Simple and Generalized Synthesis of Semiconducting Metal Sulfide Nanocrystals

By *Sang-Hyun Choi, Kwangjin An, Eung-Gyu Kim, Jung Ho Yu, Jeong Hyun Kim,* and *Taeghwan Hyeon**

Uniform-sized semiconducting nanocrystals of binary metal sulfides are synthesized from the thermolysis of metal-oleate complexes in alkanethiol. The size of the Cu_2S nanocrystals can be tuned from 7 to 20 nm by varying the reaction conditions. Various shaped nanocrystals of CdS, ZnS, MnS, and PbS are synthesized from the thermal reaction of metal-oleate complex in alkanethiol.

1. Introduction

Nanocrystalline materials have attracted a great deal of attention from researchers in various areas for both their fundamental size- and shape-dependent properties and their many important technological applications.[1–7] Among the various nanocrystals,[8] transition metal chalcogenide nanocrystals have been investigated for many applications including biological labeling[9,10] and photovoltaic devices.[11–13] Over the past several years, several groups have reported the synthesis of metal sulfide nanocrystals[14] using various synthetic routes, including the thermolysis of single-source precursors,[15–18] solventless synthesis,[19,20] the thermolysis of metal-alkanethiolate precursors,[21–26] thermolysis of metal-oleylamine complexes,[27] and a simple organic amine-assisted hydrothermal process.[28]

Very recently, we reported ultra-large-scale synthesis of various uniform-sized transition metal oxide nanocrystals from the thermal decomposition of metal-oleate complexes.[29,30] In the continuation of the development of a simple method of synthesizing uniform-sized nanocrystals, we herein report on the generalized synthesis of uniform-sized nanocrystals of semiconducting metal sulfides from the thermolysis of a metal-oleate complex in alkanethiol.

[*] Prof. T. Hyeon, Dr. S.-H. Choi, Dr. K. An, E.-G. Kim, J. H. Yu, Dr. J. H. Kim
National Creative Research Initiative Center for Oxide Nanocrystalline Materials and School of Chemical and Biological Engineering
Seoul National University
Seoul 151-744 (Korea)
E-mail: thyeon@snu.ac.kr

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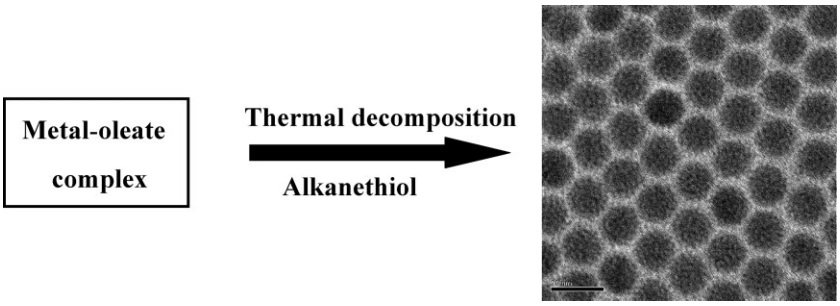
2. Results and Discussion

Metal sulfide nanocrystals were synthesized by the solution-phase thermal decomposition of metal-oleate complexes in alkanethiol (Scheme 1).[29,30] For the synthesis of copper sulfide nanocrystals, 3.18 g (5.088 mmol) of the Cu-oleate complex was dissolved in a solvent mixture containing 50 mL of oleylamine (152 mmol) and 50 ml of dodecanethiol ($C_{12}H_{25}SH$, 209 mmol) at room temperature, and the resulting reaction mixture was heated to 230 °C under argon flow and kept at this temperature for 20 min. Transmission electron microscopy (TEM) images (Fig. 1a and b) showed that the nanocrystals are highly uniform with a particle diameter of 18 nm. The high-resolution transmission electron microscopy (HRTEM) image (Fig. 1c) exhibited a distinct lattice fringe, demonstrating the high crystallinity of the nanocrystals. The electron diffraction (ED) pattern (Fig. 1d) can be clearly indexed to the standard chalcocite Cu_2S structure (JCPDS 84-0206), which is also confirmed by the X-ray diffraction (XRD) pattern shown in Figure 4a. GC–MS spectrum of the byproducts obtained from the thermal decomposition of the Cu-oleate complex in dodecanethiol showed two peaks corresponding to oleic acid and 1-dodecene, demonstrating that the following reaction seems to be responsible for the synthesis of the Cu_2S nanocrystals: $C_{12}H_{25}SH + 2\ \text{Cu-(OC(=O)}C_{17}H_{33} \rightarrow Cu_2S + 2\ C_{17}H_{33}C(=O)OH + C_{12}H_{24}$ (see Fig. S1 of the Supporting Information). Inductive coupled plasma-mass spectroscopy (ICP-MS) and elemental analysis (EA) of the 18-nm-sized Cu_2S nanocrystals revealed atomic percentage of 54% and 26%, respectively. Recently, Korgel and his co-workers reported the solventless synthesis of copper sulfide nanocrystals from the thermolysis of copper-alkanethiol complex without using co-ordinating solvent.[20] Comparing with the solventless synthesis, we speculate that the excess oleic acid in the co-ordinating solvent is responsible for the production of monodisperse Cu_2S nanocrystals.

