Electronic supplementary information

Phase control in the colloidal synthesis of well-defined nickel sulfide nanocrystals

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Table S1. Summary of the reaction conditions to obtain various Ni–S nanocrystal phases

Phase	Sulfur precursor	S:Ni ratio	Solvent/Ligand	Temperature (˚C)	Time
Ni_3S_2	*N*,*N*'-dibutyl thiourea	10.0	oleylamine & 1-dodecanethiol	180	1 h
Ni_9S_8	*N*,*N*'-diphenyl thiourea	3.0	oleylamine & 1-dodecanethiol	180	4 h
Ni_3S_4	*N*,*N*'-diphenyl thiourea	1.5	oleylamine	180	4 h
α-NiS	*N*,*N*'-diphenyl thiourea	5.0	dodecylamine	180	5 min
β-NiS*	*N*,*N*'-diphenyl thiourea	8.0	oleylamine	220	4 h

*β-NiS phase also contains minor α-NiS impurities.

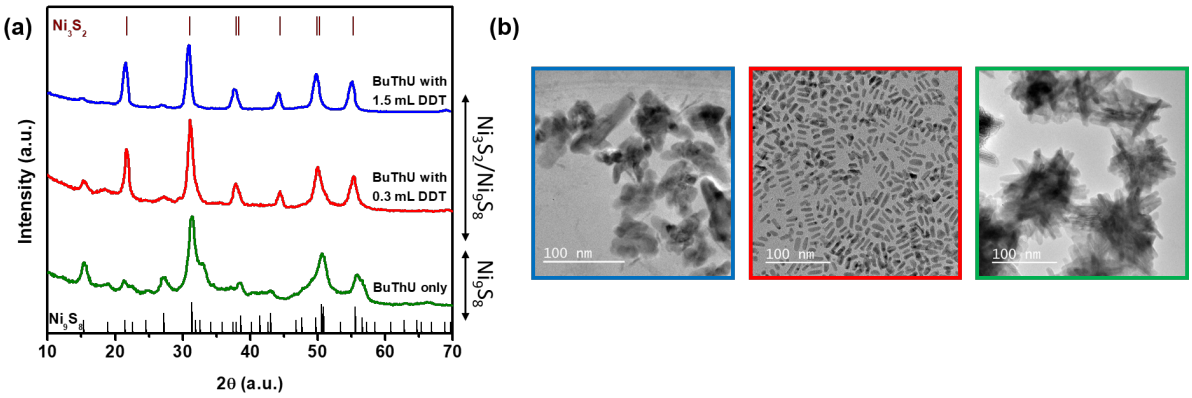

Fig. S1 (a) Powder XRD patterns and (b) TEM micrographs of the products from the reaction of NiI_2 and *N*,*N*'-dibutyl thiourea (BuThU) in the presence of various amounts of 1-dodecanethiol (DDT) at 180 ˚C for 1 h.

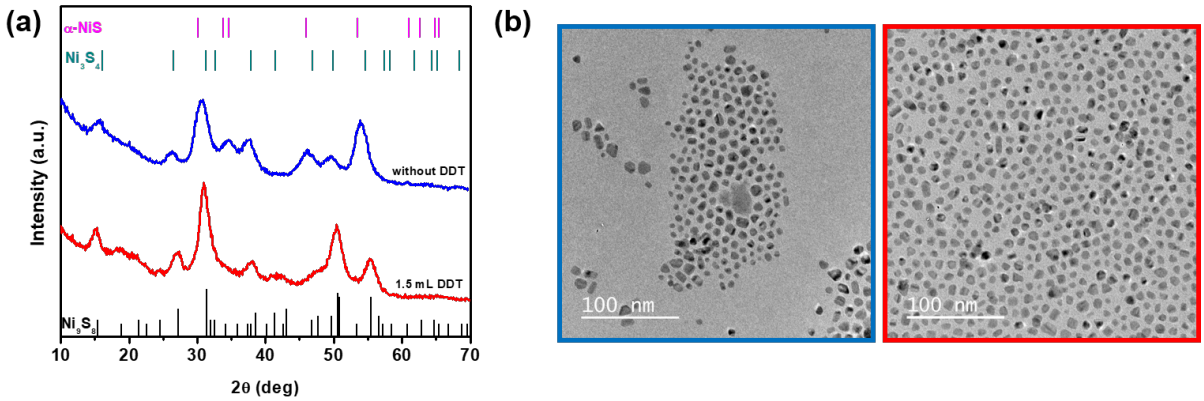

Fig. S2 (a) Powder XRD patterns and (b) TEM micrographs of the products from the reaction of NiI_2 and 3.0 molar equivalents of *N*,*N*'-diphenyl thiourea in the presence and absence of 1-dodecanethiol (DDT) in oleylamine.

