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Liquid-Phase Syntheses and Material Properties of Two Dimensional Nanocrystals of Rare Earth-Selenium Compound Containing Planar Se-Layers: RESe₂ Nanosheets and RE₄O₄Se₃ Nanoplates

Jun Gu, Ze-Qiong Zhao, Yi Ding, Hong-Liang Chen, Ya-Wen Zhang, and Chun-Hua Yan

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Liquid-Phase Syntheses and Material Properties of Two Dimensional Nanocrystals of Rare Earth-Selenium Compound Containing Planar Se-Layers: RESe₂ Nanosheets and RE₄O₄Se₃ Nanoplates

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ABSTRACT: Synthesis of diverse two dimensional nanostructures with unique material properties is of current interests and multidisciplinary importance, but remains a challenge for trivalent rare earth (RE) - selenium (Se) compounds because of the weak affinity between hard rare earth cations and soft selenium anions. In this article, for the first time, we report a mild solution approach towards a series of two dimensional trivalent RE-Selenium compound nanocrystals, namely RESe₂ nanosheets (RE = La to Nd, for EuSe₂, nanobars were obtained) and RE₄O₄Se₃ nanoplates (RE = Nd, Sm, Gd to Ho), under a high chemical potential of selenium obtained by activating SeO₂ powder with oleylamine in high-boiling-point organic solvents. Both kinds of nanocrystals contain Se with -1 valence in planar Se-layers, allowing for a great variability in their crystal structures. Satellite diffraction peaks were observed in the electron diffraction pattern of LaSe₂ nanosheets, indicating the presence of Peierls distortion in the Se-layers. In the RE₄O₄Se₃ nanoplates, the interaction between Se²⁻ ions and [Se-Se]²⁻ dumbbells in the Se-layers increases when the radii of the RE³⁺ ions decrease along the lanthanide series, resulting in a narrower optical band gap (from 1.96 eV to 1.73 eV). The LaSe₂ nanosheet films fabricated by drop-casting exhibited good electrical conductivity at room temperature (about 1 Ω·cm⁻¹). Further, the RE₄O₄Se₃ nanoplates showed very high light extinction capacity in the visible region (extinction coefficient μ_i : 4.4×10⁵ cm⁻¹ for Nd₄O₄Se₃, and 3.1×10⁵ cm⁻¹ for Gd₄O₄Se₃), comparable to that (5×10⁵ cm⁻¹) of CuInS₂ commonly used in solar cells.

INTRODUCTION

Colloidal methods have been used to synthesize numerous two-dimensional (2D) nanocrystals (NCs).^{1,2} Chalcogenide (sulfide, selenide and telluride) compounds with layered structures, such as topological insulators³, ferromagnets⁴, charge density wave conductors⁵⁻⁷ and superconductors⁸, are one family of the most important 2D materials. They demonstrate practical applications including transistors^{9,10}, supercapacitors¹¹ and thermoelectric devices¹², etc. Compared with micromechanical exfoliation⁹ and vapor deposition¹⁰, colloidal methods promise highly efficient preparation of free-standing 2D chalcogenide nanomaterials at lower cost.¹³⁻²¹ For example, Hyeon and co-workers synthesized CdSe nanoribbons with uniform thickness of 1.4 nm through a Lewis acid-base reaction between cadmium cations and selenocarbamate anions at low temperature.¹³ Dubertret and co-workers realized the thickness controlled synthesis of CdSe platelets.¹⁴ Weller and co-workers showed that single-crystal ultrathin PbS nanosheets could be synthesized by oriented attachment of smaller PbS nanocubes, and the as-formed nanosheets could be further integrated into a photo-detector device through a simple spin-coating method.¹⁷ Additionally, colloidal 2D nanomaterials, including chalcogenides of d-block elements^{15,16,19}, In₂S₃²⁰, SnSe²¹, have been synthesized.

Among chalcogenides and oxy-chalcogenides of various metals, those of rare earth (RE) elements possess interesting structures and properties. Doert and co-workers explored a series of RE polychalcogenide crystals prepared by chemical

transport reaction of elementary substances, containing infinite planar layers of chalcogen atoms, with the chemical formulas as REX₂²², REXY²³, REX₂-₆^{24,25} and REXY₂^{26,27} (X, Y = S, Se, Te). Many of these materials were described to be 2D charge density wave compounds. Due to the special electronic structure, the chalcogen layers in the crystals adopt Peierls distortion, resulting in satellite reflections in diffraction characterization. RE oxy-selenide with the formula of RE₄O₄Se₃ is another type of material containing Se-planes with parallel -Se²⁻-[Se-Se]²⁻- chains. Schleid and co-workers prepared RE₄O₄Se₃ (RE = La to Nd, Sm) through the solid state reactions of RE metal, elemental selenium and SeO₂, and investigated their optical and magnetic properties.^{28,29} It is of great interest to examine the properties of these materials when the thickness of the crystal is confined within several nanometers.

In recent years, a lot of efforts have been devoted to the syntheses of colloidal NCs of different types of compounds of trivalent RE, including oxide (RE₂O₃)^{30,31}, fluoride (REF₃)^{32,33}, NaREF₄^{34,35}, oxy-halide (REOX, X = F, Cl)^{36,37} and oxysulfide (RE₂O₂S)³⁸⁻⁴¹. Among these materials, RE oxide, fluoride and oxysulfide NCs exhibit 2D disk morphology. According to hard soft acid base (HSAB) theory⁴², trivalent RE ions are classified as hard acid, possessing strong affinity towards oxygen and halide ions but weak affinity towards S²⁻, Se²⁻ and Te²⁻ ions. The syntheses of EuS⁴³, EuSe⁴⁴ and EuSe₂⁴⁵ NCs have been reported previously, but in all of these materials Eu element is divalent. In our previous work, by introducing alkali metal ions (e.g. Na⁺) as mediator and dopant, doped RE₂O₂S

nanoplates^{39,40} and NaRES₂ NCs⁴⁶ were prepared. So far, the synthesis of trivalent RE selenide and oxy-selenide NCs has still remained a big challenge in this field.

In this work, for the first time, two types of 2D NCs, RESe₂ nanosheets (RE = La to Nd, for EuSe₂, nanobars were obtained) and RE₄O₄Se₃ nanoplates (RE = Nd, Sm, Gd to Ho), were synthesized in a mixture of oleic acid, oleylamine and 1-octadecene. Excess SeO₂ was used as Se-source and activated by oleylamine to provide high chemical potential of Se element in the reaction mixture. The formation conditions of these two types of NCs are discussed. Among these NCs, LaSe₂ nanosheets with side length of about 1 μm were generated from screw dislocation driven growth. Satellite diffraction peaks were observed in the electron diffraction pattern of LaSe₂ nanosheets, indicating the distortion of the Se-layers. Furthermore, LaSe₂ nanosheet films fabricated with a spin-coating method exhibited good electrical conductivity at room temperature. RE₄O₄Se₃ nanoplates displayed high light-extinction property in visible light region, which might endow them with promising applications in light filters and solar cells. The optical band gap of RE₄O₄Se₃ nanoplates decreased from light RE to heavy RE, possibly due to the interaction between Se²⁻ ions and [Se-Se]²⁻ dumbbells caused by lattice shrinkage.

