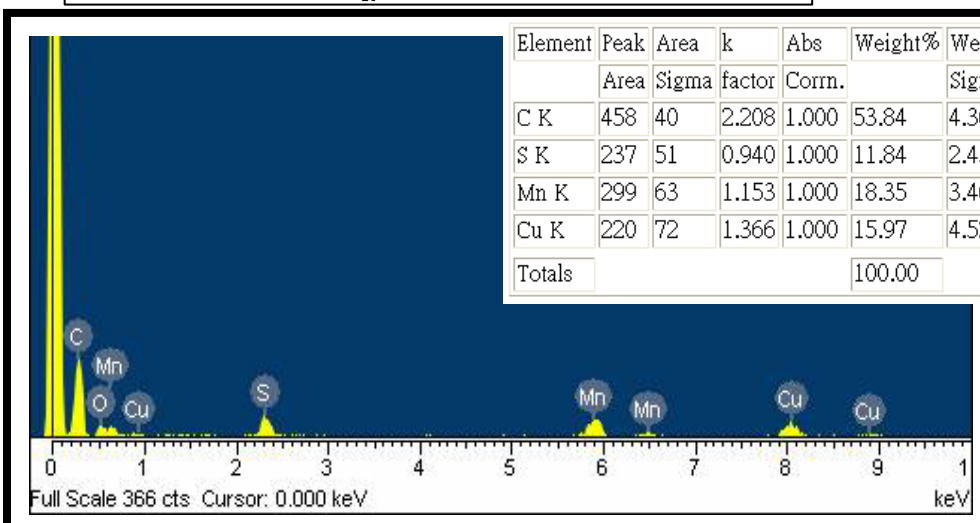


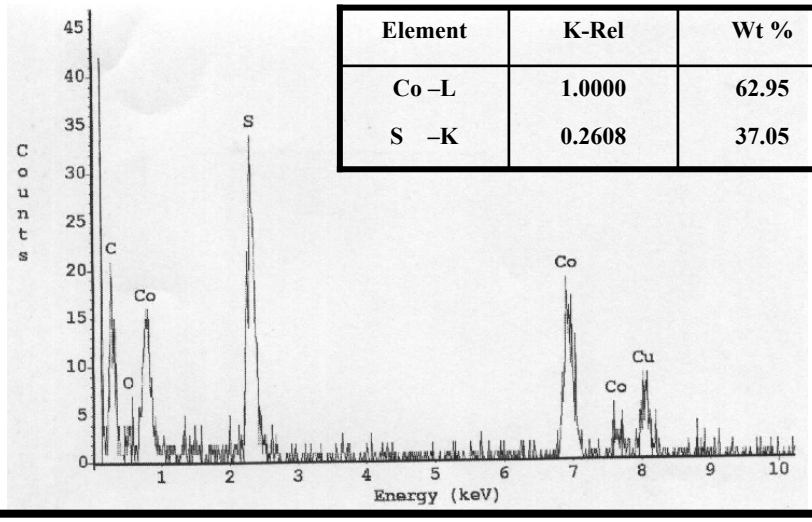
Elemen	Wt %	Atom %
S K	38.61	52.28
Fe K	61.39	47.72

$Fe_{1-x}S$



Element	Peak Area	Area Sigma	k factor	Abs Corrn.	Weight%	Weight% Sigma	Atomic%
C K	458	40	2.208	1.000	53.84	4.36	82.44
S K	237	51	0.940	1.000	11.84	2.45	6.79
Mn K	299	63	1.153	1.000	18.35	3.46	6.14
Cu K	220	72	1.366	1.000	15.97	4.52	4.62
Totals					100.00		

MnS



Element	K-Rel	Wt %	Atom %
Co –L	1.0000	62.95	48.05
S –K	0.2608	37.05	51.95

CoS

Figure S3. EDS spectra of the products of hollow $Fe_{1-x}S$, MnS and CoS NPs.

