Research article

Yuan Liu, Gongxun Bai*, Li Jiang, Youjie Hua, Liang Chen and Shiqing Xu*

Lanthanide Nd ion-doped two-dimensional In_2Se_3 nanosheets with near-infrared luminescence property

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Abstract: Ultrathin two-dimensional (2D) materials have drawn great attention in recent years due to their promising applications in biomedicine and atomically optoelectronic devices. In this work, we have fabricated a 2D In_2Se_3 nanosheet doped with Nd^{3+} ions via the two-step method of solid phase synthesis and liquid exfoliation. Owing to the special inner 4f-4f energy level transitions, lanthanide ions can emit photons with almost the same energy in different environments. Here, a stable near-infrared luminescence from Nd^{3+} -doped 2D In_2Se_3 nanosheets has been realized, which includes emission bands around 910, 1057, and 1324 nm. The doping of Nd^{3+} ions extends the emission region of In_2Se_3 nanosheets. Moreover, the photoluminescence mechanism of Nd^{3+} ions was investigated through a series of optical measurements. This work not only provides a reliable method to fabricate lanthanide ion-doped 2D materials but also possesses a great significance for luminescence study of lanthanide ions in the 2D matrix.

Keywords: 2D material; In_2Se_3 nanosheets; lanthanide ions; near-infrared; luminescence property.

1 Introduction

Two-dimensional (2D) sheet-like materials have attracted great attention in optoelectronic devices, solar cells,

photocatalysis, and biomedicine over the last few years [1–8]. Generally, nanomaterials with a thickness less than 5 nm are defined as 2D materials [9]. Thanks to its unique physical and chemical features, 2D materials possess lots of unexpected properties, such as quantum hall effect, ultrahigh carrier mobility, bright optical transparency, huge specific surface area, as well as remarkable photo-thermal effect [10–12]. Up to now, a lot of materials with 2D structure have been developed, including graphene, transition metal dichalcogenides, black phosphorus, III–VI layered semiconductor, and metal-organic frameworks [10, 13–16]. Among them, di-indium tri-selenide (In_2Se_3) is a representative III–VI layered semiconductor that exists in five crystalline phases (α , β , γ , δ , and κ) [17, 18]. In addition, γ - In_2Se_3 is a direct band gap semiconductor with bandgap of about 1.9 eV (652 nm), which suggests that the emission is limited in the visible region. The only visible emission restricts the applications in photonics to a large extent. Therefore, it is significant to seek a strategy to modulate the emission of 2D In_2Se_3 semiconductor.

By comparison, lanthanide ions are normally doped into some insulators or semiconductor materials for realizing the luminescence from the ultraviolet (UV) to the infrared region, which originates from the 4f electron orbital transitions of lanthanide ions [19–21]. There are amounts of lanthanide ions such as Eu^{3+} , Dy^{3+} , Nd^{3+} , Er^{3+} , Ho^{3+} , and Yb^{3+} , whose luminescence properties contain abundant emission bands, narrow bandwidth, long lifetime, and high light stability [22–24]. Among them, Nd^{3+} ion is a typical lanthanide dopant with luminescence peaks at 900, 1100, and 1300 nm, which are widely applied to near-infrared (NIR) photonics areas [25]. Over recent research, Bai and coworkers incorporated the lanthanide ion Er^{3+} into MoS_2 thin film with bilayer thickness for the first time through chemical vapor deposition (CVD) method. They confirmed the possibility of lanthanide ion-doped 2D materials and doping lanthanide ions can modulate the emission of semiconductor nanosheets [26].

There are numerous methods of doping lanthanide ions into matrix, such as solid state reaction, hydrothermal

*Corresponding authors: Gongxun Bai and Shiqing Xu, Institute of Optoelectronic Materials and Devices, China Jiliang University, Hangzhou 310018, People's Republic of China, e-mail: baigx@cjl.u.edu.cn. <https://orcid.org/0000-0002-4066-0359> (G. Bai); shiqingxu@cjl.u.edu.cn (S. Xu)

Yuan Liu and Youjie Hua: Institute of Optoelectronic Materials and Devices, China Jiliang University, Hangzhou 310018, People's Republic of China