EXPERIMENTAL SECTION

Materials. Oleic acid (OA; 90%, Aldrich), oleylamine (OM; > 80%, Acros), 1-octadecene (ODE; > 90%, Acros), cerium(III) acetate hydrate (Ce(Ac)₃·xH₂O; 99.9% metals basis, Aldrich), RE oxides (RE₂O₃, RE = La, Pr, Nd, Sm to Ho; > 99.99%), acetylacetone (Hacac; A. R. grade), selenium dioxide (SeO₂, A. R. grade), trioctylphosphine (TOP; 90%, Aldrich), nitric acid (HNO₃; A. R. grade), ammonia (NH₃·H₂O; A. R. grade), sodium hydroxide (NaOH; > 96%), absolute ethanol (> 99.7%) and cyclohexane (>99.5%) were used as received.

Synthesis of RESe₂ (RE = La to Nd, Eu) and RE₄O₄Se₃ (RE = Nd, Sm, Gd to Ho) NCs. RE acetylacetonate (RE(acac)₃, RE = La, Pr, Nd, Sm to Ho) was prepared by following the previously-reported procedure.³¹ The reaction parameters for every sample were listed in Table S1. Schlenk line was used under N₂ atmosphere. RE(acac)₃ or Ce(Ac)₃ (0.5 mmol), SeO₂, OA (1.41 g), OM (4.55 g) and ODE (5.05 g) were loaded into a three-neck flask (100 mL) on a heater with a magnetic stirrer at room temperature. The mixture was heated under vacuum and kept at 80 °C for 5 min and at 100 °C for 20 min, to remove water and oxygen and to form RE oleate in situ.⁴⁶ The mixture was then heated to the synthetic temperature listed in Table S1 at a rate of 20 °C·min⁻¹ and kept at this temperature for a certain duration (as listed in Table S1) under N₂. Then the mixture was air-cooled to 160 °C and TOP (0.7 mL when 0.222 g of SeO₂ was added, 1.5 mL when 0.444 g of SeO₂ was added) was injected into the flask to reduce elemental Se byproduct. The mixture was kept at 120 °C for 5 min, and then was cooled to room temperature. 40 mL ethanol was added, followed by centrifugation at 7800 rpm for 10 min. The supernatant was discarded and the precipitate was dispersed in 10 mL cyclohexane under ultrasonic wave. After centrifugation at 3000 rpm for 3 min, the black or dark brown precipitate A and the supernatant B were separated by decantation.

To purify RESe₂ NCs, the precipitate A should be washed by cyclohexane for three times. For each time, the precipitate

was dispersed in 10 mL cyclohexane and the mixture was treated under ultrasonic wave for 5 min, followed by centrifugation at 3000 rpm for 3 min. Then the supernatant was discarded. Finally, the precipitate was dried in vacuum or re-dispersed in cyclohexane for further characterization.

To obtain RE₄O₄Se₃ nanoplates, 20 mL of ethanol was added into the supernatant B, followed by centrifugation at 18000 rpm for 10 min. The supernatant was discarded and the precipitate was re-dispersed in 10 mL of cyclohexane. The same procedure was conducted once again. At last, the nanoplates could be preserved in cyclohexane or as powder sample after vacuum drying.

Resistivity measurement of LaSe₂ nanosheet films. The LaSe₂ films for electrical measurements were prepared by drop-casting 150 μL of the dispersion of as-synthesized LaSe₂ nanosheets (10 mg·mL⁻¹) onto silicon wafers (1 cm × 1 cm) covered with 300 nm thick thermally grown octadecyltrichlorosilane-modified silicon dioxide surface. Then the thickness of the film was about 2 μm. The as-deposited samples were dried at 80 °C for 30 min, followed by thermal treatment at 300 °C in air for 30 min. Four-electrode configuration was used to minimize the contact resistance. Thermal evaporation was used to deposit metal electrodes, with chromium/gold (5 nm/50 nm) through a shadow mask. The channel length and width were 700 μm and 4 mm, respectively. Resistivity measurements of as-prepared films were carried out on a CHI 840B electrochemical analyzer (CH Instrument, TX, USA). Constant current was loaded on the outer two electrodes and the voltage between the inner two electrodes was measured.

Instrumentation. X-ray diffraction (XRD) patterns of the dry powders were characterized on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2° at a scanning speed of 2°·min⁻¹ using Cu Kα radiation. Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of cyclohexane dispersion of the NCs on copper grids coated by amorphous carbon. TEM, selected area electron diffraction (SAED), High resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDS) analyses were performed on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV. Particle sizes were counted from at least 50 NCs. Samples for scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses were prepared by drying a drop of diluted cyclohexane dispersion of NCs on silicon wafers. SEM analyses were conducted on a FEG-SEM (S-4800, Hitachi, Japan) operated at 8.0 kV. The AFM images were acquired with Nanoscope IIIA multimode AFM (Digital Instruments) using tapping mode at room temperature. The absorption spectra were taken on a UV-vis spectrophotometer (UV-3100, Shimadzu, Japan). Quartz absorption cells with optical length of 1 cm were used. Infrared (IR) spectra were taken on a Bruker Vector22 FTIR spectrometer (Germany). The concentrations of the NCs in the dispersions were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, PROFILE SPEC, Leeman, USA). To prepare the solution for ICP-AES analysis, 1.000 mL of NCs dispersion in a crucible was firstly dried on a vapor bath. Then the crucible was put into a muffle furnace and kept at 800 °C for 3 h. After the crucible cooled down, the residue was dissolved by concentrated nitric acid and transferred to a volumetric flask. C-H-N elemental analysis was conducted on a vario EL elemental analyzer (Elementar Analysensysteme GmbH, Germany). X-ray photoelectron spectroscopy (XPS)

analysis was taken on an Axis Ultra imaging photoelectron

spectrometer (Kratos Analytical Ltd., UK).