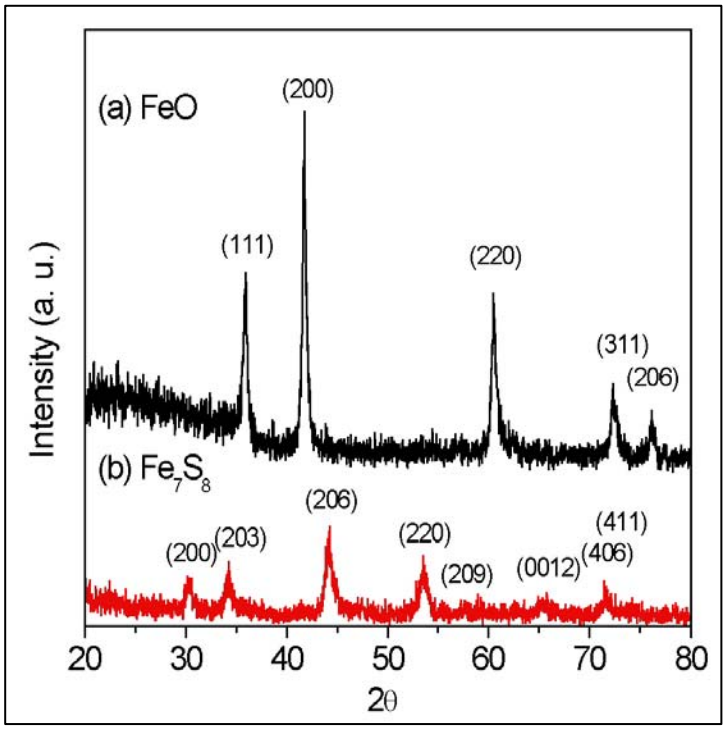


Figure S4. XRD pattern of the $F_{1-x}O$ cube samples before (a) and after (b)the sulfidation reaction.

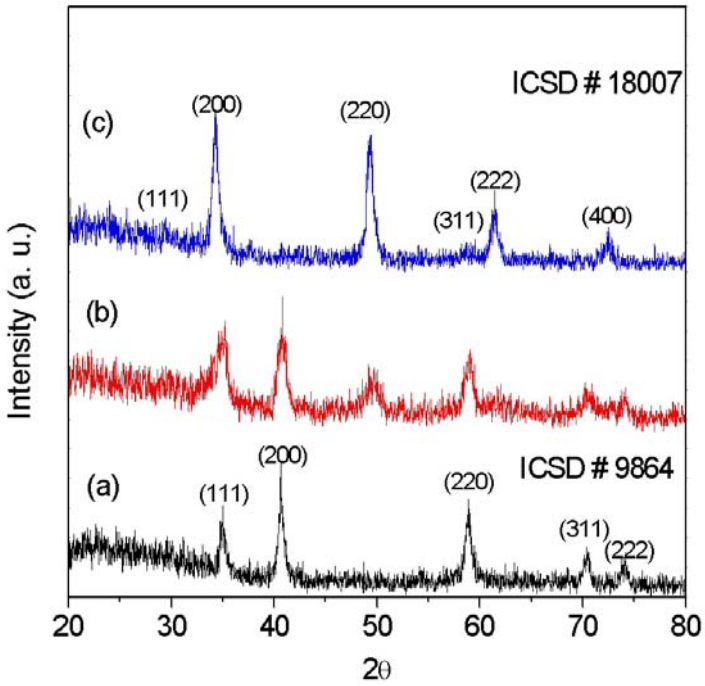


Figure S5. XRD patterns of (a) as-prepared MnO NP precursors showing peaks consistent with rock-salt structure, (b) sulfidation products with insufficient S powder showing a mixture of MnO and α-MnS, and (c) the hollow MnS NPs products showing peaks consistent with rock-salt α-MnS structure.

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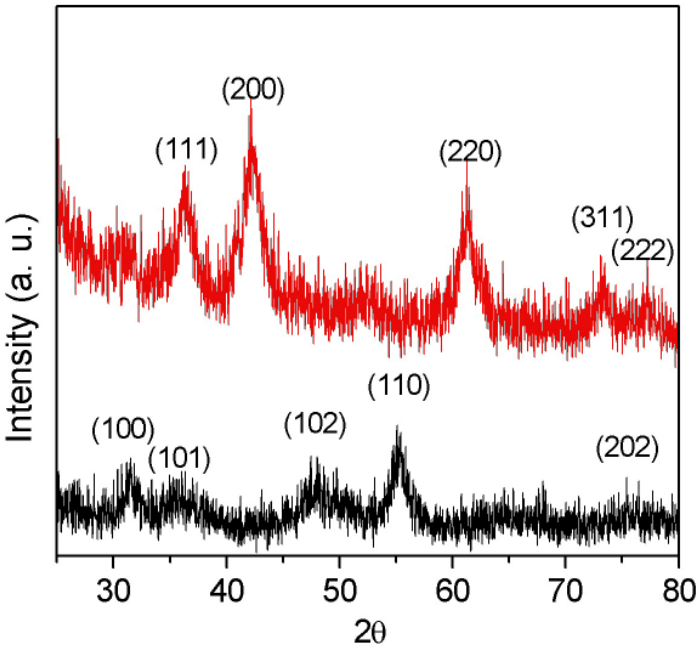

Figure S6. XRD patterns of CoO NP precursors (a) before and (b) after the sulfidation reaction indicating the complete transformation.