The particle sizes of the Cu_2S nanocrystals could be controlled by varying reaction temperature, time, and the molar ratio of oleylamine and dodecanethiol. When the amount of dodecanethiol was decreased to 10% of that used for the above synthesis of 18-nm-sized nanocrystals and the reaction was conducted at 215 °C for 60 min, 7-nm-sized Cu_2S nanocrystals were produced (Fig. 2a). When the synthesis was performed at 215 °C for 20 min with keeping other reaction conditions the same as those employed for the synthesis of 18-nm-sized nanocrystals, 15-nm-sized Cu_2S nanocrystals were obtained



Scheme 1. The overall synthetic procedure for metal sulfide nanocrystals.

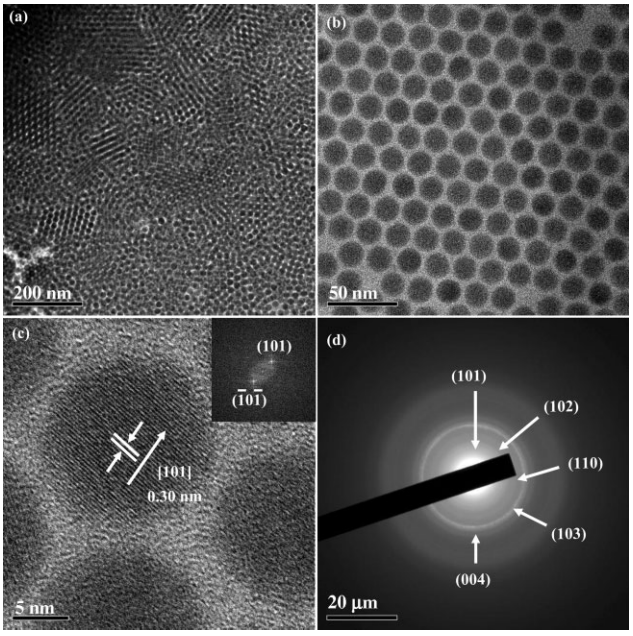


Figure 1. a, b) TEM images, c) HRTEM image (inset: FFT image), and d) ED pattern of 18-nm-sized Cu_2S nanocrystals.

(Fig. 2b). When the reaction was performed at the same temperature of 215 °C for longer 60 min, 19-nm-sized Cu_2S nanocrystals were generated (Fig. 2c). When the reaction mixture used for the synthesis of 18-nm-sized nanocrystals was heated to 230 °C, and cooled down to 150 °C and kept at this temperature for 17 h, 20-nm-sized nanocrystals were produced (Fig. 2d).