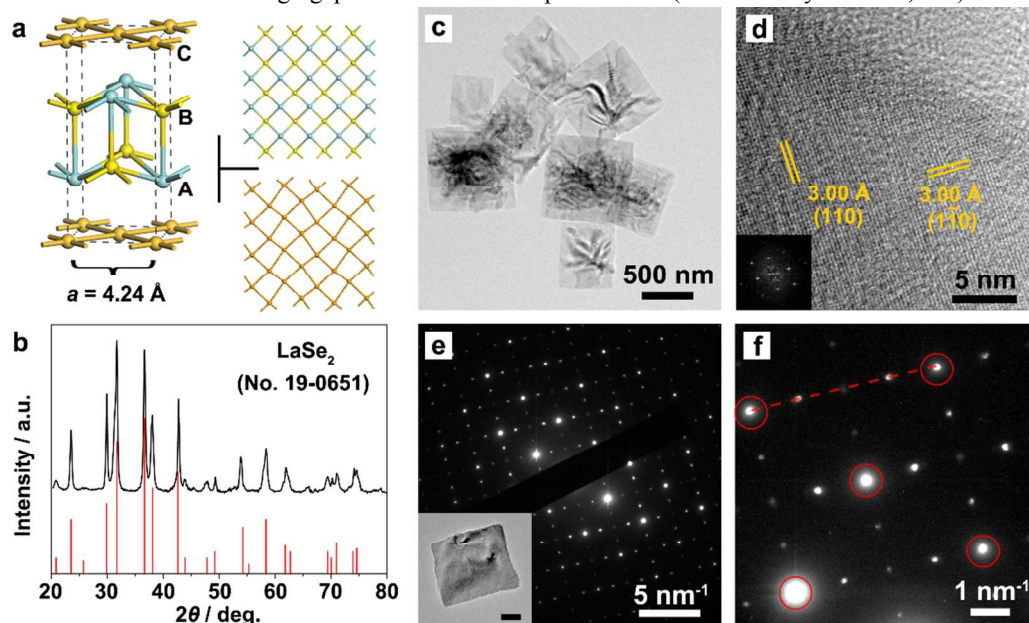


Figure 1. Structure characterizations of LaSe₂ nanosheets: (a) the crystal structure of LaSe₂. Left part shows a tetragonal ZrSSi-type unit cell divided into three layers, i.e. A, B and C. In LaSe₂, La³⁺, Se²⁻ and Se⁻ occupy Zr-sites (blue ball), S-sites (yellow ball) and Si-site (orange ball), respectively. The cell parameter *a* for LaSe₂ is 4.24 Å. Right-top part shows the top-view of A and B layers without distortion. Right-bottom part shows the top view of C layer (planar Se-layer), which distorts due to Peierls' theorem; (b) XRD pattern, compared with the standard XRD pattern of orthorhombic LaSe₂ (JCPDS No. 19-0651); (c) TEM images; (d) HRTEM images and corresponding FFT pattern (inset); (e) SAED pattern of the LaSe₂ nanosheets shown in the inset (scale bar: 200 nm); (f) SAED pattern of the same LaSe₂ nanosheets shown in panel (e) obtained at a longer camera length (main diffraction peaks are highlighted by red circles and satellite peaks appear between two main peaks, as indicated by the dashed red line).

RESULTS AND DISCUSSION

Structure characterizations of RESe₂ nanosheets. (RE = La to Nd, Eu) NCs could be prepared with the method presented in the experimental section. Among them, RESe₂ (RE = La to Nd) nanosheets appeared black powders while EuSe₂ nanobars were brown powder. When the black powder of LaSe₂ nanosheets was compressed, metallic luster could be observed on the surface of the sample, indicating that LaSe₂ nanosheets may possess high conductivity. A detailed structure characterization of the LaSe₂ nanosheets is shown in Figure 1. The crystal structure of LaSe₂ was derived from that of ZrSSi in tetragonal phase. Left part of Figure 1a shows a cell in ZrSSi type. La³⁺ ions occupy the Zr-sites (blue balls) and Se²⁻ ions occupy the S-sites (yellow balls) in layer A and B. Furthermore, Si-sites (orange balls) in layer C are also occupied by Se element. To balance the charge in LaSe₂ cell, every Se atom on Si-site has to gain one more electron to form Se⁻ ion.^{47,48} Since an unpaired electron exists in Se⁻ ions, Se⁻ monolayer will distort due to Peierls' theorem, as illustrated in the lower right part of Figure 1a.

Black line in Figure 1b is the XRD pattern of LaSe₂ nanosheets, which is in good accordance with the standard XRD pattern of LaSe₂ bulk material (red line, JCPDS No. 19-0651). Calculated from the XRD pattern, the lattice parameters of tetragonal LaSe₂ nanosheets were *a* = 4.2432(5) Å and *c* = 8.588(2) Å. Figure 1c shows the TEM image of LaSe₂ nanosheets. All of the LaSe₂ nanosheets show the square shape and the average side length of the nanosheets is 1.0 ± 0.2 μm. The molar ratio between La and Se obtained from EDX analysis (Figure S1a) is 36:64, which is near the stoichiometric ratio

of 1:2. Figure 1d shows the HRTEM image of the edge of a LaSe₂ nanosheets and the inset shows the corresponding fast Fourier transformation (FFT) pattern. The distance between two nearest lattice fringes is 3.00 Å, which equals the spacing between two nearest (110) planes (crystal indices here are defined based on the unit cell shown in the left part of Figure 1a). This indicates that the basal plane of the nanosheet is perpendicular to the *c* axis of the unit cell and the edge of the nanosheet is parallel to the *a* axis.

Figure 1e shows the SAED pattern of a LaSe₂ nanosheet shown in the inset, and Figure 1f is an SAED pattern of the same nanosheet obtained at a longer camera length. Main diffraction peaks in Figure 1f are highlighted by red circles. The reciprocal of the length of the red dashed line equals *a*/2, i.e. 2.12 Å. Since the (100) diffraction peaks should disappear due to systematic extinction, only diffraction peaks in red circles should be observed if the atomic arrangement in LaSe₂ nanosheets keeps all the symmetry of ZrSSi. The appearance of other diffraction peaks indicates the distortion in layer C and the breaking of the original tetragonal symmetry. Satellite diffraction peaks appear at 1/4 positions between two nearest main diffraction peaks along the <100> direction, indicating that the Se⁻ layers distort into a commensurate modulated structure.

The TEM images of RESe₂ (RE = Ce to Nd, Eu) NCs are shown in Figure S2 (the insets show the corresponding SAED patterns). Square nanosheets with side length of 400±30 nm were obtained in the case of CeSe₂, while PrSe₂ and NdSe₂ nanosheets curled into nanotubes with the length of several micrometers. Both of CeSe₂ and PrSe₂ nanosheets were well crystallized single crystals, while NdSe₂ nanosheets were

poorly crystallized. $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates existed as impurities together with PrSe_2 and NdSe_2 nanosheets. Single-crystalline EuSe_2 nanobars with a size distribution from 100 to 350 nm were obtained. The SEM image of EuSe_2 nanobars is shown in Figure S3. The results of EDX analyses of these four samples are listed in Figure S1b to e and Table S2. The atomic ratios of $\text{RE}:\text{Se}$ in CeSe_2 and EuSe_2 NCs are near the stoichiometric ratio of 1:2, but deviating from this ratio in PrSe_2 and NdSe_2 NCs, due to the existence of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates as impurities. The XRD patterns of these samples are shown in Figure S4. All of these patterns are in accordance with the corresponding standard XRD peaks. In the pattern of CeSe_2 nanosheets, the appearance of some extra diffraction peaks may be caused by the modulated ZrSSi-type structure in this sample.

Spiral structure of LaSe_2 nanosheets. Figure 2 and Figure S5 show the TEM, AFM and SEM images of LaSe_2 nanosheets obtained with different growth durations. As shown in these images, the as-synthesized LaSe_2 nanosheets are not planar sheets but helicoids, as a result of the spiral growth at screw dislocations. Different from the cases studied by Jin and co-workers⁴⁹, Moire fringes appear in the TEM images (Figure 2a, c and Figure S5c), which indicates that the lattice direction on different layers rotated slightly and spaces existed between different slices on one helicoid. SEM images (Figure 2d, f and Figure S5f) also show that each slice was separated from the upper and lower ones.

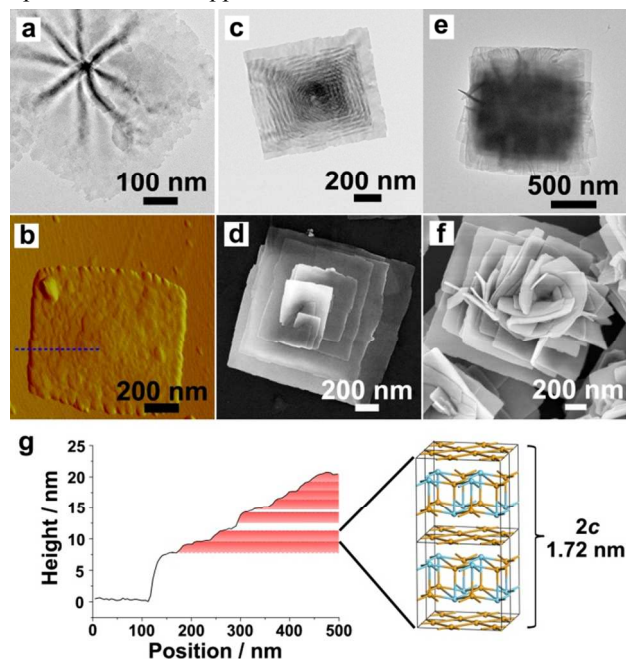


Figure 2. Morphology characterization of LaSe_2 nanosheets obtained with different growth durations. 1 min: (a) TEM image and (b) AFM phase image; 15 min: (c) TEM image and (d) SEM image; 30 min: (e) TEM image and (f) SEM image. (g) Height diagram along the blue dashed line in panel b. Every red stripe represents two layers of LaSe_2 .