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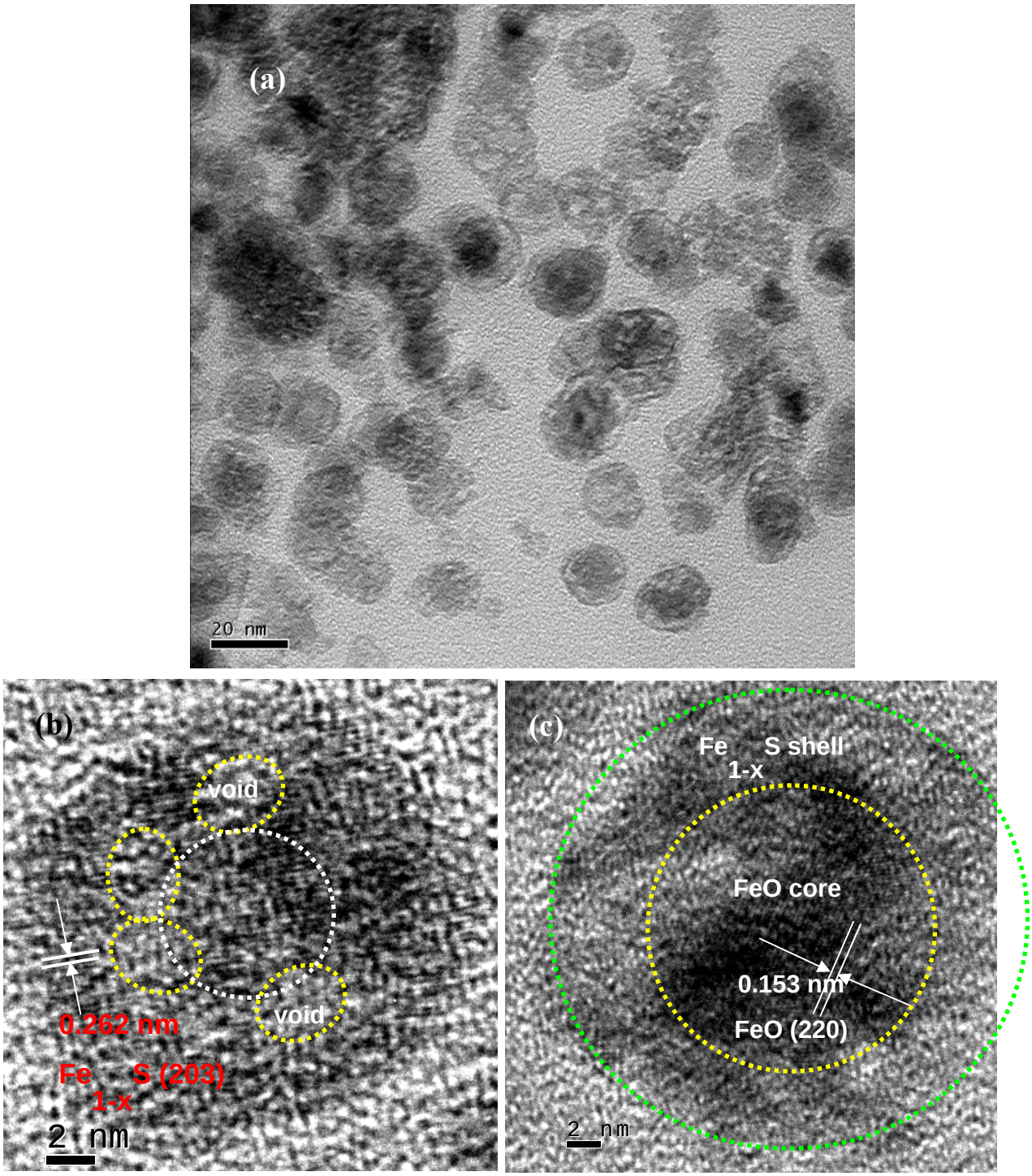