The monodisperse Cu_2S nanocrystals could be synthesized not only in a size-controlled manner but also in a shape-controlled manner. When the amount of Cu-oleate complex was doubled and the amount of dodecanethiol was decreased to 50% of that used for the above synthesis of 18-nm-sized nanocrystals, disk-shaped Cu_2S nanocrystals were obtained (Fig. 3). The TEM images obtained by tilting along the *x*-axis from –27.2 ° to + 27.2 ° (Fig. 3a–c) clearly showed the disk-shaped nanocrystals with an average diameter of ~30 nm. The HRTEM image (Fig. 3d) showed highly crystalline chalcocite Cu_2S structure. The reduction of the amount of dodecanethiol, which acted as the sulfur source, with respect to Cu-oleate complex, was responsible for the formation of the disk-shaped Cu_2S nanocrystals. The results are very similar to our group's previous results on the generalized synthesis of uniform-sized metal sulfide nanocrystals, where the ratio of metal-oleylamine complex and sulfur was responsible for the shape control of the CdS nanocrystals.[14]

Using a similar thermal decomposition of metal-oleate complexes in dodecanethiol, nanocrystals of ZnS, CdS, MnS, and PbS were synthesized. Figure 5 shows TEM images of tetrahedron-shaped ZnS nanocrystals with an average side dimension of 10 nm (Fig. 5a), tetrahedron-shaped CdS nanocrystals with an average side dimension of 10 nm (Fig. 5b), pseudo-spherical shaped MnS nanocrystals with an average diameter of 11 nm (Fig. 5c, XRD of Fig. S2), and cube-shaped PbS nanocrystals with an average side dimension of 47 nm (Fig. 5d). Figure 4 shows the XRD patterns of ZnS nanocrystals with zinc blende structure (Fig. 4b, JCPDS No. 80-0020), CdS nanocrystals with wurtzite structure (Fig. 4c, JCPDS No. 80-0006), and PbS nanocrystals with cubic structure (Fig. 4d, JCPDS No. 78-1901).

The optical properties of nanocrystals of ZnS and CdS were characterized by UV/vis absorption and photoluminescence (PL) spectroscopy. The UV/vis absorption spectrum of the 10-nm-sized ZnS nanocrystals (Fig. 6a) showed an absorption band at around 340 nm, which is similar to the bulk bandgap. The photoluminescence spectrum of the ZnS nanocrystals showed a strong peak at 342 nm and a weak shoulder at ~400 nm, which can be assigned to a band-edge emission and shallow-trap emission peak, respectively. The small peak at ~450 nm can be attributed to the deep-trap emission.[23,24] As in case of our previous report on the synthesis of ZnS nanocrystals, the excess alkanethiol seems to be responsible for the reduction of trap-state emission, which is

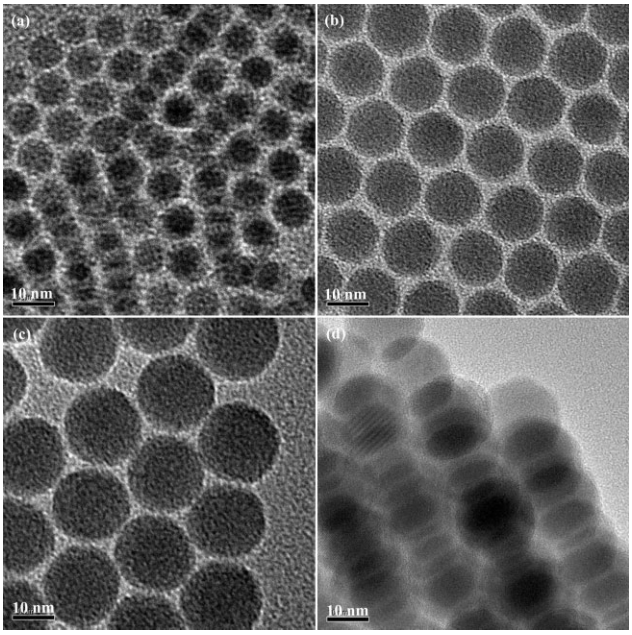


Figure 2. TEM images of Cu_2S nanocrystals with particle diameters of a) 7 nm, b) 15 nm, c) 19 nm, and d) 20 nm.