Figure 2a, b, Figure S5a and b show the TEM, AFM and SEM images of the sample taken out from the flask at 1 min after the reaction solution turned black. Square LaSe_2 nanosheets with a side length of about 1 μm formed within 1 min of the growth regime. The edge of the nanosheets was very rough. Regions of different contrasts in the TEM images and steps on the upper surface of the nanosheet shown in the

AFM image indicate that one as-formed nanosheet here was composed of several thinner slices. The SEM image (Figure S5b) shows that the spiral structure had formed in this early stage. Figure 2g shows the height diagram along the blue dashed line in Figure 2b. Many steps can be seen in this height diagram. Most of the heights of these steps are approximately equal to or larger than twice of the height of one unit cell of LaSe_2 , i.e. 1.72 nm, as indicated by the red stripes in Figure 2g. Therefore, it is highly possible that every slice was composed of two layers of cells. Due to the weak layer-layer interaction in LaSe_2 , solvent molecules might insert into the layered structure of LaSe_2 and separate two slices. Consequently, the heights of some steps in Figure 2g are larger than 1.72 nm. The existence of solvent molecules inserted between slices could be confirmed by removing these inserted molecules by thermal treatment followed by measuring the change in step height. Figure S6 shows an AFM image of LaSe_2 nanosheets (growth duration: 1 min) after thermal treatment at 300 $^\circ\text{C}$ in air for 30 min and Figure S7 compares the statistical results of the height of steps on LaSe_2 nanosheets before and after thermal treatment obtained from AFM measurements. It can be seen that the steps higher than 2.2 nm disappeared after thermal treatment, indicating the removal of the solvent molecules inserted between slices.

Figure 2c, d, Figure S5c and d show the TEM and SEM images of LaSe_2 nanosheets obtained after growing for 15 min. Spiral structure was well-developed in these nanosheets and distinct Moire fringes can be seen in the TEM images. In some cases, several centers of screw dislocation exist in one nanosheet, as shown in Figure 2d, Figure S5c and d. As a result of ripening process, the edge of the nanosheets became smoother as the growth time extended. If the growth period was further extended to 30 min, the newly formed slices would roll up and the nanosheets would grow into rose-shaped NCs, as shown in Figure 2e, f, Figure S5e and f.

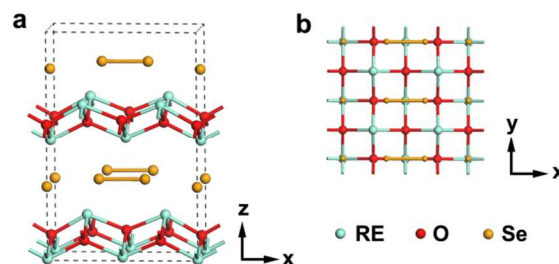


Figure 3. Crystal structure of orthorhombic $\text{RE}_4\text{O}_4\text{Se}_3$: (a) side-view and (b) top-view.

Structure characterization of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates. $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = La to Nd, Sm) bulk materials (orthorhombic phase) have been reported earlier by other groups.^{28,29,50} Similar to RESe_2 , the crystal structure of $\text{RE}_4\text{O}_4\text{Se}_3$ also shows layered feature. As shown in Figure 3, two kinds of basic layers, $\infty\{[\text{RE}_4\text{O}_4]^{4+}\}$ layers and $\infty\{[\text{Se}_3]^{4-}\}$ layers, alternately build up the crystals. $\infty\{[\text{RE}_4\text{O}_4]^{4+}\}$ layers are formed by $[\text{ORE}_4]^{10+}$ tetrahedrons with common edges and $\infty\{[\text{Se}_3]^{4-}\}$ layers by parallel Se-chains composed of Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells. It is predictable that if the ionic radii of RE^{3+} ions decrease, the unit cell will shrink on x direction, resulting in the interaction between Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells.

With the method presented in the experimental section, $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = Pr, Nd, Sm, Gd to Ho) nanoplates could be

obtained together with RESe₂ nanosheets or some amorphous membranous impurities. Therefore, low-speed centrifugation procedure was needed to separate RE₄O₄Se₃ nanoplates from those byproducts with larger sizes. However, since the yield of Pr₄O₄Se₃ nanoplates was quite low and most of Pr₄O₄Se₃ nanoplates were rolled up in PrSe₂ nanosheets, it was very hard to get powder sample of Pr₄O₄Se₃ nanoplates separated from PrSe₂ nanosheets. Figure S8 shows the TEM images, SAED pattern and EDS analysis of the mixed sample of PrSe₂ nanosheets and Pr₄O₄Se₃ nanoplates. The SAED pattern of Pr₄O₄Se₃ nanoplates was similar to those of other RE₄O₄Se₃ nanoplates, confirming that the nanoplates were orthorhombic Pr₄O₄Se₃. The atomic ratio of Pr:Se was 42:58, indicating the existence of the mixture of PrSe₂ and Pr₄O₄Se₃. Thus Pr₄O₄Se₃ nanoplates will not be discussed in the following paragraphs. The powder samples of Nd₄O₄Se₃ and Sm₄O₄Se₃ were brown, while other four samples showed very dark violet color. Calculated from ICP-AES results, the yields of NdSe₂ nanosheets, Nd₄O₄Se₃ nanoplates and Gd₄O₄Se₃ nanoplates were 62.8 %, 28.3 % and 46.7 %, respectively.

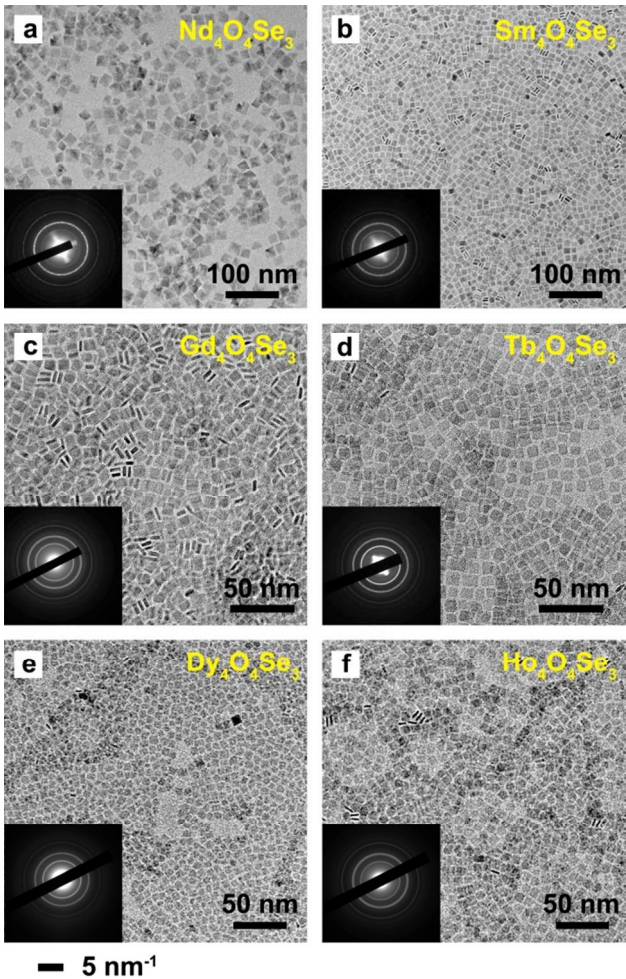


Figure 4. TEM images and corresponding SAED patterns (insets) of the nanoplates of (a) Nd₄O₄Se₃, (b) Sm₄O₄Se₃, (c) Gd₄O₄Se₃, (d) Tb₄O₄Se₃, (e) Dy₄O₄Se₃, (f) Ho₄O₄Se₃.