Li Jiang and Liang Chen: Institute of Optoelectronic Technology, China Jiliang University, Hangzhou 310018, People's Republic of China

process, sol-gel method, and microwave synthesis. It is a simple way of solid state reaction for doping lanthanide ions into the host on account of the advantages for high yield and good crystallinity. In addition, massive efforts have been used for fabrication of 2D materials, including micromechanical cleavage, CVD, wet-chemical synthesis, liquid exfoliation, and pulsed laser deposition [27–30]. For instance, Gu and Tao fabricated 2D In_2Se_3 thin layers with a thickness of $\sim 4\text{--}5$ nm via mechanical exfoliation method [14]. Hao's group synthesized the Yb/Er codoped layered WSe_2 nanosheets through the pulsed laser deposition process [31]. Unfortunately, the fabricated yields of existing approaches are still at an extremely low level; it is significant to adopt an effective approach to improve the yield of the doped 2D materials. Due to its superiority in terms of wide applicability, well controllability, and high yield, the liquid assistant exfoliation technique is the most widely used, practical approach for manufacture of 2D materials. Hence, it is crucial to find a tactic to dope the lanthanide ions into the host and make them in the 2D form as efficiently as possible. In addition, 2D materials fabricated by the liquid exfoliation method also have wide applications in photothermal areas and photoelectric nanodevices owing to their small particle size and convenient preparation [11, 32–34].

In this report, we adopted a two-step method of solid state reaction and liquid phase exfoliation to fabricate lanthanide-doped 2D In_2Se_3 nanosheets. The as-prepared material possessed not only good crystallinity after lanthanide ion doping but also 2D nanosheet structure. After the doping of lanthanide Nd^{3+} ions, the emission region of intrinsic In_2Se_3 semiconductor was extended from visible to NIR, which has promising applications in NIR photonic filed. A down-conversion process of single photon was also observed from the lanthanide Nd^{3+} ions in the 2D In_2Se_3 nanosheets under 808 nm excitation.

2 Experiment section

The bulk In_2Se_3 with a grain size of $80\text{ }\mu\text{m}$ was purchased from Foshan QIANLIMU Technology Co., Ltd (Foshan, China). NdF_3 powders with high purity of 99.99% were purchased from Aladdin Industrial Corporation (Shanghai, China). Analytically pure ethanol was provided by Hangzhou Gaojing Fine Chemical Industry Co., Ltd (Hangzhou, China). The 2D $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets were fabricated by a two-step method of solid state reaction and liquid phase exfoliation. First, the solid state reaction was executed for preparing bulk In_2Se_3 doped with lanthanide Nd ions. The raw materials of 99% In_2Se_3 and 1% NdF_3 with molar percentage were mixed and abraded in an agate mortar. Next,

the mixed powders were placed in a tube furnace and heated to 650°C for 4 h in protective gas Ar. Finally, the Nd-doped In_2Se_3 powders were cooled to room temperature and grinded fine for further disposing. Posteriorly, we adopted the liquid phase exfoliation technique to acquire the $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. The doped In_2Se_3 powders were dispersed in ethanol with a ratio of 2 mg/ml. Then, the mixture was exfoliated with probe sonication for 24 h. Ultimately, the nanosheets were gained from the supernatant after controlled centrifugation.

The crystal phase for microcrystals and nanosheets of Nd^{3+} -doped In_2Se_3 was identified via X-ray diffraction (XRD; D2 PHASER, Bruker, Karlsruhe, Germany) measurement with Cu $K\alpha$ radiation in the range of $10\text{--}65^\circ$. To investigate micromorphology, a Tecnai FEI transmission electron microscope (TEM), type of G2 F20, was used to observe the structure and size of as-prepared nanosheets at nanoscale. Atomic force microscopy (AFM) (D3100, Veeco, Plainview, NY, USA) was applied for thickness detection to figure out the morphology of nanosheets. X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Fisher, Waltham, MA, USA) detection with a monochromated Al $K\alpha$ source ($h\nu = 1361$ eV) was carried out to determine the situation for doping of Nd^{3+} ions. Raman spectra were acquired by a Renishaw inVia-Reflex Raman spectrograph with a 532 nm laser for investigation of microstructure. Absorbance spectra in the range of 300–1300 nm were collected by PerkinElmer Lambda 750S UV-VIS-NIR spectrophotometer (Perkin Elmer, Waltham, MA). The intrinsic luminescence spectra of as-prepared nanosheets were gained by Renishaw Raman spectrograph in the photoluminescence (PL) mode. And the NIR emission spectra of nanosheets were obtained through a Fluorolog-3 (Jobin Yvon, Paris, France) fluorescence spectrometer with an 808 nm laser diode.