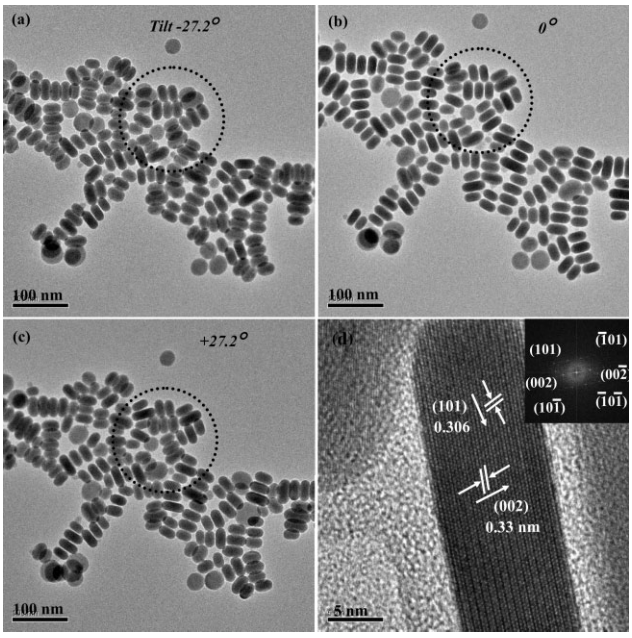


Figure 3. TEM images of disk-shaped Cu_2S nanocrystals by tilting along the *x*-axis: a) −17.2°, b) 0°, c) +17.2°, and d) HRTEM image.

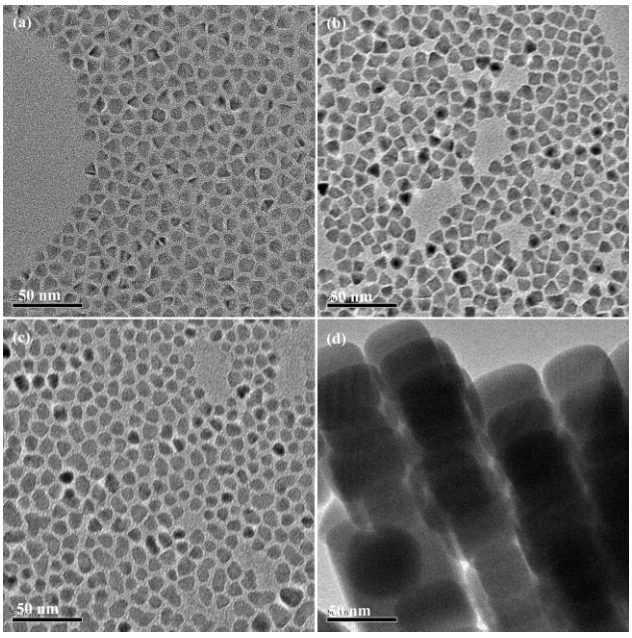


Figure 5. TEM images of nanocrystals of a) ZnS, b) CdS, c) MnS, and d) PbS.

