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# Bandgap regulation and doping modification of Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets†

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Ga<sub>2</sub>Se<sub>3</sub>, an important direct wide bandgap semiconductor with excellent optoelectronic properties, has wide application potential in the fields of photodetectors, photoelectric sensors and solar cells. Herein, we describe the synthesis of Ga<sub>2</sub>Se<sub>3</sub> semiconductor nanoparticles using a high temperature organic liquid phase method. Post-annealing treatment at different temperatures can not only improve the crystallinity of Ga<sub>2</sub>Se<sub>3</sub> nanoparticles, but also regulate its optical band gap ranging from 2.50 to 2.80 eV. We further synthesized Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets by doping CrCl<sub>3</sub>·6H<sub>2</sub>O in the reaction process. By adjusting the Cr doping concentration, Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets can achieve a continuously tunable band gap in the range of 2.23 eV to 2.42 eV. Both Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets and Ga<sub>2</sub>Se<sub>3</sub> nanoparticles exhibit excellent and stable photoelectric switching performance. With Cr doping, Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> exhibits reduced Nyquist impedance and enhanced electrocatalytic activity, which is attributed to its ultrathin nanosheet morphology and large specific surface area. In addition, the diamagnetic behavior of pure Ga<sub>2</sub>Se<sub>3</sub> changes to ferromagnetism with different Cr doping concentrations, and its magnetization is as high as 18.0 emu g<sup>-1</sup> at x = 0.4. These findings demonstrate that Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets have significant potential in future optoelectronic and magnetoelectric applications.

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## 1. Introduction

Band engineering is an important tool for modulating the electronic structure of semiconductor materials and studying their physical properties. Current strategies for bandgap manipulation primarily include surface modification, doping/alloying, applying strain, constructing heterojunctions, *etc.*<sup>1-4</sup> These approaches can effectively alter the band structure of semiconductor materials, thereby affecting their electron transport, optical properties, and chemical activity.<sup>5,6</sup> Therefore, controlling the bandgap of semiconductors through various physical or chemical methods is essential for meeting specific application requirements.

China is the world's largest producer of Ga and Ge, and its Ga reserves rank first in the world.<sup>7-9</sup> III-VI compounds such as NX (N = Ga, In, and X = S, Se) have been enthusiastically studied due to their scientific merits of strong light absorption, high carrier mobility, flexibility, ultrathinness, larger

area and thickness-tunable band gap modulation.<sup>10-13</sup> Ga<sub>2</sub>Se<sub>3</sub> is a typical III<sub>2</sub>VI<sub>3</sub> natural defective semiconductor, which crystallizes in a defect zincblende structure with one-third of cationic vacancy.<sup>14-16</sup> Ga<sub>2</sub>Se<sub>3</sub> is a p-type semiconductor with a wide bandgap of 2.5 eV and has excellent photoelectric performances with a high photosensitivity (9.2 A W<sup>-1</sup>) and a fast response time (rise/fall time of <4/3 ms).<sup>17-20</sup> And the constituents of Ga and Se are also low cost, nontoxic, and environmental friendly.<sup>21,22</sup> Thus, Ga<sub>2</sub>Se<sub>3</sub> is attractive in next-generation high performance photodetection and photovoltaic.

In this work, defective Ga<sub>2</sub>Se<sub>3</sub> nanoparticles and Cr-doped Ga<sub>2</sub>Se<sub>3</sub> nanosheets were synthesized by a simple high temperature organic liquid phase method and their photoelectric response behavior and magnetic properties were systematically explored. Annealing treatment at different temperatures not only improved the crystallinity of Ga<sub>2</sub>Se<sub>3</sub>, but also finely tuned its optical band gap ranging from 2.50 to 2.80 eV. Meanwhile, Cr doping not only effectively adjusted the bandgap but also enhanced the material's magnetization performance and electrocatalytic activity. The Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets demonstrated an adjustable band gap ranging from 2.23 to 2.42 eV. At a Cr concentration of x = 0.4, these nanosheets showed a significant magnetization intensity of up to 18.0 emu g<sup>-1</sup> and exhibited excellent and stable photoelectric switching performance. Furthermore, Ga<sub>1.6</sub>Cr<sub>0.4</sub>Se<sub>3</sub>

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nanosheets displayed reduced Nyquist impedance and enhanced electrocatalytic activity, which can be attributed to their ultrathin morphology and large specific surface area compared to the Ga<sub>2</sub>Se<sub>3</sub> nanoparticles. Thus, the Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> nanosheets are promising for the next-generation diverse optoelectronic and magnetoelectric applications.

## 2. Experimental

### 2.1. Materials

Gallium acetylacetonate [Ga(acac)<sub>3</sub>, 99.99%], chromium trichloride hexahydrate (CrCl<sub>3</sub>·6H<sub>2</sub>O, 98%), selenium powder (Se, 200 mesh, 99.999%), oleylamine (OLA, 80–90%) and octadecylene (ODE) were purchased from Alfa Aesar. Ethanol (99.7%) was purchased from Tianjin Kermel, and hexane (99.5%) was obtained from Tianjin Fengchuan Chemical Reagent Co. All chemicals and solvents were used as received without any further purification.

### 2.2. Synthesis

0.5 mmol Ga(acac)<sub>3</sub>, 1.0 mmol Se and solvents (OLA/ODE, 20 ml) added into a four-neck round-bottom flask at room temperature, sealed, and then degassed at 120 °C for 20 min with N<sub>2</sub> atmosphere. Then the mixture was heated up to 200 °C

at the rate of ~2 °C min<sup>-1</sup>, and allowed to be aged for another 2 h at this temperature in N<sub>2</sub> atmosphere. Finally, the solution was cooled down to room temperature naturally, and excess ethanol was added to precipitate the products, which can be harvested through centrifugation at 8000 rpm for 5 min. The Ga<sub>2</sub>Se<sub>3</sub> nanoparticles can be obtained by rewashing the precipitates with ethanol and hexane for three times. And the Ga<sub>2-x</sub>Cr<sub>x</sub>Se<sub>3</sub> (x = 0.2, 0.4, 0.6) nanosheets were synthesized by adding CrCl<sub>3</sub>·6H<sub>2</sub>O (0.05 mmol, 0.10 mmol, 0.15 mmol) under the similar synthesis conditions.