Figure S7. (a) The sulfidation of FeO NPs with insufficient S powder showing a core-shell structure. (b-c) HRTEM image of core-shell NPs showing the $Fe_{1-x}S$ shell formed around unreacted FeO cores

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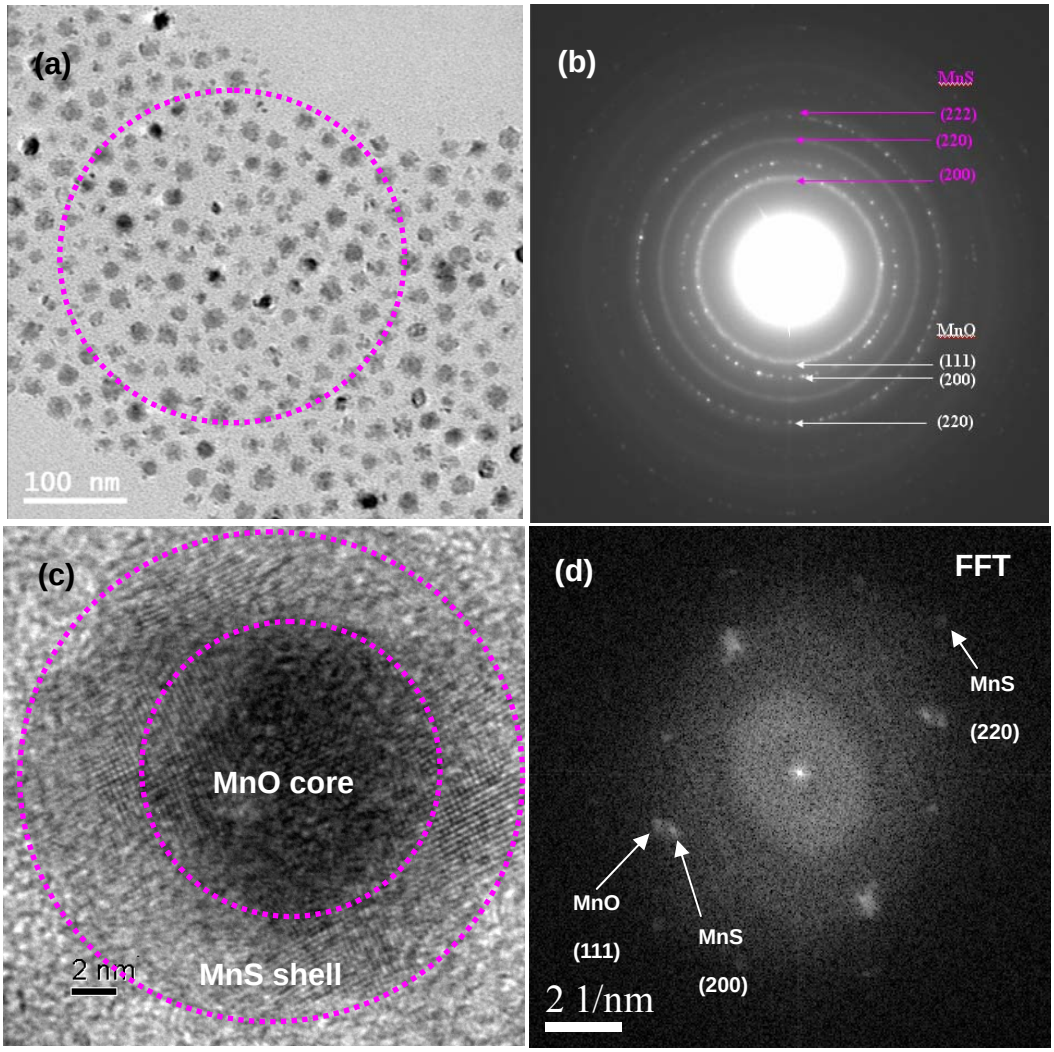

Figure S8. (a) TEM images of sulfidation products with insufficient S powder. (b) SAED pattern of NPs showing the rings can be assign to MnO and MnS (c). HRTEM image of a core-shell NP showing a MnS shell formed around an unreacted FeO core (b). FFT pattern of a core-shell NP showing the spots can be assign to MnO and MnS.