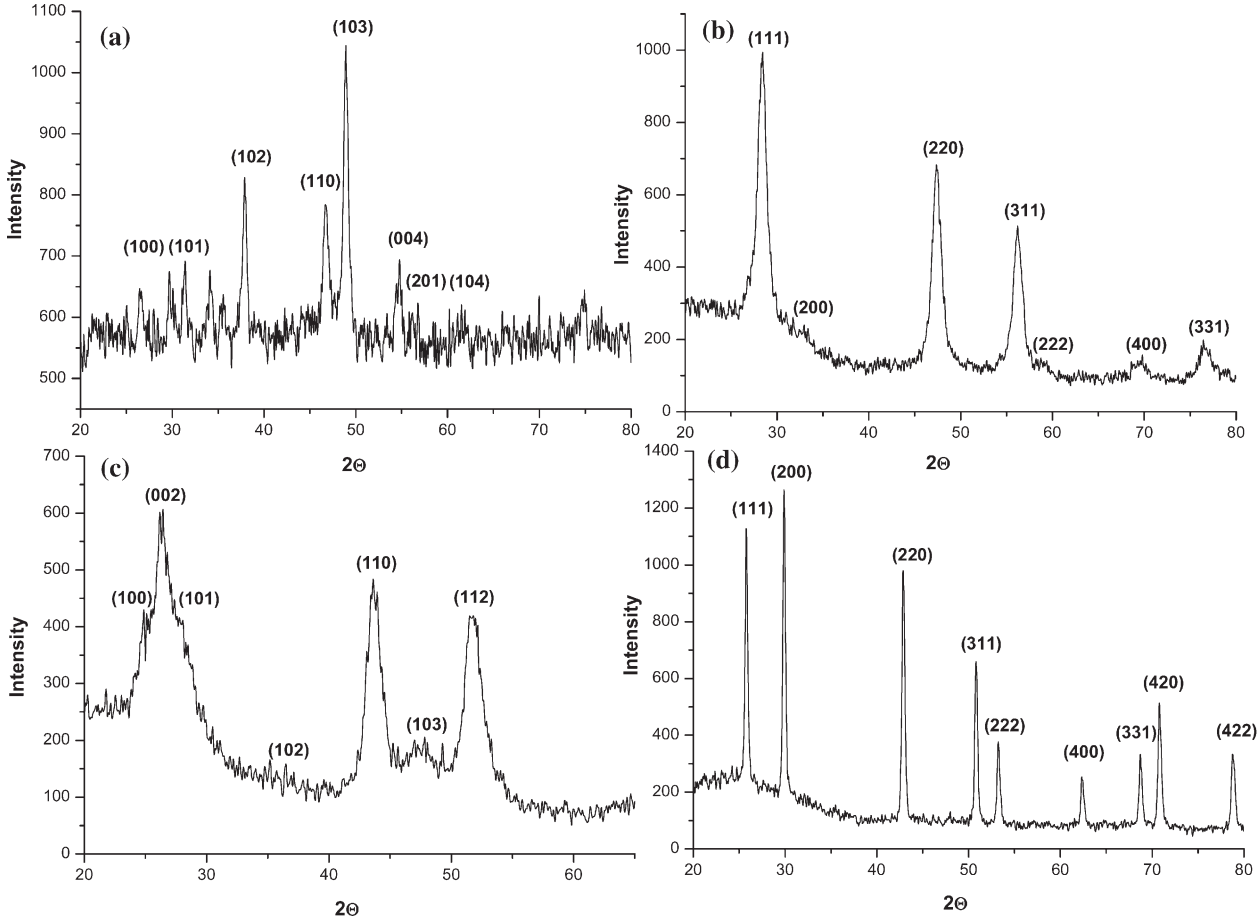


Figure 4. XRD patterns of nanocrystals of a) Cu_2S, b) ZnS, c) CdS, and d) PbS.

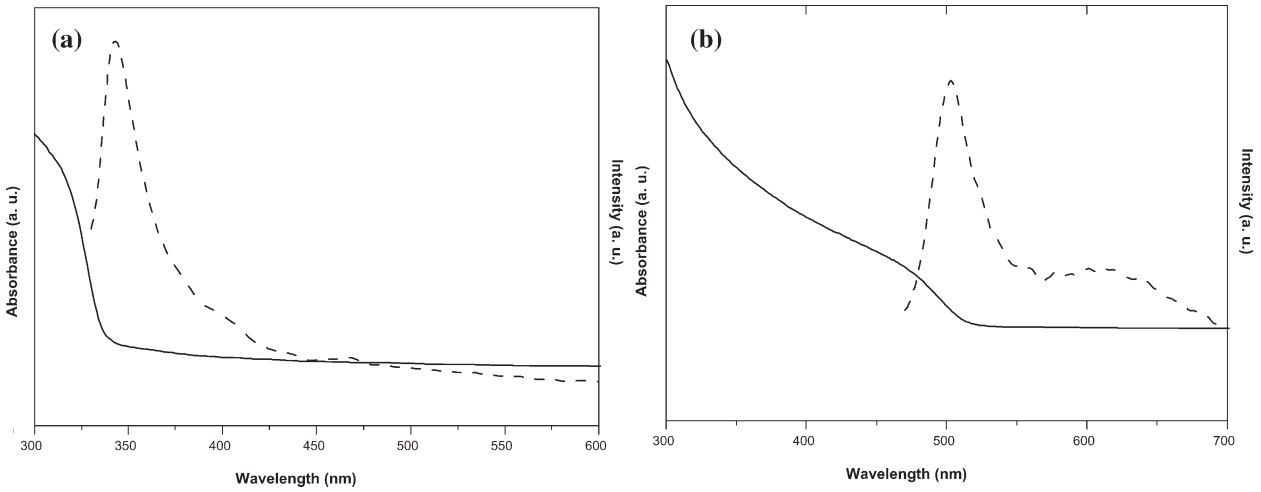


Figure 6. UV/vis absorption spectra (solid lines) and the PL spectra (dashed lines) of a) ZnS nanocrystals and b) CdS nanocrystals.