### 2.3. Analysis and characterizations

The phase structures were identified by using powder X-ray diffraction (XRD, D8 Advance) with a Cu K $\alpha$  radiation source ( $\lambda = 0.154$  nm). The morphologies and element valences were investigated by scanning electron microscope (SEM, JSM-7500F), transmission electron microscope (TEM, JEM-F2100) equipped with energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha). The magnetic hysteresis loops (*M-H*) were performed using a physical property measurement system (PPMS, QD Dyna Cool) with a field of up to 5 T. The N<sub>2</sub> adsorption/desorption isotherms and pore size distribution curves were obtained by Micromeritics ASAP 2020. And all the electrochemical

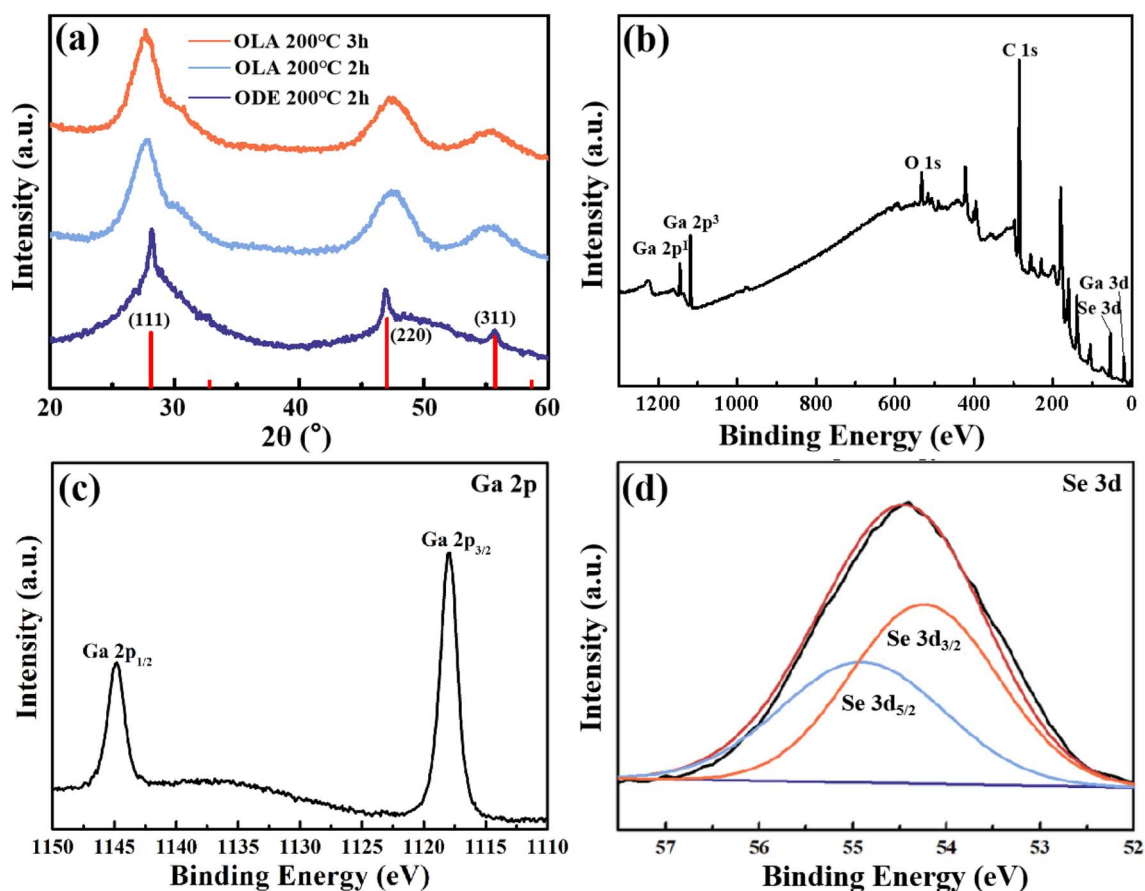


Fig. 1 (a) XRD patterns, (b–d) XPS spectra and high-resolution Ga 2p, Se 3d spectra of Ga<sub>2</sub>Se<sub>3</sub> nanoparticles.



measurements were carried out on a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) with a standard three-electrode setup.

#### 2.4. Electronic structure calculations

The theoretical calculations were based on density functional theory (DFT). The exchange–correlation potential of Perdew–Burke–Ernzerhof (PBE) with the generalized-gradient approximation (GGA) was used for structural relaxations of  $\text{Ga}_2\text{Se}_3$  unit cell. The energy band structures and density of states (DOS) of original  $\text{Ga}_2\text{Se}_3$ , expand  $\text{Ga}_2\text{Se}_3$  and  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  were performed with HSE06 functional.

### 3. Results and discussions

Colloidal  $\text{Ga}_2\text{Se}_3$  nanoparticles were synthesized by a facile high temperature organic liquid phase method, employing gallium acetylacetonate and selenium in various solvents and at different reaction times. As depicted in Fig. 1a, all of the diffraction peaks could be indexed to the cubic  $\text{Ga}_2\text{Se}_3$  (JCPDS 05-0724), revealing that the as-synthesized  $\text{Ga}_2\text{Se}_3$  sample is a pure phase. XPS was utilized to further analyze the elemental