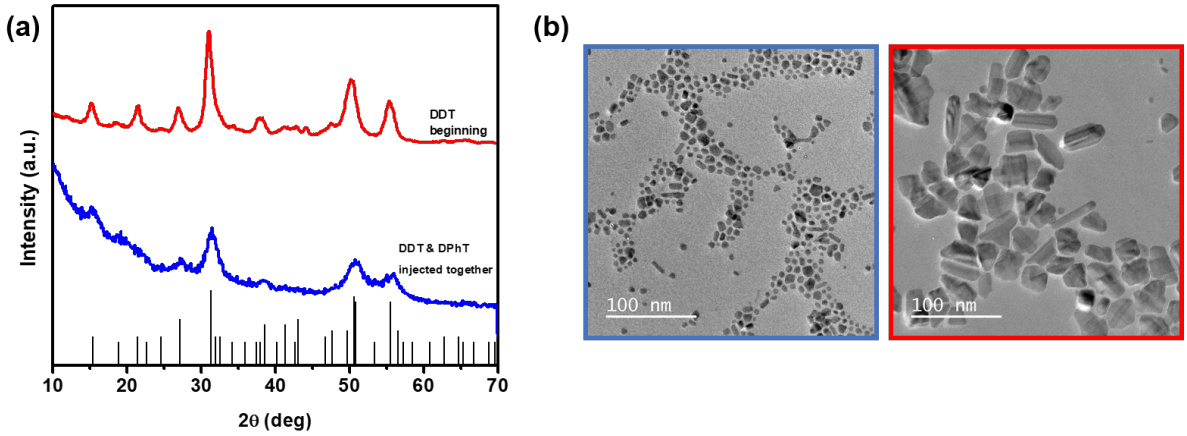

Fig. S3 (a) Powder XRD patterns and (b) TEM micrographs of the products from the reaction of NiI_2 and 3.0 molar equivalents of *N*,*N*'-diphenyl thiourea (DPhT) in the presence of 3.0 mL of 1-dodecanethiol (DDT) in oleylamine.

The effect of the injection time of 1-dodecanethiol was also explored (Figure S3). Simultaneous injection of 1-dodecanethiol and *N*,*N*'-diphenyl thiourea resulted in the formation of relatively more polydispersed Ni_9S_8 nanocrystals with a variety of shapes including rods, rectangles, quasi-spheres (Figure S3b). Alternately, larger nanocrystals with an ill-defined shapes were observed when 1-dodecanethiol was added to the reaction flask along with oleylamine before the injection of *N*,*N*'-diphenyl thiourea (Figure S3b). In this case, 1-dodecanethiol decomposed before the injection of *N*,*N*'-diphenyl thiourea. By the time *N*,*N*'-diphenyl thiourea is injected at 180 ˚C, nucleation and growth of nanoparticles have already been initiated and 1-dodecanethiol became the primary sulfur precursor. Larger and polydispersed nanocrystals can be attributed to slower conversion kinetics in the case of 1-dodecanethiol that leads to a low monomer concentration subsequently resulting in Ostwald ripening. These control experiments clearly indicate that injection time of 1-dodecanethiol has no significant impact on the phase of nanocrystals; that is, they all crystalize into the same orthorhombic structure, whereas the injection time of 1-dodecanethiol primarily dictates the morphology of the resulting nanocrystals rather than their phase.