mainly originated from the surface-vacant sites.[27] Figure 6b shows the representative absorption and photoluminescence spectra of the 10-nm-sized CdS nanocrystals in chloroform. The UV/vis absorption spectrum of the 10-nm-sized CdS nanocrystals exhibited an excitonic peak at 470 nm, and their PL spectrum shows a band-edge emission at around 503 nm and a broad trap state emission at around 605 nm.

3. Conclusions

In summary, we describe a generalized synthetic procedure for uniform-sized metal sulfide nanocrystals from the thermolysis of metal-oleate complexes in dodecanethiol. The current synthetic procedure is simple and highly reproducible. Furthermore, the resulting metal sulfide nanocrystals can be produced in large quantity, which is important for industrial applications.

4. Experimental

Chemicals: Hexane, ethanol, toluene, distilled water, and acetone were used as received. Copper(II) chloride ($CuCl_2 \cdot 2H_2O$, 99%) and manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 98%) were purchased from Aldrich Chemicals. Lead(II) nitrate ($Pb(NO_3)_2$, 98%) was purchased from Strem Chemicals. Potassium oleate ($C_{17}HCOOK$, 95%) and sodium oleate ($C_{17}HCOONa$, 95%) were purchased from TCI organic Chemicals. Cadmium chloride 2.5-hydrate ($CdCl_2 \cdot 2.5H_2O$, 98%) was purchased from Kanto Chemicals. Dodecanethiol ($CH_3(CH_2)_{11}SH$, 98%), octanethiol ($CH_3(CH_2)_7SH$, 97%), hexadecanethiol ($CH_3(CH_2)_{15}SH$, 92%), octadecanethiol ($CH_3(CH_2)_{17}SH$, 96%), phenylthiol (C_6H_5SH, 99%), zinc chloride ($ZnCl_2$, 98%), and oleylamine ($CH_3(CH_2)_7CH{=}CH(CH_2)_8NH_2$, 90%) were purchased from Acros Chemicals.

Synthesis of Cu_2S Nanocrystals: Cu-oleate complex was prepared by reacting copper chloride and sodium oleate. In a typical synthesis of the Cu-oleate complex, 5.45 g of copper chloride ($CuCl_2 \cdot 2H_2O$, 40 mmol, Aldrich, 99%) and 24.35 g of sodium oleate (80 mmol, TCI, 95%) were dissolved in a solvent mixture composed of 80 mL of ethanol, 60 mL of distilled water and 140 mL of hexane. The resulting solution was heated to 70 °C and kept at this temperature for 4 h. When the reaction was complete, the upper organic layer containing the Cu-oleate complex was washed three times with 30 mL of distilled water in a separatory funnel. After washing, the hexane was evaporated off, yielding the Cu-oleate complex in solid form. In a typical synthesis of the 18-nm-sized Cu_2S nanocrystals, 3.18 g (5.088 mmol) of the Cu-oleate complex was dissolved in a mixture containing 50 mL of oleylamine and 50 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 230 °C under argon flow and kept at this temperature for 20 min. The solutions gradually changed from yellow to a deep-brown colloidal solution. The solution was then cooled to room temperature, and excess ethanol was added to yield a deep brown precipitate, which was then separated by centrifuging.

For the synthesis of 7-nm-sized nanocrystals, 3.18 g (5.10 mmol) of the Cu-oleate complex was dissolved in a solvent mixture containing 50 mL of oleylamine and 5 ml of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 215 °C and kept at this temperature for 60 min. For the synthesis of 15-nm-sized nanocrystals, 3.18 g (5.088 mmol) of the Cu-oleate complex was dissolved in a mixture containing 50 mL of oleylamine and 50 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 215 °C under argon flow and kept at this temperature for 20 min. When the reaction mixture used for the synthesis of 18-nm-sized nanocrystals was heated to 230 °C, and cooled down to 150 °C and kept at this temperature for 17 h, 20-nm-sized nanocrystals were produced. For the synthesis of disk-shaped nanocrystals, 6 g (9.6 mmol) of the Cu-oleate complex was dissolved in a solvent mixture containing 50 mL of oleylamine and 25 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 230 °C and kept at this temperature for 20 min.