compositions and chemical states of the  $\text{Ga}_2\text{Se}_3$  nanoparticles. Low-resolution XPS survey confirms the presence of Ga, Se, O and C signals in  $\text{Ga}_2\text{Se}_3$  sample (Fig. 1b). The observed oxygen peak can be attributed to the adsorption of air on the sample surface. In the magnified Ga-2p spectrum (Fig. 1c), two peaks located at 1144.8 eV and 1117.9 eV correspond with the Ga  $2p_{1/2}$  and  $2p_{3/2}$  of  $\text{Ga}^{3+}$ .<sup>23,24</sup> By fitting the Se-3d spectrum (Fig. 1d), the characteristic peaks at 55.1 eV and 54.2 eV correspond with the Se  $3d_{3/2}$  and  $3d_{5/2}$  binding energies of  $\text{Se}^{2-}$ , agreeing well with previous reports.<sup>25</sup> Moreover, the representative SEM images are shown in Fig. 2a–c,  $\text{Ga}_2\text{Se}_3$  exhibit as highly uniform irregular nanoparticles with a diameter of about 500 nm. The TEM image and corresponding elemental mappings in Fig. 2d reveal that colocalization of the Ga and Se elements on the  $\text{Ga}_2\text{Se}_3$  nanoparticles with an average atomic ratio of 38.18% : 61.82% (2 : 3) (Fig. 2e), in good agreement with the above XRD results.

Although  $\text{Ga}_2\text{Se}_3$  pure phase has been prepared, it exhibits a wide diffraction peak (Fig. 1a). To further improve the crystallinity of  $\text{Ga}_2\text{Se}_3$ , the synthesized samples were annealed under vacuum conditions at temperatures of 150 °C, 200 °C, 250 °C, and 300 °C for 2 h. The XRD results (Fig. 3a) show that

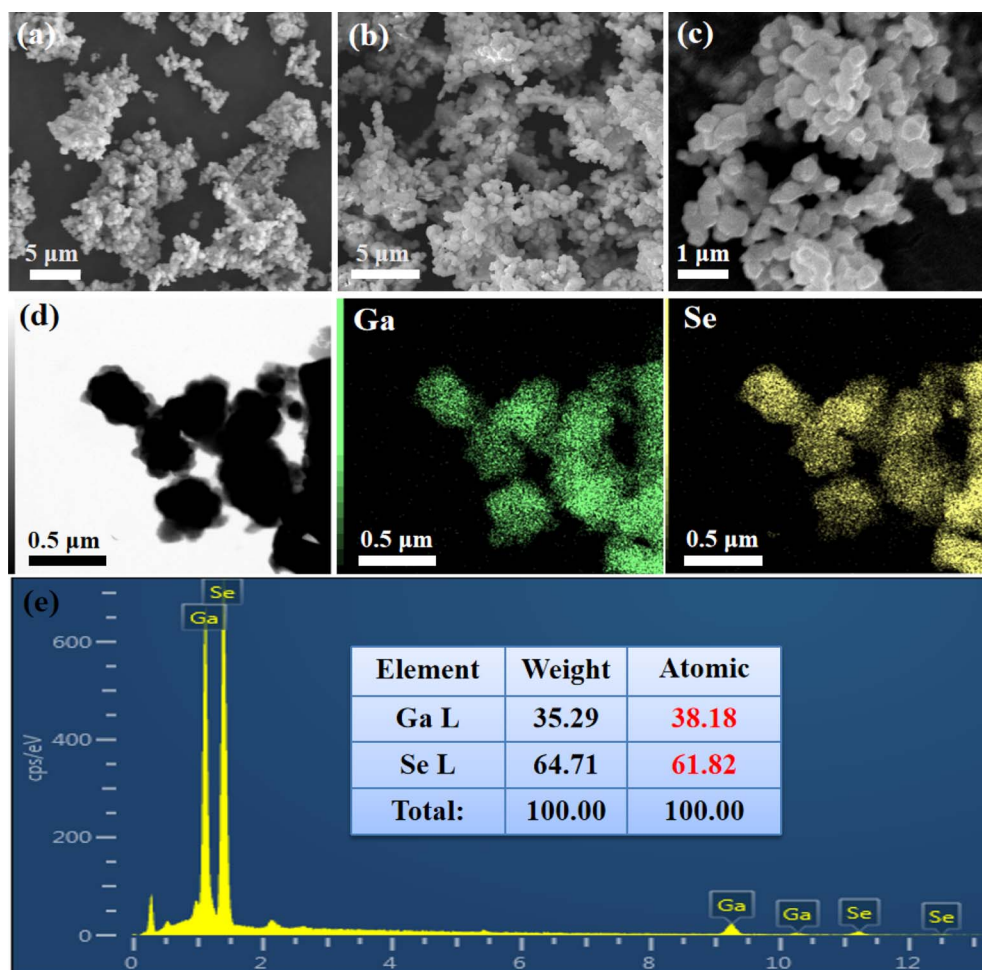


Fig. 2 (a–c) SEM images, (d) corresponding TEM elemental mappings and (e) EDX spectrum of the as-prepared  $\text{Ga}_2\text{Se}_3$  nanoparticles.