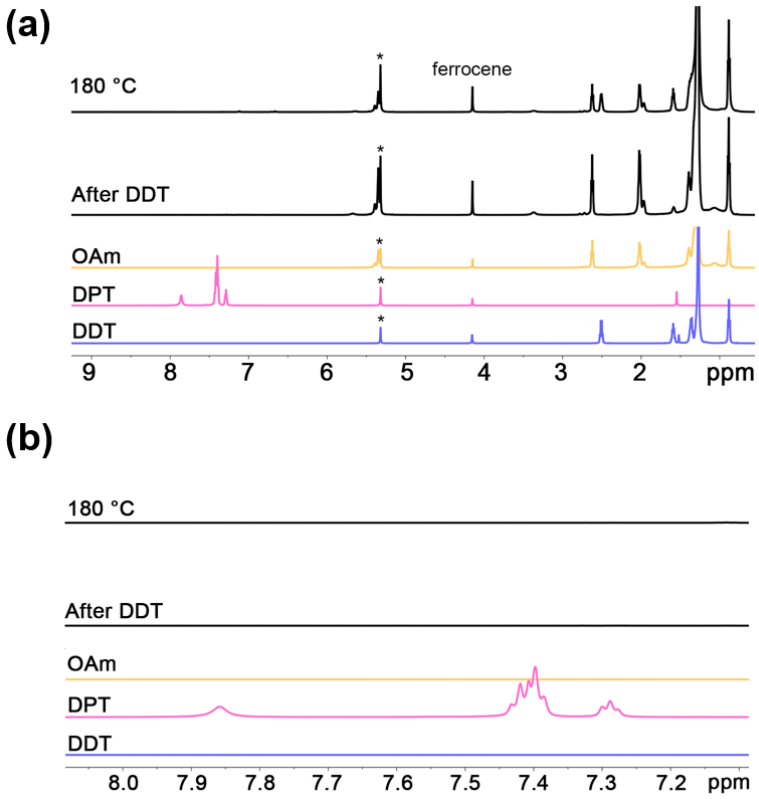

Fig. S4 ^{1}H NMR of spectra in dichloromethane-d_2 of *N*,*N*'-diphenyl thiourea heated in oleylamine at 180 ˚C for 10 min, and then 5 min after 1-dodecanethiol (DDT) was added. (a) and (b) are showing full spectra and aromatic region only, respectively. ^{1}H NMR spectra of starting materials (*i.e.*, oleylamine (OAm) (yellow), *N*,*N*'-diphenyl thiourea (PhThU) (pink), and 1-dodecanethiol (DDT) (blue)). Residual solvent is denoted by *.

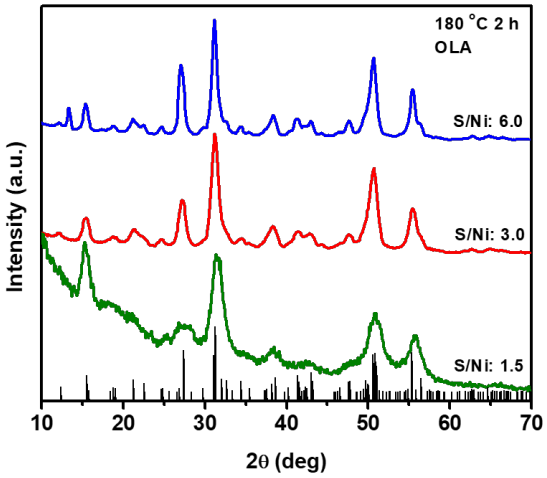

Fig. S5 Powder XRD patterns of the products from the reaction of NiI_2 and various amounts of 1-dodecanethiol in oleylamine (OLA).