Figure 4 shows the TEM images and corresponding SAED patterns of RE₄O₄Se₃ nanoplates. All of these nanoplates show near square shape. The size distributions of these nanoplates are listed in Table 1. As the RE element changes from light RE to heavy RE, the size of RE₄O₄Se₃ nanoplates became smaller and the thickness became thinner. Meanwhile, their

SAED patterns show systematic outward shifts, indicating that these RE oxy-selenide share similar crystal structure and the lattice shrinks from Nd₄O₄Se₃ to Ho₄O₄Se₃. The results of corresponding EDS analyses are shown in Table 1 and Figure S9. The atomic ratios of RE:Se of these nanoplates were close to their stoichiometric ratio of 4:3.

Table 1. Size distributions and elemental analysis results of RE₄O₄Se₃ nanoplates.

	Side length (nm)	Thickness (nm)	Atomic ratio of RE:Se
Nd ₄ O ₄ Se ₃	20±2	3.5±0.4	52:48
Sm ₄ O ₄ Se ₃	10.3±0.9	3.2±0.4	54:46
Gd ₄ O ₄ Se ₃	8.5±0.7	2.7±0.3	55:45
Tb ₄ O ₄ Se ₃	8.3±0.8	1.7±0.2	59:41
Dy ₄ O ₄ Se ₃	6.4±0.7	1.9±0.2	60:40
Ho ₄ O ₄ Se ₃	7.9±0.7	2.1±0.2	64:36

From Nd₄O₄Se₃ to Ho₄O₄Se₃, the gradual decreasing of the Se element may be caused by a gradual increasing of the concentration of Se-vacancies in the nanoplates. The atomic ratio of O:Se in the lattice of RE₄O₄Se₃ nanoplates could be estimated from the results of C-H-N elemental analysis (Table S4) and XPS analysis (Table S5) of the nanoplates. The amount of OA adsorbed on nanoplates could be obtained from C-H-N elemental analysis and the atomic ratio of C:O:Se could be obtained from XPS analysis. After subtracting the contribution from the oxygen atoms in OA, the atomic ratios of O:Se in the lattices of Nd₄O₄Se₃ nanoplates and Gd₄O₄Se₃ nanoplates were calculated to be 1.0:1 and 1.2:1, respectively, which were close to the stoichiometric ratio of 4:3.

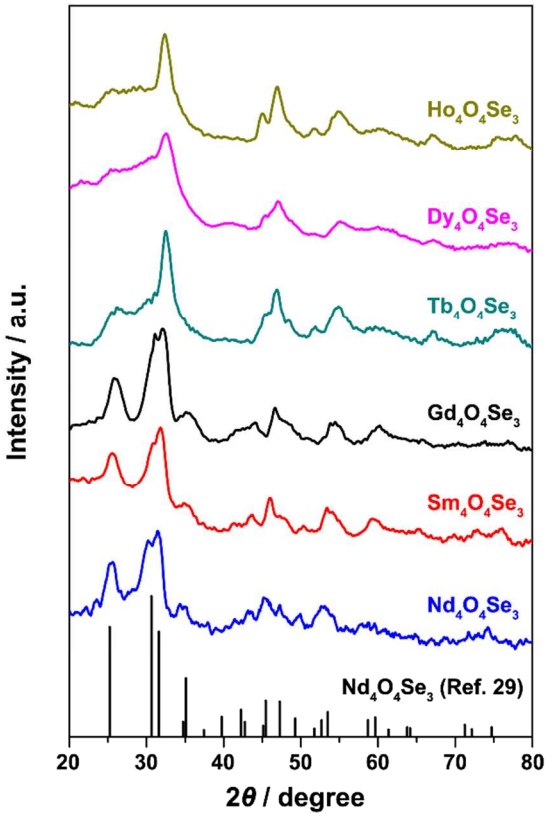


Figure 5. XRD patterns of $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = Nd, Sm, Gd to Ho) nanoplates, compared with the XRD pattern of bulk $\text{Nd}_4\text{O}_4\text{Se}_3$ calculated from the crystallographic data reported in ref. 29.

Figure 5 shows the XRD patterns of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates compared with that of $\text{Nd}_4\text{O}_4\text{Se}_3$ bulk material, which was calculated from previously reported crystallographic data²⁹ (using PowderCell for Windows, Version 2.4). The indices of the calculated diffraction peaks are listed in Table S3. The XRD pattern of $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates can match the calculated one. The diffraction peaks of other $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates show gradual systematic shifts toward high angle, indicating the lattice contraction caused by the decreasing of the ionic radii from Nd^{3+} to Ho^{3+} . However, the crystal structures for $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = Gd to Ho) have not been reported, they cannot be solved from the nanoplates samples due to the broadening of the diffraction peaks. Supposing $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = Gd to Ho) crystals possess the same orthorhombic crystal structure as $\text{Nd}_4\text{O}_4\text{Se}_3$ and can be described by the model shown in Figure 3, the lattice parameters of $\text{Gd}_4\text{O}_4\text{Se}_3$ are $a = 8.2412(5)$ Å, $b = 3.9298(2)$ Å and $c = 12.5311(8)$ Å, which were calculated from ten strongest diffraction peaks in the XRD pattern of $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates. Compared with the lattice parameters of $\text{Nd}_4\text{O}_4\text{Se}_3$ ($a = 8.4568(4)$ Å, $b = 3.9883(2)$ Å, $c = 12.8245(7)$ Å), the unit cell of $\text{Gd}_4\text{O}_4\text{Se}_3$ was compressed. Since $\text{Tb}_4\text{O}_4\text{Se}_3$, $\text{Dy}_4\text{O}_4\text{Se}_3$ and $\text{Ho}_4\text{O}_4\text{Se}_3$ nanoplates were smaller and thinner than other $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates and contained high concentration of Se-vacancies, some weak diffraction peaks cannot be observed in their XRD patterns.