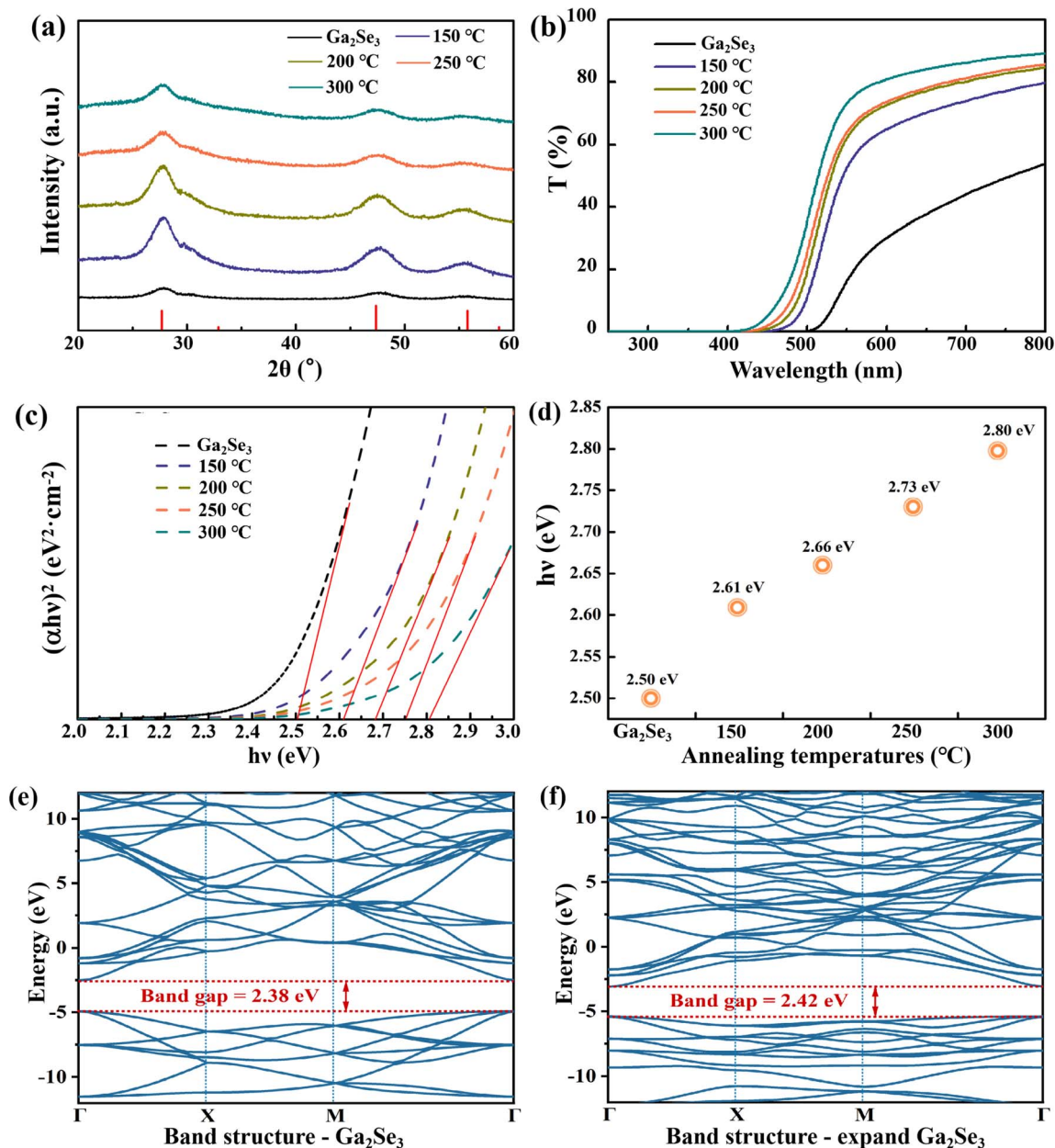


Fig. 3 (a) XRD patterns, (b) transmission spectra, (c)  $(\alpha h\nu)^2 - h\nu$  curves and (d) band gap values of Ga<sub>2</sub>Se<sub>3</sub> sample at different annealing temperatures. (e and f) Calculated energy band structures of Ga<sub>2</sub>Se<sub>3</sub> and expand Ga<sub>2</sub>Se<sub>3</sub> using HSE06 functional.

the main peaks of Ga<sub>2</sub>Se<sub>3</sub> are still present and without any impurities are observed, which further confirms that the Ga<sub>2</sub>Se<sub>3</sub> samples did not undergo phase transformation after annealing. Post-annealing promotes the diffusion of atoms within a material, leading to an orderly realignment of atomic structures. This process effectively reduces grain boundaries and defects.<sup>26</sup> As a result, the crystallinity of Ga<sub>2</sub>Se<sub>3</sub> samples is significantly improved after undergoing annealing. Notably, the sample annealed at 200 °C has the strongest XRD diffraction peak intensity, followed by a decrease in peak intensity with increasing annealing temperature. This suggests that the grain growth may be effectively promoted at

200 °C. Next, to further clarify the changes in XRD diffraction peaks after annealing, the thermal stability of the Ga<sub>2</sub>Se<sub>3</sub> sample was carried out (Fig. S1†). From the thermogravimetric curve of Ga<sub>2</sub>Se<sub>3</sub>, weight loss is observed starting around about 200 °C, which is consistent with the decomposition temperature of selenium.<sup>27</sup> Moreover, upon annealing at 300 °C, the weight of Ga<sub>2</sub>Se<sub>3</sub> nanoparticles decreases to 80% of the initial mass. Consequently, the decrease in peak intensity beyond 200 °C can be ascribed to the formation of selenium vacancies and the concomitant reduction in Ga<sub>2</sub>Se<sub>3</sub> mass.

The optical bandgaps of Ga<sub>2</sub>Se<sub>3</sub> samples were determined by UV-vis-NIR transmission spectra, as shown in Fig. 3b. The