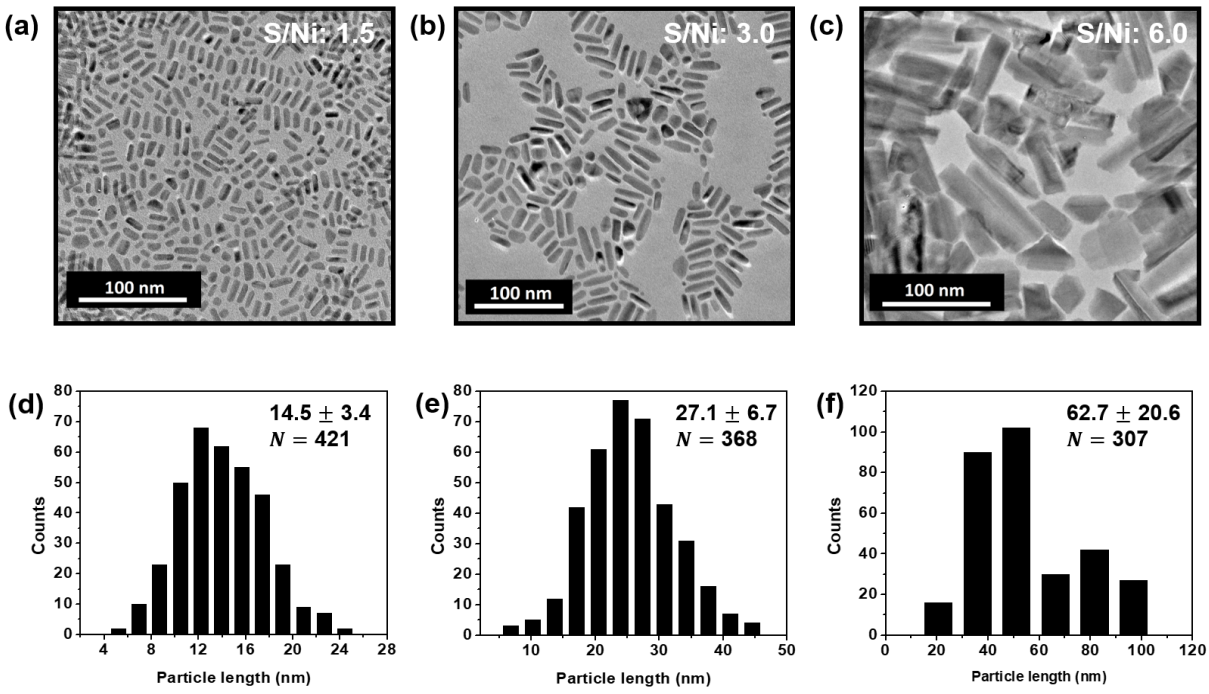

Fig. S6 TEM micrographs of Ni_9S_8 nanocrystals synthesized by the reaction of NiI_2 with 1-dodecanethiol at 180 ˚C for 2 h with thiol:Ni ratios of (a) 1.5, (b) 3.0 and (c) 6.0. Histograms of the particle length distributions for nanocrystals synthesized with (d) 1.5, (e) 3.0, and (f) 6.0 molar equivalents of 1-dodecanethiol.

Ni_9S_8 nanorod synthesis: Ni_9S_8 nanorods were synthesized by a similar synthetic approach. In this case, 1-dodecanethiol was used as the sole sulfur precursor. In a typical reaction, 0.38 mmol (0.12 g) of NiI_2 was dissolved in 5.0 mL of oleylamine. Various amounts of 1-dodecanethiol (*i.e.*, 1.5, 3.0 and 6.0 molar equivalents) were rapidly injected into the solution of NiI_2 in oleylamine at 180 ˚C. The reaction mixture was allowed to react for 2 h with stirring under flowing N_2, followed by thermally quenching the reaction by placing it in a water bath and allowing it to cool to room temperature.

Figure S5 provides the XRD patterns of the products from the reaction of NiI_2 with various amounts of 1-dodecanethiol at 180 ˚C for 2 h. Analysis of the as-synthesized products reveal that the particles crystallize into the same orthorhombic Ni_9S_8 structure. The diffraction peaks of the product synthesized using a molar thiol:Ni ratio of 1.5 are broader than those for ratios of 3.0 and 6.0. A sharpening of all the diffraction lines was observed upon increasing the thiol:Ni ratio, suggesting an increase in the particle size. Figure S6 provides the TEM images of the resulting nanocrystals synthesized using various amounts of 1-dodecanethiol. These micrographs indicate that when 1-dodecanethiol is used as the sole sulfur precursor, rod-like Ni_9S_8 nanocrystals are produced. The nanocrystal lengths were found to be 14.5 ± 3.4, 27.1 ± 6.7 and 62.7 ± 20.6 nm for 1.5, 3.0, and 6.0 molar equivalents of 1-dodecanethiol, respectively (Table S2). The TEM micrographs and particle length distributions show that the length of the nanorods becomes longer and edge lengths are more polydispersed as the amount of 1-dodecanethiol increased in the reaction.

Table S2. Synthetic conditions for the preparation of shape-controlled Ni_9S_8 nanoparticles. NiI_2 is reacted with various sulfur sources in oleylamine at 180 ˚C.