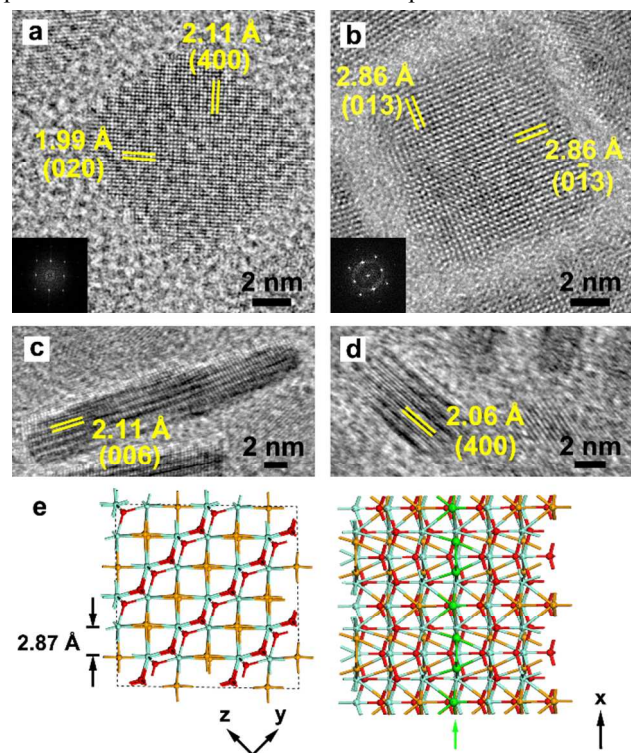


Figure 6. Growth directions of $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates. Top view (a and b) and side view (c and d) HRTEM images of $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates (a and c) and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates (b and d) are shown. FFT patterns of the top view images are shown in the corresponding insets. The interplanar spacing and corresponding indices are marked on the images. (e) Structure model of $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates: left part is the top view and right part is the side view. A Se-chain in the side view is highlighted by green color.

Figure 6 shows the top-view and side-view HRTEM images of $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates. Although $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates were similar in crystal structure and morphology, the growth directions of these two kinds of nanoplates were different. Considering the layered structure of $\text{RE}_4\text{O}_4\text{Se}_3$ shown in Figure 3, it is very likely that the nanoplates expose (001) and (00-1) facets as the upper and lower surfaces, which was the case for $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates. The side surfaces of $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates were $\{210\}$ facets. However, each $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplate exposed two $\{100\}$ facets as the upper and lower surfaces and four $\{013\}$ facets as the side surfaces. Figure 6e schematically shows the structure of $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates. In this structure, Se-chains are perpendicular to the upper and lower surfaces. This structure may be caused by a relatively low growth rate of Se-chains in the compressed lattice of $\text{Gd}_4\text{O}_4\text{Se}_3$ compared with that of $\text{Nd}_4\text{O}_4\text{Se}_3$. Since the $\{013\}$ facets of $\text{Gd}_4\text{O}_4\text{Se}_3$ possess the maximum atomic density, thus low surface energy, these facets were exposed as the side surfaces of $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates.

Formation conditions for RESe_2 NCs and $\text{RE}_4\text{O}_4\text{Se}_3$ NCs along RE series. $\text{RE}(\text{acac})_3$ (RE = La, Pr, Nd, Sm to Ho) and $\text{Ce}(\text{Ac})_3$ were used as precursors of RE elements in this work, which were also used in the synthesis of RE oxide³¹, oxysulfide³⁹⁻⁴¹ and NaRES_2 NCs. These precursors could transform into RE oleate under vacuum in the mixed solvent of OA, OM and ODE. Then RE monomers could be released steadily as the oleate decomposed at 310 °C. Moreover, using SeO_2 as the precursor of Se was another key factors in the synthesis of RESe_2 and $\text{RE}_4\text{O}_4\text{Se}_3$ NCs. SeO_2 could be easily reduced by OM and dissolved in solvent, and it was possible to prepare NCs contain Se (-1) in this condition.

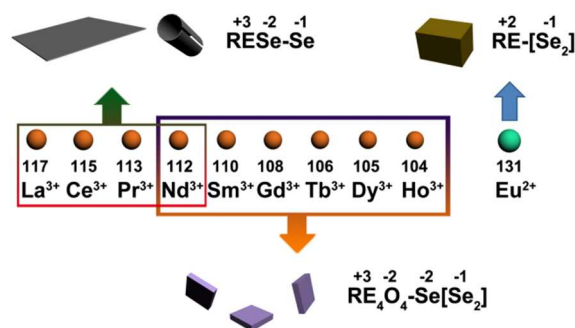


Figure 7. Formation competition between RESe_2 and $\text{RE}_4\text{O}_4\text{Se}_3$ based on HSAB theory. The values on the element symbols are the ionic radii of the corresponding ions (unit: pm).

The structures of RESe_2 and $\text{RE}_4\text{O}_4\text{Se}_3$ are both layered structure containing Se-layers. In RESe_2 , Se-layers with Se (-1) grids are sandwiched between $\infty\{[\text{RESe}]^+\}$ layers. The $\infty\{[\text{RESe}]^+\}$ layers can be regarded as $[\text{SeRE}_3]^{13+}$ square pyramids with shared edges. In $\text{RE}_4\text{O}_4\text{Se}_3$, Se-layers consisting of $-\text{Se}^{2-}-[\text{Se-Se}]^{2-}-$ chains are sandwiched between $\infty\{[\text{RE}_4\text{O}_4]^{4+}\}$ layers. Figure 7 schematically shows the formation competition between RESe_2 and $\text{RE}_4\text{O}_4\text{Se}_3$. Whether RESe_2 NCs or $\text{RE}_4\text{O}_4\text{Se}_3$ NCs would be obtained was decided by the properties of RE^{3+} ions and the reaction conditions. Since the ionic radii of the trivalent ions decrease from La to Lu, according to the HSAB theory, the affinity of RE^{3+} ions toward Se^{2-} ions weakens while that toward O^{2-} ions strengthens. Consequently, $\infty\{[\text{RESe}]^+\}$ layers of light RE elements could form in RESe_2 NCs, while only $\infty\{[\text{RE}_4\text{O}_4]^{4+}\}$ layers could form for

middle RE elements in $\text{RE}_4\text{O}_4\text{Se}_3$ NCs. Furthermore, the crystallinity of LaSe_2 nanosheets and $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates was much better than that of NdSe_2 nanosheets and $\text{Ho}_4\text{O}_4\text{Se}_3$ nanoplates, respectively, as shown in the XRD patterns. High concentration of Se-vacancies in $\text{Dy}_4\text{O}_4\text{Se}_3$ and $\text{Ho}_4\text{O}_4\text{Se}_3$ nanoplates is another consequence of the weak affinity between Se and Dy or Ho. All of these phenomena strongly suggest that the bonding between Se and light RE were more thermodynamically favored than that between Se and middle or heavy RE. Another reason for the formation of Se-vacancies in $\text{Dy}_4\text{O}_4\text{Se}_3$ and $\text{Ho}_4\text{O}_4\text{Se}_3$ nanoplates is that, due to the smaller size of Dy^{3+} and Ho^{3+} ions compared with trivalent ions of light RE, the unit cells of $\text{Dy}_4\text{O}_4\text{Se}_3$ and $\text{Ho}_4\text{O}_4\text{Se}_3$ are more compressed and too crowded for Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells, resulting in the escape of some Se atoms from the lattice.

While it seems an exception for the formation of EuSe_2 nanobars instead of $\text{Eu}_4\text{O}_4\text{Se}_3$ nanoplates according to the trend we discussed above. This result is comprehensible because the crystal structure of EuSe_2 (tetragonal phase) is totally different from that of other RESe_2 ⁵¹, as shown in Figure S10. Eu atoms are divalent in EuSe_2 , and previous works have shown that the divalent RE ions are much softer compared to trivalent ones, leading to higher affinity to soft bases, i.e. S⁴³ and Se.^{44,45}

In addition, if $\text{Na}(\text{acac})$ (3 mmol) was introduced into the reaction solution together with $\text{RE}(\text{acac})_3$, NaRESe_2 (RE = La, Ce) NCs in cubic phase could be obtained, similar to NaRESe_2 NCs in our previous report.⁴⁶ The XRD patterns and TEM images of NaRESe_2 were shown in Figure S11 and S12, respectively. Calculated from EDS results in Figure S13, the atomic ratios of Na:RE:Se are 18:26:56 for NaLaSe_2 NCs and 16:28:56 for NaCeSe_2 NCs.