3 Results and discussion

Structure and morphology play an important role in material properties. Figure 1A shows the XRD patterns of bulk and nanosheets of In_2Se_3 doped with Nd^{3+} ions. The doped In_2Se_3 bulk exhibits a perfect accordance with XRD patterns of the standard card (PDF#40-1407), which suggests the bulk belonging to hexagonal system. And it shows that the characteristic of the doped γ -phase is similar with former works of Marsillac and coworkers [17]. The XRD patterns of nanosheets also show the feature of γ -phase, which demonstrates that the exfoliation will not alter the phase of as-prepared materials. TEM was used to reveal the microscopic morphology of the prepared $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. As shown in Figure 1B,

Figure 1: Morphology and crystalline structure.

(A) XRD patterns of bulk and nanosheets of the $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ samples. (B) TEM image of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. (C) HR-TEM image of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. (D) AFM image of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. Inset: Height profile of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets.

the contrast of nanosheets is almost at the same level, which demonstrates that the nanosheets are quite thin to a large extent. And it can be observed that the size of as-prepared nanosheets is at tens to hundreds of nanometers scale. Figure 1C indicates the high-resolution TEM (HR-TEM) image of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. It reveals a lattice spacing of around 0.319 nm. According to the formula:

$$d = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \left(\frac{a}{c}\right)^2 l^2}},$$

which indicates the relationship between interplanar spacing (d) and Miller index (h, k, l) and lattice constant (a, c); the observed plane is consistent with (110) face of hexagonal $\gamma\text{-In}_2\text{Se}_3$ crystal after calculation.

The AFM image further shows that the as-prepared nanosheets are extremely flat. It can be obtained from the AFM image that the plane size of as-prepared nanosheets is around hundreds of nanometers, but the thickness is just 4.5 nm, which is far less than the flat size. According

to the above results of XRD, TEM, and AFM, it can be concluded that 2D-structure nanosheets with good crystallinity have been successfully fabricated.

XPS was carried out to investigate whether Nd^{3+} ions have been already doped into In_2Se_3 nanosheets. Figure 2A shows the XPS pattern of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets in full scale. Apparently, the In, Se and Nd elements can be observed in the full-scale spectrum; however, C and O are introduced from the measurement. Among them, HR-XPS spectrum of Nd 3d is presented in Figure 2B. Peaks located at 974.2 and 995.2 eV originated from Nd $3d_{5/2}$ and Nd $3d_{3/2}$ binding energies, respectively. Figure 2C and D expressed the HR-XPS spectra of In_2Se_3 nanosheets with undoped and doped Nd^{3+} ions. It can be observed that the core-level peaks of In and Se in the $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ sample show a slightly shift toward higher binding energies compared with the undoped In_2Se_3 sample, which reveals the transformation of chemical microenvironment. Therefore, the intensities of In and Se elements are both lower than the undoped sample, which means the electric pairs of chemical bonds are attracted to them. This change suggests that

Figure 2: XPS spectra of In_2Se_3 nanosheets with and without Nd ions.

(A) Full-scale XPS spectrum of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. (B) HR-XPS spectrum of Nd 3d core levels in $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. Contrastive HR-XPS spectra of (C) In 3d and (D) Se 3d core levels in undoped In_2Se_3 and $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets.

Nd^{3+} ions have been introduced into the In_2Se_3 matrix. This may be due to facts that the electronegativities of In and Se are larger than that of the Nd element from Allred-Rochow scale [35]. Besides, no apparent binding energy peaks of NdF_3 can be discerned here. Therefore, it can be confirmed from the above results that the Nd^{3+} ions have been successfully doped into In_2Se_3 nanosheets.