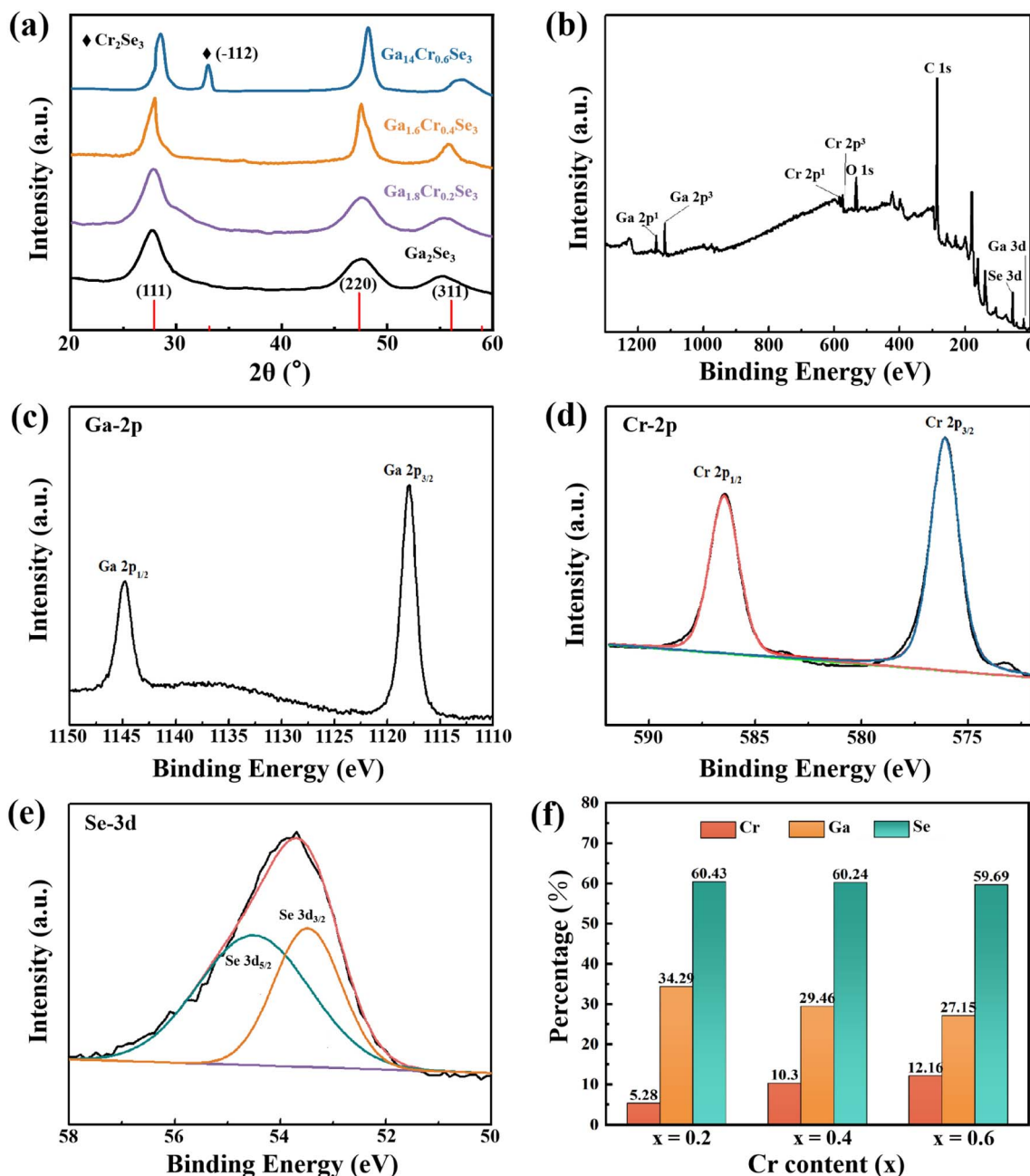


Fig. 4 (a) XRD patterns of different Cr-doped  $\text{Ga}_2\text{Se}_3$  nanomaterials. (b) XPS spectra and (c–e) high-resolution spectra of Cr 2p, Ga 2p and Se 3d in  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  sample. (f) EDX analyses of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  (0 ≤ x ≤ 0.6) with different Cr concentrations.

transmittance of  $\text{Ga}_2\text{Se}_3$  nanoparticles had a sharply decline at about 570 nm and decreased almost to zero near 400 nm. And the absorption band edge of  $\text{Ga}_2\text{Se}_3$  samples are continuously blue-shifted with increasing annealing temperatures. The bandgap was calculated according to the equation  $(\alpha h\nu)^n = C(h\nu - E_g)$ , where  $C$  is a constant,  $\alpha$  is the absorption coefficient,  $E_g$  is band gap,  $h\nu$  is the photon energy and  $n$  equals to 2 for direct inter-band transition.<sup>28</sup> By plotting  $(\alpha h\nu)^2 - h\nu$  curves

(Fig. 3c) and extrapolating the linear sections of the curves to the  $x$ -axis, the band gaps were determined to be 2.50, 2.61, 2.66, 2.73, and 2.80 eV for the untreated and annealed samples at 150, 200, 250, and 300 °C, respectively (Fig. 3d). Table S1† shows the lattice constants and cell volumes calculated from the XRD patterns in Fig. 3a. It is observed that annealing at various temperatures leads to a large lattice constant ( $a$ ) compared to the original  $\text{Ga}_2\text{Se}_3$ . The non-monotonic increase



in lattice constants ( $a$ ) at 250 °C may be attributed to lattice distortion effects. And the lattice distortion relative to  $\text{Ga}_2\text{Se}_3$  for annealing at 150, 200, 250, and 300 °C is  $\Delta V = 3.46, 4.85, 3.37$  and  $4.40 \text{ \AA}^3$ . At high temperatures, atomic or phonon vibrations significantly affect the band gap through electron-phonon interactions and lattice thermal expansion, as observed in semiconductors like black phosphorus and  $\text{CsSnI}_3$ .<sup>29,30</sup> To further investigate the influence of lattice parameters and chemical bonds on the band gap of  $\text{Ga}_2\text{Se}_3$ , we conducted first-principles calculations. As depicted in the band structure in Fig. 3e, the untreated  $\text{Ga}_2\text{Se}_3$  has a band gap

of 2.38 eV, which is a direct band gap material due to the alignment of the valence band maximum and conduction band minimum at the same high-symmetry point. As the lattice constant of  $\text{Ga}_2\text{Se}_3$  increases from 5.219 Å to 5.438 Å, the lattice expansion weakens the interaction between atoms, resulting in a decrease in the overlap of Ga and Se atomic orbitals (Fig. 3f). This separation of electronic states in the valence band and conduction band leads to an increase in the band gap to 2.42 eV.