Electronic transport property of LaSe_2 nanosheet films.

Lots of RE compounds containing 2-D sheets of Se or Te atoms are considered as 2-D charge density wave conductor with special electronic transport properties. For instance, LaSeTe_2 exhibit metal-semiconductor transition at about 270 K.²⁶ The resistivity of LaSeTe_2 powder was about $0.9 \Omega\cdot\text{cm}$ at 300 K, and reached the minimum value of $0.7 \Omega\cdot\text{cm}$ at 270 K. When the temperature decreased to 4 K, the resistivity increased to $1.4 \Omega\cdot\text{cm}$.

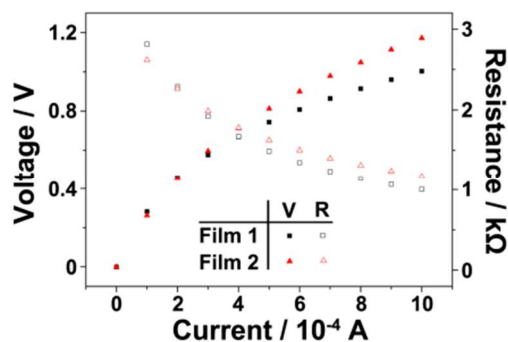


Figure 8. Resistance measurement of two LaSe_2 nanosheet films.

Herein, two LaSe_2 films with good electrical conductivity were fabricated by drop-casting the cyclohexane dispersion of LaSe_2 nanosheets on SiO_2 substrates. Thermal treatment at 300°C in air was used to remove the organic ligands adsorbed on the surface of the nanosheets. As shown in the XRD pattern (Figure S14) and TEM image (Figure S15) of LaSe_2 nanosheets after the thermal treatment for 30 min, the as-

synthesized LaSe_2 nanosheets were stable under this procedure. Figure S16 shows the IR spectra of LaSe_2 nanosheets before and after the thermal treatment. The stretching vibrational peaks of C-H bonds around 2800 cm^{-1} dropped dramatically, which indicates that most of the OA and OM molecules adsorbed on the surface of LaSe_2 nanosheets were successfully removed. Four-electrode method was used to measure the resistivity of the LaSe_2 nanosheet films under different currents. The result of the resistivity measurements of these two films was repeatable, as shown in Figure 8. When the current went through the films increased, the resistivity of the films decreased. According to the definition of resistivity:

$$\rho = \frac{b \cdot h}{l} R \quad (1)$$

where b , h and l represent the width, thickness and length of the channel, respectively, and R stands for the resistance of the film, the resistivity of as-prepared LaSe_2 films ranged from $3.4 \Omega\cdot\text{cm}$ to $1.1 \Omega\cdot\text{cm}$ as the current increased from 0.1 mA to 1.0 mA. These values are comparable in magnitude with the resistivity of bulk LaSeTe_2 ²⁶, which possesses similar structure with LaSe_2 . Because the interfacial resistance between LaSe_2 nanosheets contributed a lot to the total resistance of the films, the intrinsic resistivity of LaSe_2 nanosheets is significantly lower than the values listed above, and the non-ohmic contact between LaSe_2 nanosheets is a possible reason for the non-linear I-V relationship shown in Figure 8. Due to their comparatively large size ($1 \mu\text{m}$) and low resistivity ($< 1 \Omega\cdot\text{cm}$), LaSe_2 nanosheets are ideal candidates to fabricate nano-field-effect transistor^{9,10} and in-plane supercapacitor.¹¹

Light extinction property of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates. Figure 9b shows the photo of the cyclohexane dispersion of $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = Nd, Sm, Gd to Ho) nanoplates. The dispersions of $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Sm}_4\text{O}_4\text{Se}_3$ nanoplates present similar brown colors and the dispersions of the other four kinds of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates appear similar violet colors. Figure 9a shows the absorption spectra of these samples. Two main peaks below 3 eV were observed in the spectrum of $\text{Sm}_4\text{O}_4\text{Se}_3$ dispersion, while only one obvious peak could be seen in the spectra of other samples.

Table 2. The absorption edge energy of each peak in the absorption spectra of the dispersions of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates.

	E_g (eV)
$\text{Nd}_4\text{O}_4\text{Se}_3$	1.95
$\text{Sm}_4\text{O}_4\text{Se}_3$	1.79, 1.96
$\text{Gd}_4\text{O}_4\text{Se}_3$	1.74
$\text{Tb}_4\text{O}_4\text{Se}_3$	1.73
$\text{Dy}_4\text{O}_4\text{Se}_3$	1.78
$\text{Ho}_4\text{O}_4\text{Se}_3$	1.73

The absorption edge energy (E_g) of each peak was defined as the energy of the intersection point of the spectral baseline along the energy axis and the extrapolated line of the linear part at the lower-energy side of the peak, as illustrated by the dashed lines in Figure 9a. E_g of each peak was listed in Table 2. These peaks could be divided into two classes according to E_g values: peaks with E_g about 1.95 eV and peaks with E_g between 1.73 and 1.79 eV. E_g with lower energy here can be assigned to the optical band gap of the sample. According to former report²⁹, the optical band gaps of $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = La, Pr, Nd, Sm) bulk materials were approximately 1.9 eV. It is

comprehensive, due to the small-size effect, the band gap of $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates was wider than that of the bulk counterpart. But the band gap of other $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates decreased.

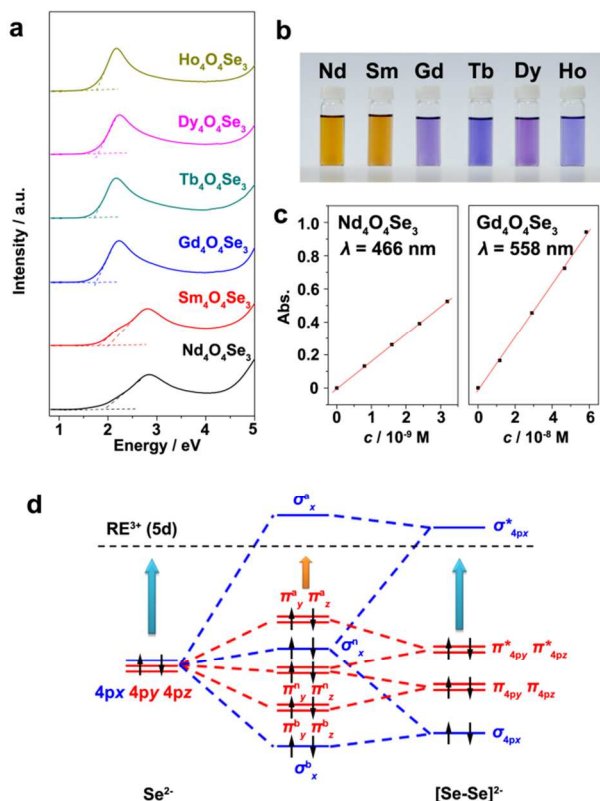


Figure 9. Light extinction property of the cyclohexane dispersions of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates: absorption spectra (a) and photos (b) of $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates dispersions. (c) Absorbance of the dispersions of $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates at corresponding maximum absorption wavelength depends on the concentrations of nanoplates. (d) Scheme of the interaction between Se^{2-} ion and $[\text{Se-Se}]^{2-}$ dumbbell along x direction in vacuum. Blue lines show σ -interactions and red lines show π -interactions. The superscripts, b, n and a, stand for bonding, non-bonding and anti-bonding, respectively. The energy level of RE (5d) is marked with black dashed line.