Sulfur precursor	S:Ni ratio	Reaction time (h)	Shape	Size (nm)
N,*N*'-diphenyl thiourea / 1-dodecanethiol	3.0 w/ 3.0 mL of 1-dodecanethiol	4	Spherical	8.8 ± 1.8
N,*N*'-dibutyl thiourea	10.0	1	Rod-like aggregates	~ 100
1-dodecanethiol	1.5	2	Rods	14.5 ± 3.4
1-dodecanethiol	3.0	2	Rods	27.1 ± 6.7
1-dodecanethiol	6.0	2	Bricks	62.7 ± 20.6

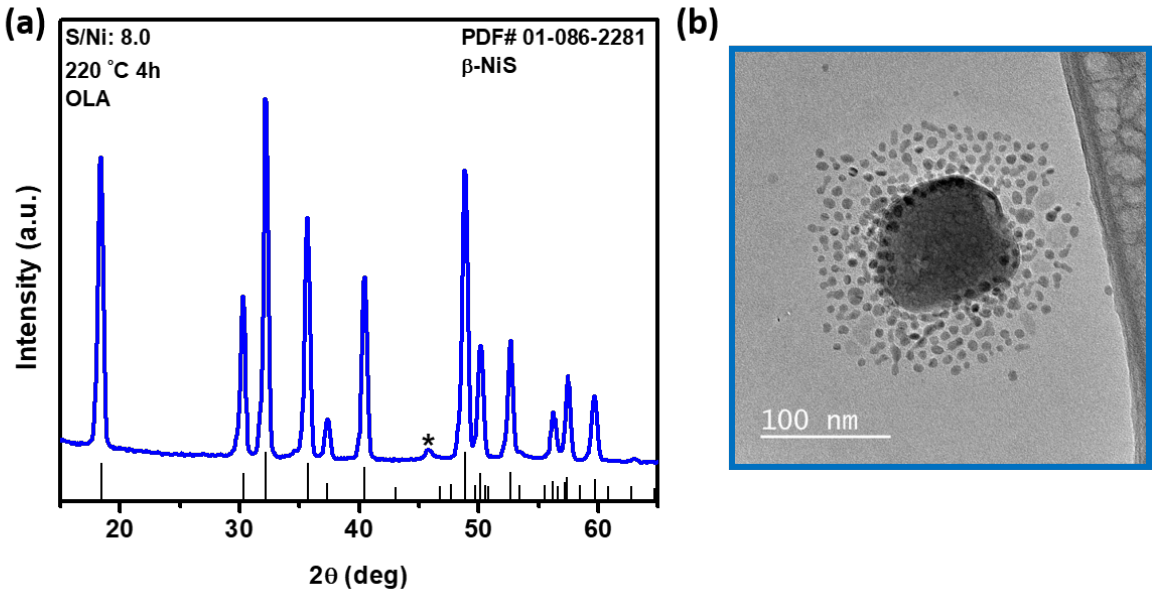

Fig. S7 (a) Powder XRD patterns of rhombohedral β-NiS nanocrystals synthesized by *N*,*N*'-diphenyl thiourea with the α-NiS impurity shown by (*). (b) TEM micrograph of β-NiS nanocrystals.

β-NiS Nanocrystal Synthesis. NiI_2 (0.38 mmol, 0.12 g) and degassed oleylamine (15.2 mmol, 5.0 mL) were added to a three-neck flask fitted with a reflux condenser and rubber septa. The solution was heated to 120 ˚C and degassed for 30 min under vacuum. *N*,*N*'-diphenyl thiourea (3.04 mmol, 0.70 g) was dissolved in dibenzylamine (20.8 mmol, 4.0 mL) and the solution was sparged by bubbling N_2 through it for 15 min. The solution of NiI_2 in oleylamine was heated for 220 ˚C, and then the *N*,*N*'-diphenyl thiourea solution was quickly injected into the reaction flask and allowed to react for 4 h with stirring under flowing N_2. The reaction was quenched by placing it in a water bath and allowing it to cool to room temperature.

The reaction of NiI_2 with an 8.0 molar excess of *N*,*N*'-phenyl thiourea in oleylamine at 220 ˚C for 4 h gives a colloidally unstable product with large particles and XRD analysis of the product reveals β-NiS nanocrystals with minor α-NiS impurities (Figure S7).