Raman and intrinsic PL spectra were further used to reveal the structural characteristics of the prepared $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. As shown in Figure 3A, the Raman spectra of bulk and nanosheets of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ samples were collected under 532 nm excitation. Five Raman peaks located at around 81, 150, 179, 206, and 227 cm^{-1} are observed in both bulk and nanosheets, which agree well with the previous reports of $\gamma\text{-In}_2\text{Se}_3$ [17, 36, 37]. The full width at half maximum of the main Raman peak located at about 150 cm^{-1} is approximately 9 cm^{-1} , which is consistent with former research as well [37]. Furthermore, there is almost no peak position difference between bulk and nanosheets, which suggests that the sonification hardly changed the phase structure of In_2Se_3 nanosheets. Considering the above results, it can be further proved that the as-prepared nanosheets are γ -phase with 2D structure.

Figure 3B shows the intrinsic PL spectra of bulk and nanosheets of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ under 532 nm (2.33 eV, which is larger than the band gap of 2D In_2Se_3) excitation. Apparently, the PL intensity of nanosheets is stronger than bulk, whose peaks are both located at around 675 nm (1.84 eV). According to previous reports, the intensity of PL emission is relevant with the thickness (z-axis) and plane size (xy-plane) of the prepared sample [38–40]. It can be speculated that the PL performance of bulk and nanosheets is related to the combined effects of carrier confinement through the xy-plane together with along the z-axis [41, 42]. Our intrinsic result is consistent with the previous report [42].

UV-VIS-NIR absorption spectroscopy was applied to investigate the band gap and optical response. Figure 4A indicates the absorption spectrum of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. It can be observed that the nanosheets possess a broadband absorption in the range from 300 nm (UV) to 1200 nm (NIR). After calculation with Tauc plot method (as shown in right insert), the band gap of as-prepared nanosheets is around 1.83 eV (677 nm), which is nearly consistent with the above intrinsic PL emission. As shown in Figure 4B, the absorption signals decrease

Figure 3: Raman and intrinsic PL spectra of the prepared $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ samples. (A) Raman and (B) intrinsic photoluminescence spectra of bulk and nanosheets under 532 nm excitation.

Figure 4: Absorption spectra of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. (A) UV-VIS-NIR absorption spectrum of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. Insert: Tauc plot with its calculation of band gap. (B) UV-VIS-NIR absorption spectra of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets at different rates of centrifugation. Insert: photos with suspension of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets at different centrifugal speeds.

with the increase in centrifugation speed. This is owing to a smaller particle size and thinner concentration of the obtained supernatant, which results in weaker absorption signals. Moreover, the colors of supernatants with various centrifugal speeds are not the same because of the different sizes of the nanoparticles, which is just like the optical photo displayed in the insert.

The PL performance demonstrates that the $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets possess intrinsic emission at a range of visible. In order to extend the emission range, Nd^{3+} ions were doped into the In_2Se_3 matrix. We then investigated the luminescence properties of lanthanide Nd^{3+} ions in 2D In_2Se_3 nanosheets. Figure 5A illustrates the emission spectra of In_2Se_3 nanosheets with doped and undoped Nd^{3+} ions by pump laser of 808 nm. It can be clearly seen that three PL peaks appear after Nd^{3+} ion doping. The emission peaks located at 910, 1057, and 1324 nm are consistent with the energy transitions of Nd^{3+} ions from excited state $^4\text{F}_{3/2}$ toward $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, and $^4\text{I}_{13/2}$, respectively [25]. On the contrary, emission peaks of undoped nanosheets in the range of NIR are hardly observed. Therefore, the doping of Nd^{3+} ions did increase the emission region from visible

to NIR spectra. Figure 5B indicates the emission spectra of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets with different concentrations from 100 ppm to 500 ppm. The emission signal of nanosheets exhibits a stronger trend as the increment of concentration. This can be attributed to positive correlation between emission intensity and consistency of lanthanide Nd^{3+} under some conditions.