Herein, we attribute this abnormal phenomenon to the interaction between Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells. In the former report²⁹, the top of the valence band and the bottom of the conduction band were attributed to Se (4p) states and RE (5d) states, respectively. The as-mentioned Se (4p) states may come from the Se (4p) orbitals of Se^{2-} ions or $[\text{Se-Se}]^{2-}$ dumbbells. The interaction between Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells can result in the rise of energy of the top of the valence band. Figure 9d schematically shows the interaction between the 4p orbitals of Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells along x direction in vacuum. Since the energy of π_y^a and π_z^a , the highest occupied orbitals in interaction case, is higher than the energy of 4p orbitals of isolated Se^{2-} ions or π_{4py}^* orbitals of $[\text{Se-Se}]^{2-}$ dumbbells, the energy gap between Se (4p) and RE (5d) decreases as Se^{2-} ions interact with $[\text{Se-Se}]^{2-}$ dumbbells. Considering the periodicity of the crystal, every energy level in Figure 9d will generate a band, but the band gap will still be smaller in the interaction case than in the non-interaction case. In $\text{Nd}_4\text{O}_4\text{Se}_3$, the distance between Se^{2-} ions and $[\text{Se-Se}]^{2-}$

dumbbells is relatively large. Therefore, Se^{2-} ions cannot interact effectively with $[\text{Se-Se}]^{2-}$ dumbbells. When Nd^{3+} ions here are replaced by middle RE^{3+} ions with smaller ionic radii, the lattice of $\text{RE}_4\text{O}_4\text{Se}_3$ will shrink, leading to stronger interaction between Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells. Consequently, the optical band gaps of $\text{RE}_4\text{O}_4\text{Se}_3$ (RE = Sm, Gd to Ho) nanoplates were smaller than that of $\text{Nd}_4\text{O}_4\text{Se}_3$ nanoplates. Interaction and non-interaction cases may exist simultaneously in $\text{Sm}_4\text{O}_4\text{Se}_3$ nanoplates, resulting in the appearance of two absorption peaks. Considering that σ_x^* orbital, an occupied orbital in the interaction case, partially comes from σ_{4px}^* orbital, an anti-bonding orbital of $[\text{Se-Se}]^{2-}$ dumbbells, the interaction between Se^{2-} ions and $[\text{Se-Se}]^{2-}$ dumbbells would weaken and stretch the Se-Se bond in $[\text{Se-Se}]^{2-}$ dumbbells. This inference was tested by density functional theory simulation. Figure S17 shows the optimized structure of $\text{Gd}_4\text{O}_4\text{Se}_3$ crystal. Compared with the crystal structure of $\text{Nd}_4\text{O}_4\text{Se}_3$, the unit cell of $\text{Gd}_4\text{O}_4\text{Se}_3$ was compressed on x direction, but the Se-Se bond length in $[\text{Se-Se}]^{2-}$ dumbbells increased.

The as-synthesized $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates exhibit high light extinction ability in the visible light region. Figure 9c shows the diagrams of the peak absorbance for each sample depending on the concentrations of $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates in the cyclohexane dispersions. The concentrations of nanoplates here were calculated from the concentration of Nd^{3+} and Gd^{3+} ions obtained from ICP-AES analysis and the average volume of a single $\text{Nd}_4\text{O}_4\text{Se}_3$ or $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplate obtained from the TEM images. According to Lambert-Beer's law, the molar extinction coefficients of $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates were calculated to be 1.6×10^8 and $1.6 \times 10^7 \text{ M}^{-1} \cdot \text{cm}^{-1}$, respectively. The intrinsic absorption coefficient μ_i was defined as:

$$\mu_i = \frac{\ln 10}{N_A \cdot V_{\text{NC}}} \epsilon \quad (2)$$

In this equation, N_A , V_{NC} and ϵ stand for Avogadro constant, the volume of a single NC, and the molar extinction coefficient of the NCs, respectively.⁵² μ_i of $\text{Nd}_4\text{O}_4\text{Se}_3$ and $\text{Gd}_4\text{O}_4\text{Se}_3$ nanoplates were 4.4×10^5 and $3.1 \times 10^5 \text{ cm}^{-1}$. These values are higher than μ_i of various quantum dots, such as PbS^{53} and CdSe^{54} , and comparable to that of CuInS_2 ($5 \times 10^5 \text{ cm}^{-1}$)⁵⁵, in visible light region. Thus, $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates have potential application in light filters and solar cells.

CONCLUSIONS

Two types of 2D NCs of trivalent RE selenides and oxy-selenides, namely RESe_2 nanosheets (RE = La to Nd, for EuSe_2 , nanobars were obtained) and $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates (RE = Nd, Sm, Gd to Ho), could be synthesized in mixed solvents of OA-OM-ODE. SeO_2 could be used as efficient Se-source in the reaction. Both kinds of these NCs contain Se-layers involving Se atoms in -1 valence. Since trivalent ions of middle RE, compared with that of light RE, possess stronger affinity towards O^{2-} ions but weaker affinity towards Se^{2-} ions, according to HSAB theory, RESe_2 nanosheets were obtained for light RE (La to Nd) and $\text{RE}_4\text{O}_4\text{Se}_3$ nanoplates were obtained for middle RE (Nd, Sm, Gd to Ho). EuSe_2 nanobar was an exception because Eu atoms were divalent in this material. LaSe_2 nanosheets with side-length about $1 \mu\text{m}$ could form from the screw dislocation driven growth. The number of slices in one nanosheet increased as the reaction duration was prolonged. Satellite diffraction peaks were observed in the SAED pattern of LaSe_2 nanosheets, indicating the modulated

structure in Se-layers. LaSe₂ nanosheet films fabricated by drop-casting displayed low electronic resistance at room temperature. The light absorption property of RE₄O₄Se₃ nanoplates was characterized. RE₄O₄Se₃ nanoplates exhibited high light extinction ability in visible light region. The optical band gap of Nd₄O₄Se₃ nanoplates was broader than that of the bulk counterpart, while those of other RE₄O₄Se₃ nanoplates were narrower. We ascribe this phenomenon to the interaction between Se²⁻ ions and [Se-Se]²⁻ dumbbells in the Se-layers caused by the lattice shrinkage from Nd₄O₄Se₃ to Gd₄O₄Se₃.

Since numerous fascinating phenomena have been discovered in different layer-structured selenide compounds, it is of great interest to study the behaviors of these materials on nanoscale. The synthesis method of RESe₂ nanosheets and RE₄O₄Se₃ nanoplates developed in this work could guide the large-scale synthesis of 2D NCs of other selenide compounds, laying the foundation of the development of new types of transistors, thermoelectric devices and wave-absorbing materials.

ASSOCIATED CONTENT

Supporting Information. The detailed reaction conditions for the syntheses of different NCs, more TEM, SEM, AFM images, EDS analyses, XRD spectra, IR spectra, structure models and DFT calculation results are included in supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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