Fig. 4a shows the XRD patterns of different Cr-doped  $\text{Ga}_2\text{Se}_3$  nanomaterials. The main peaks (111) and (220) of  $\text{Ga}_2\text{Se}_3$  shift

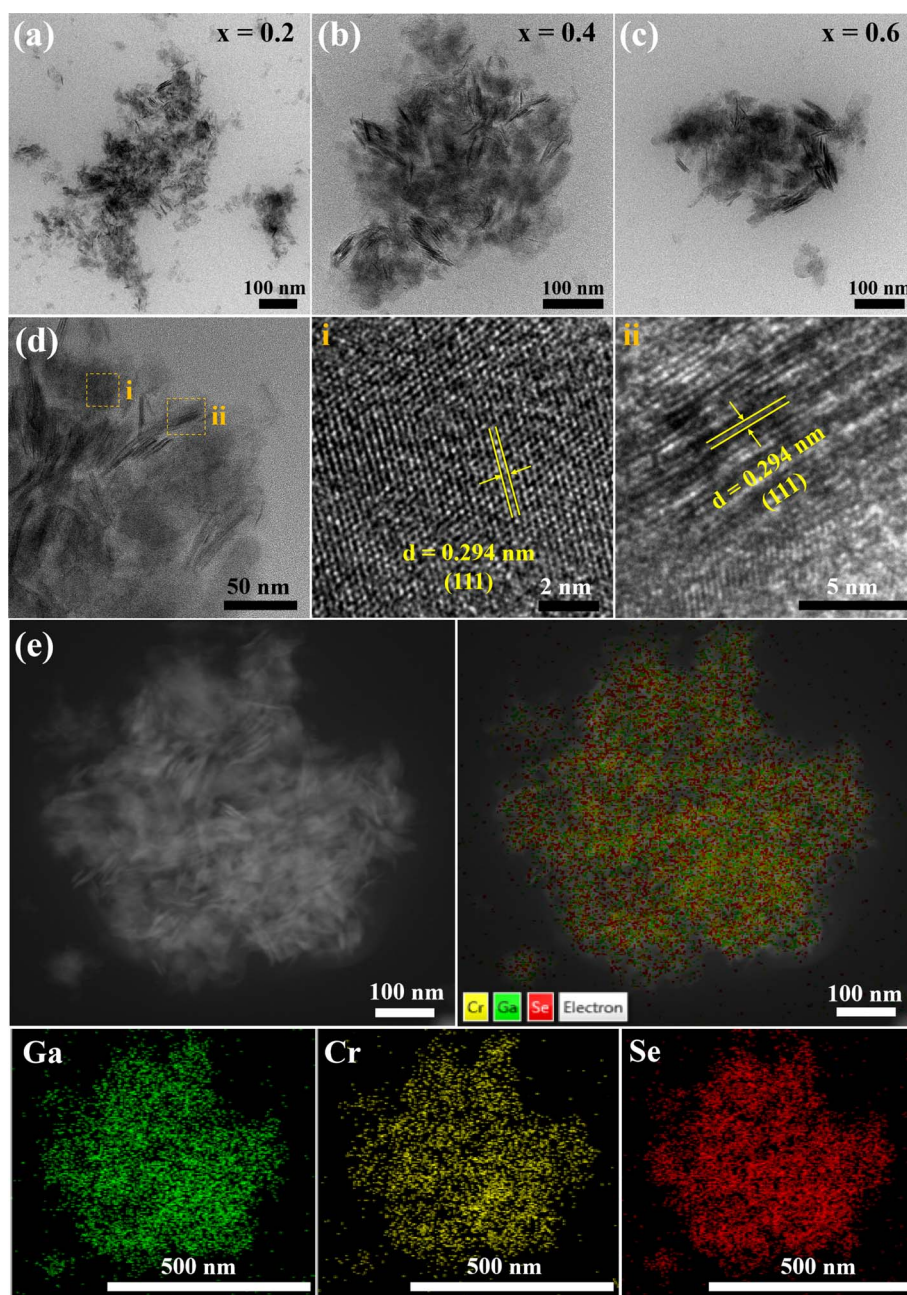


Fig. 5 (a–c) TEM images of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  ( $0 \leq x \leq 0.6$ ) nanosheets with different Cr concentrations. (d) Enlarged TEM, HRTEM and (e) corresponding elemental mappings images of  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  nanosheets.





to the higher angle with increasing Cr dopant content ( $0 < x \leq 0.6$ ), which is attributed to the replacement of  $\text{Cr}^{3+}$  (69 pm) by the smaller  $\text{Ga}^{2+}$  (62 pm). And the corresponding lattice constants and unit cell volumes of the  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  were summarized in Table S2.† However, when the Cr doping content reaches 0.6, the diffraction peak at  $33^\circ$  can correspond to the hexagonal  $\text{Cr}_2\text{Se}_3$  ( $-112$ ) crystal plane. These results indicate that Cr ions can be successfully doped into  $\text{Ga}_2\text{Se}_3$  lattice, while the excessive Cr ions will combine with Se ions to form new phase  $\text{Cr}_2\text{Se}_3$ . XPS spectra (Fig. 4b) further confirm the presence of Ga, Se and Cr in the  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  ( $x = 0.4$ ) sample. From Cr-3d spectrum in Fig. 4c, the chemical states of Cr  $2p_{1/2}$  and  $2p_{3/2}$  can be identified from the peaks at binding energies of 586.5 eV and 576.2 eV, which proves the sample is indeed doped with Cr element.<sup>31</sup> And the Ga-2p and Se-3d spectra in  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  ( $x = 0.4$ ) are the same as those in  $\text{Ga}_2\text{Se}_3$  (Fig. 4d and e). The content of Cr, Ga and Se elements in  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  samples was analyzed using EDX spectra, as shown in Fig. S3 and Table S3.† The histogram in Fig. 4 signifies that as the doping amount ( $x$ ) increases, the amount of chromium gradually increases, while the content of gallium gradually decreases. Significantly, the total cation content ( $\text{Cr}^{3+} + \text{Ga}^{3+}$ ) and the total anion content ( $\text{Se}^{2-}$ ) maintained a constant ratio of 2 : 3. This further confirms the partial substitution of Ga

cations by Cr cations, indicating a substitutional doping has occurred between cations.