Synthesis of PbS Nanocubes: In a typical synthesis of Pb-oleate complex, 13.24 g of lead(II) nitrate ($Pb(NO_3)_2$, 40 mmol, Strem, 98%) and 25.64 g of potassium oleate (80 mmol, TCI, 95%) were dissolved in a solvent mixture composed of 80 mL of ethanol, 60 mL of distilled water, and 140 mL of hexane. For the synthesis of PbS nanocubes, 3 g of the Pb-oleate complex was dissolved in a mixture containing 50 mL of oleylamine and 50 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 230 °C under argon flow and kept at this temperature for 60 min. The solution was gradually changed from white to a black colloidal solution. The solution was then cooled to room temperature, and excess ethanol was added to yield a black precipitate, which was then separated by centrifuging.

Synthesis of MnS Nanocrystals: In a typical synthesis of Mn-oleate complex, 7.92 g of manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 40 mmol, Aldrich, 99%) and 24.36 g of sodium oleate (80 mmol, TCI, 95%) were dissolved in a solvent mixture composed of 80 mL of ethanol and 60 mL of distilled water and 140 ml of hexane. To obtain the MnS nanocrystals, 3 g of the Mn-oleate complex was dissolved in a mixture containing 50 mL of oleylamine and 50 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 280 °C under

argon flow and kept at this temperature for 1 h. The solution gradually changed to a deep green colloidal solution. The solution was then cooled to room temperature, and excess ethanol was added to yield a deep-green precipitate, which was separated by centrifuging.

Synthesis of CdS Nanocrystals: Cd-oleate complex was prepared by reacting cadmium chloride 2.5-hydrate and potassium oleate. In a typical synthesis of the Cd-oleate complex, 4.57 g of cadmium chloride 2.5-hydrate ($CdCl_2 \cdot 2.5H_2O$, 20 mmol, Kanto, 98%) and 12.18 g of potassium oleate (40 mmol, TCI, 95%) were dissolved in a solvent mixture composed of 40 mL of ethanol, 30 mL of distilled water, and 70 mL of hexane. To obtain the CdS nanocrystals, 3 g of the Cd-oleate complex was dissolved in a mixture containing 50 mL of oleylamine and 50 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 300 °C under argon flow and kept at this temperature for 30 min. The solution gradually changed to a yellow colloidal solution. The solution was then cooled to room temperature, and excess ethanol was added to yield a yellow precipitate, which was separated by centrifuging.

Synthesis of ZnS Nanocrystals: Zn-oleate complex was prepared by reacting zinc chloride and sodium oleate. In a typical synthesis, 5.45 g of zinc chloride ($ZnCl_2$, 40 mmol, Acros, 98%) and 24.35 g of sodium oleate (80 mmol, TCI, 95%) were dissolved in a solvent mixture composed of 80 mL of ethanol, 60 mL of distilled water, and 140 mL of hexane. To obtain the ZnS nanocrystals, 3 g of the Zn-oleate complex was dissolved in a mixture containing 50 mL of oleylamine and 50 mL of dodecanethiol at room temperature, and the resulting reaction mixture was heated to 310 °C under argon flow and kept at this temperature for 30 min. The solution changed gradually a white colloidal solution. The solution was then cooled to room temperature, and excess ethanol was added to yield a white precipitate, which was separated by centrifuging.

Characterization of Materials: Metal sulfide nanocrystals were characterized by low- and high-resolution TEM ED and XRD. The TEM images were obtained on JEOL 2010 microscope operated at 200 kV. Powder X-ray diffraction (XRD) was performed using a Rigaku D/Max-3C diffractometer (Cu Kα radiation, $\lambda = 0.15418$ nm). UV/vis absorption and photoluminescence (PL) spectra were obtained using a Perkin-Elmer Lambda Model 20 UV/vis absorption spectrometer and JASCO FP750 spectrofluorometer, respectively.

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