Additionally, optical characteristics and luminescent transition mechanism were further researched in $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets. Figure 6A shows the emission spectra of $\text{In}_2\text{Se}_3\text{:Nd}^{3+}$ nanosheets in a concentration of 500 ppm with different pump powers under 808 nm excitation. It can be distinctly observed that the emission signal became strong with the increasing of pump power from 500 to 5000 mW, which is owing to the addition of population in unit time with excitation source. Moreover, the pump power (P) and the PL intensity (I) abide by this relation: $I \propto P^n$, where n represents the number of photons [43]. According to this relationship, the double 10 logarithm plot (log-log) was drawn, as shown in Figure 6B, and the slopes denote the number of photons. After linear fitting of data points, the slopes of emission peaks at 910,

Figure 5: NIR PL spectra of In_2Se_3 nanosheets with and without Nd ions.

(A) NIR down-shifting PL spectra of undoped and doped In_2Se_3 nanosheets under the pump at 808 nm. (B) NIR emission spectra of $\text{In}_2\text{Se}_3:\text{Nd}^{3+}$ nanosheets in various concentrations by 808 nm excitation.

Figure 6: NIR luminescence properties of Nd ions in In_2Se_3 nanosheets.

(A) NIR emission spectra of $\text{In}_2\text{Se}_3:\text{Nd}^{3+}$ nanosheets excited at 808 nm in diverse pump power. (B) Pump power dependence of emission intensity at 910, 1057, and 1324 nm. (C) NIR decay curve for 1057 nm emission of $\text{In}_2\text{Se}_3:\text{Nd}^{3+}$ nanosheets. (D) Energy level diagram of Nd^{3+} ions and the probable down-conversion mechanism.

1057, and 1324 nm are 0.35 ± 0.03 , 0.64 ± 0.04 , and 0.73 ± 0.03 , respectively. That means that the PL emission of 910, 1057, and 1324 nm possesses one photon, i.e. single photon process. The reason why the value of slopes is all lower than 1 may be attributed to factors of saturated excitation, heat accumulation, or other effects. Figure 6C shows the decay curve for Nd^{3+} ions under 808 nm pump excitation. The lifetime of Nd^{3+} ions in In_2Se_3 nanosheets with emission peak located at 1057 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) is

determined to be 0.75 ms after calculating from the decay curve.

The possible down-conversion mechanism for Nd^{3+} ions in 2D In_2Se_3 nanosheets is described in Figure 6D. The GSA, CR, and NR represent ground state absorption, cross relaxation, and nonradiative relaxation, respectively. Under the excitation of 808 nm pump, the ground state $^4I_{9/2}$ of Nd^{3+} ions are absorbed to excited state $^4F_{5/2}$. Next, it happens to the NR process from excited state $^4F_{5/2}$ to $^4F_{3/2}$.

Lastly, the radiation transitions from $^4\text{F}_{3/2}$ to $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, and $^4\text{I}_{13/2}$ are determined to be NIR emission of 910, 1057, and 1324 nm, respectively.

4 Conclusion

In summary, a reliable and effective method of solid state reaction and liquid phase exfoliation has been employed to fabricate lanthanide ion Nd^{3+} -doped 2D In_2Se_3 nanosheets. The fabricated Nd^{3+} ion-doped In_2Se_3 nanosheets are determined to be 2D in structure with a thickness of 4.5 nm via TEM and AFM characterizations. The prepared 2D In_2Se_3 nanosheets doped with Nd^{3+} ions possess γ -phase after analyses by XRD and Raman detection. The XPS measurement, combined with PL spectra, indicate that the lanthanide ions Nd^{3+} have been successfully introduced into In_2Se_3 nanosheets. Under 808 nm excitation, several emissions in the NIR region can be observed from the lanthanide ions Nd^{3+} in 2D In_2Se_3 nanosheets. The emission peaks located at 910, 1057, and 1324 nm originated from the transitions of $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$, and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$, respectively. This down-conversion luminescence of Nd^{3+} ions in the NIR region is determined to be single photon process by analysis of power-dependent emission spectra. Moreover, the introduction of Nd^{3+} ions extends the emission region of intrinsic In_2Se_3 semiconductor from visible to NIR spectra. Our work indicates that the two-step method reported here is an effective approach to embed the lanthanide ions into 2D nanosheets. The prepared 2D $\text{In}_2\text{Se}_3:\text{Nd}^{3+}$ nanosheets with excellent NIR luminescence have promising applications in NIR photonic nanodevices and biomedicine.

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