Fig. 5 shows TEM images of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  with different Cr dopants. All  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  samples are composed of ultra-thin nanosheets with a size of about 100 nm and are well dispersed (Fig. 5a–c). In the high-resolution TEM image of the  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  sample (Fig. 5d), a clear lattice fringe of 0.294 nm is observed, which is smaller than the lattice spacing (0.314 nm) on the (111) plane of cubic  $\text{Ga}_2\text{Se}_3$ . It is consistent that the (111) peak has a slight blueshift in the XRD pattern. The elements Cr, Ga and Se are uniformly distributed in  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  ultra-thin nanosheets (Fig. 5e). Thus, Cr doping in  $\text{Ga}_2\text{Se}_3$  facilitates the formation of ultrathin nanosheets.

The magnetic hysteresis loops (Fig. 6a) of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  ( $0 \leq x \leq 0.6$ ) at 5 K were obtained by PPMS. When  $x = 0$ ,  $\text{Ga}_2\text{Se}_3$  nanoparticles show a diamagnetic signal. The  $M-H$  curve is a straight line passing through the second and fourth quadrants, and the magnetic moment is almost 0. As the incorporation of Cr ions into the  $\text{Sb}_2\text{Se}_3$  lattice, the system began to exhibit ferromagnetism. When  $x = 0.4$ , the magnetization can reach up to  $18.0 \text{ emu g}^{-1}$  at 40 kOe. The 3d orbital partially occupied by Cr element is the main magnetic moment source. However, when the Cr content increases to  $x = 0.6$ , the system exhibits antiferromagnetism. This is consistent with the reported antiferromagnetism of  $\text{Cr}_2\text{Se}_3$  nanostructures with

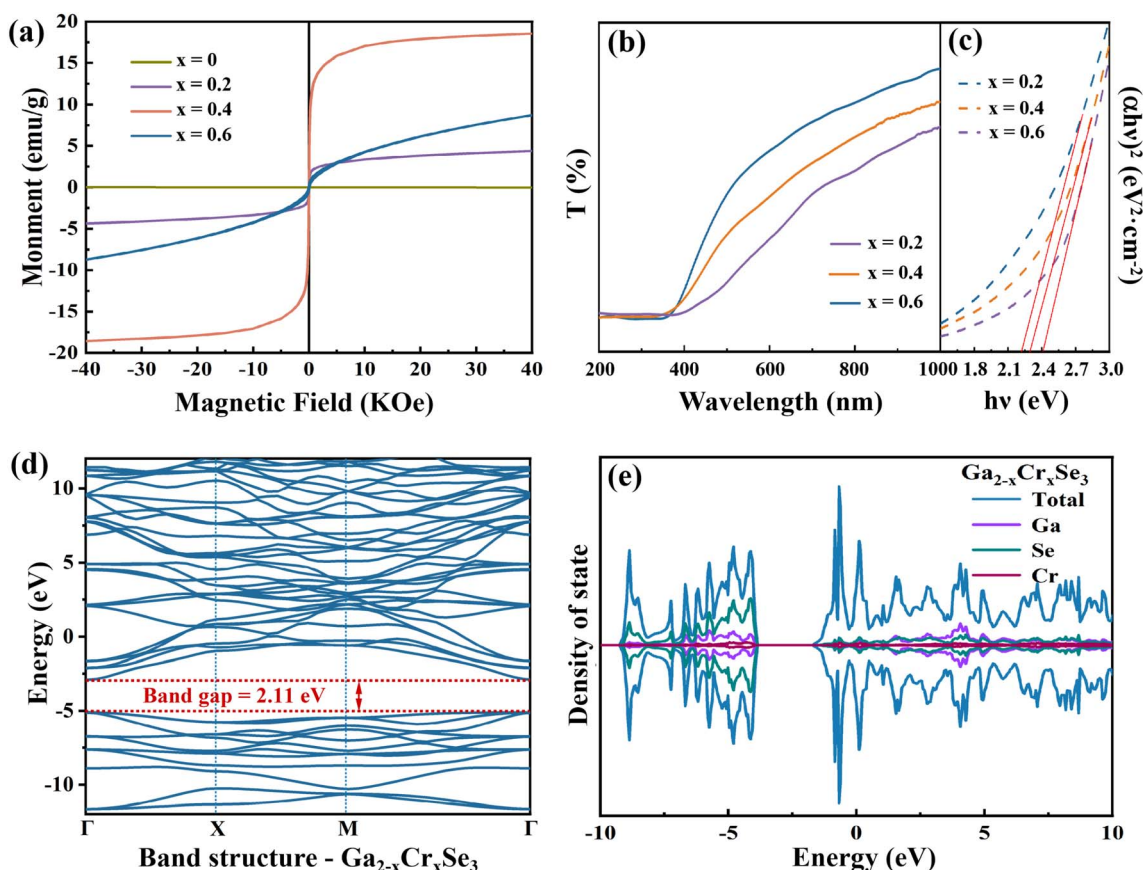


Fig. 6 (a)  $M-H$  loops measured at 5 K, (b) transmission spectra, (c)  $(\alpha hv)^2-h\nu$  curves of the  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  ( $0 \leq x \leq 0.6$ ) nanosheets with different Cr concentrations. (d and e) Calculated energy band structure and DOS plot of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  sample.

non-collinear spin configuration, which confirms the XRD results.

Cr doping not only induces ferromagnetism in  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  system, but also affects the band gaps of  $\text{Ga}_2\text{Se}_3$ . From the transmission curves and plotting  $(\alpha h\nu)^2 - h\nu$  curves (Fig. 6b and c), it can be seen that the band gaps of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  are estimated as 2.42, 2.30, and 2.23 eV when the Cr content ( $x$ ) is 0.2, 0.4 and 0.6. The introduction of Cr ions significantly alters the electronic structure of  $\text{Ga}_2\text{Se}_3$ . The detailed analysis of the band structure and DOS calculations demonstrates that the newly introduced Cr ion density peaks appear near the Fermi level, increasing the density of states around this region. This increase reduces the energy required for electrons to transition from the valence band to the conduction band, resulting in a decrease in the band gap of  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  (2.11 eV). Combined with the band gaps of  $\text{Ga}_2\text{Se}_3$  annealed at different temperatures (2.50–2.80 eV), the band gaps of the  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  nano-materials can achieve continuous changes in the range of 2.23 eV to 2.80 eV.

The photoelectrochemical performances of  $\text{Ga}_2\text{Se}_3$  and  $\text{Ga}_{2-x}\text{Cr}_x\text{Se}_3$  ( $x = 0.4$ ) were investigated through the hydrogen evolution reaction (HER) in 0.5 mol per L  $\text{H}_2\text{SO}_4$  aqueous solution. The LSV curves of both  $\text{Ga}_2\text{Se}_3$  and  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  (Fig. S4†) show positive response to simulated light (a 300 W Xe lamp) in the range of 0 to  $-0.6$  V. Notably, the doped

$\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  always displays superior onset potentials for HER compared to pure  $\text{Ga}_2\text{Se}_3$  in both light and dark conditions.  $I-t$  curves in Fig. 7a and b further indicate the  $\text{Ga}_2\text{Se}_3$  and  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  have good photocurrent response in the whole 600 s switching visible light on/off cycle. And the photocurrent densities could be effectively modulated by varying the bias voltage. Specifically, the photocurrent density of  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  increased from 0.2 to  $15.5 \text{ mA cm}^{-2}$ , with the applied bias potentials increasing from  $-0.2$  to  $-0.6$  V, respectively. This enhancement is attributed to the role of bias potentials in facilitating the separation and migration rate of photo-generated electron-hole pairs. Additionally, the lower impedance and charge transfer resistance of  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$ , confirmed by EIS measurements (Fig. 7c and d), suggest that a certain amount of Cr doping significantly improves photoelectrocatalytic hydrogen evolution performance. Additional  $\text{N}_2$  adsorption/desorption isotherms (Fig. 8a and b) display typical type IV behavior according to the IUPAC classification, and pore size distribution curves (Fig. 8c and d) confirm that both materials are primarily mesoporous. Notably, the BET surface area of  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  was measured at  $39.1 \text{ m}^2 \text{ g}^{-1}$ , significantly higher than the  $7.9 \text{ m}^2 \text{ g}^{-1}$  recorded for  $\text{Ga}_2\text{Se}_3$  (Table S4†). The large surface area should favor the rapid transfer of electrons during photoelectrocatalytic processes, which is consistent with the catalytic results.

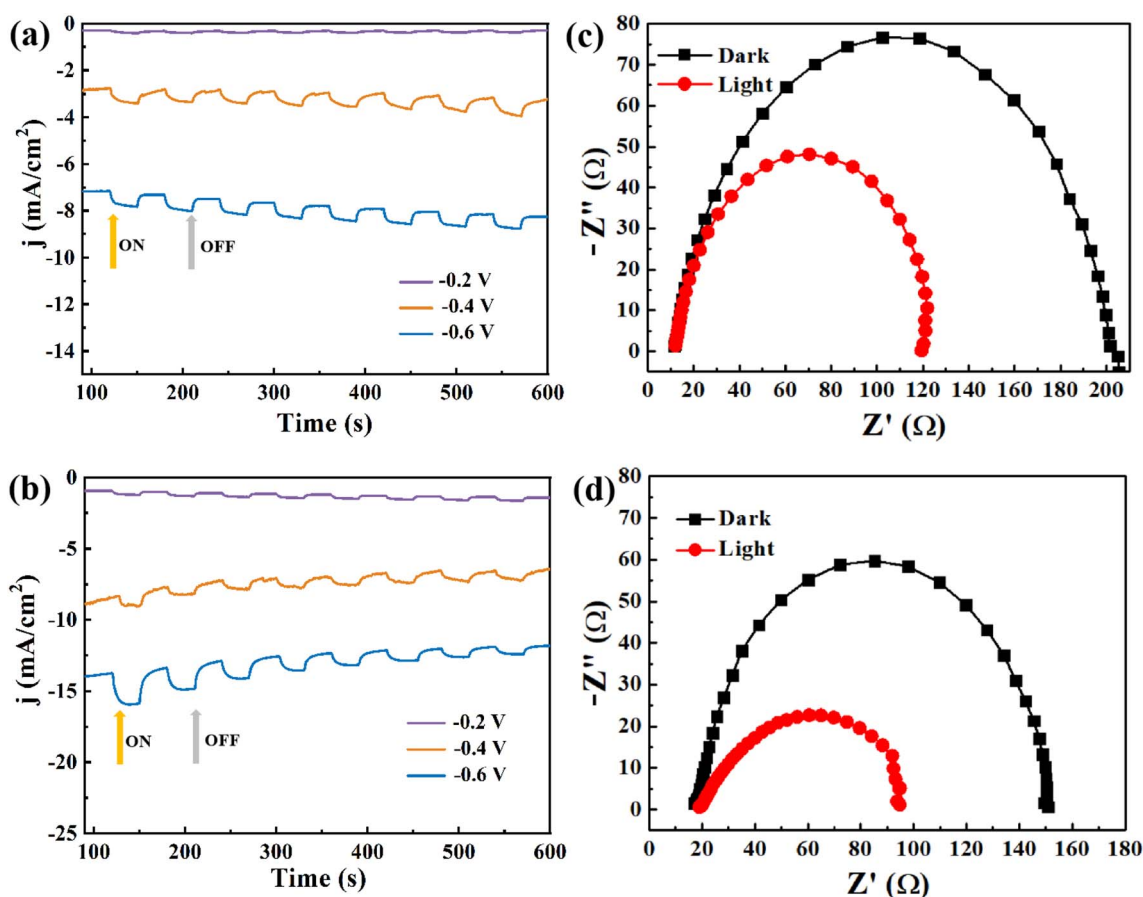


Fig. 7 (a and b)  $I-t$  curves and (c and d) EIS curves of  $\text{Ga}_2\text{Se}_3$  nanoparticles and  $\text{Ga}_{1.6}\text{Cr}_{0.4}\text{Se}_3$  nanosheets.





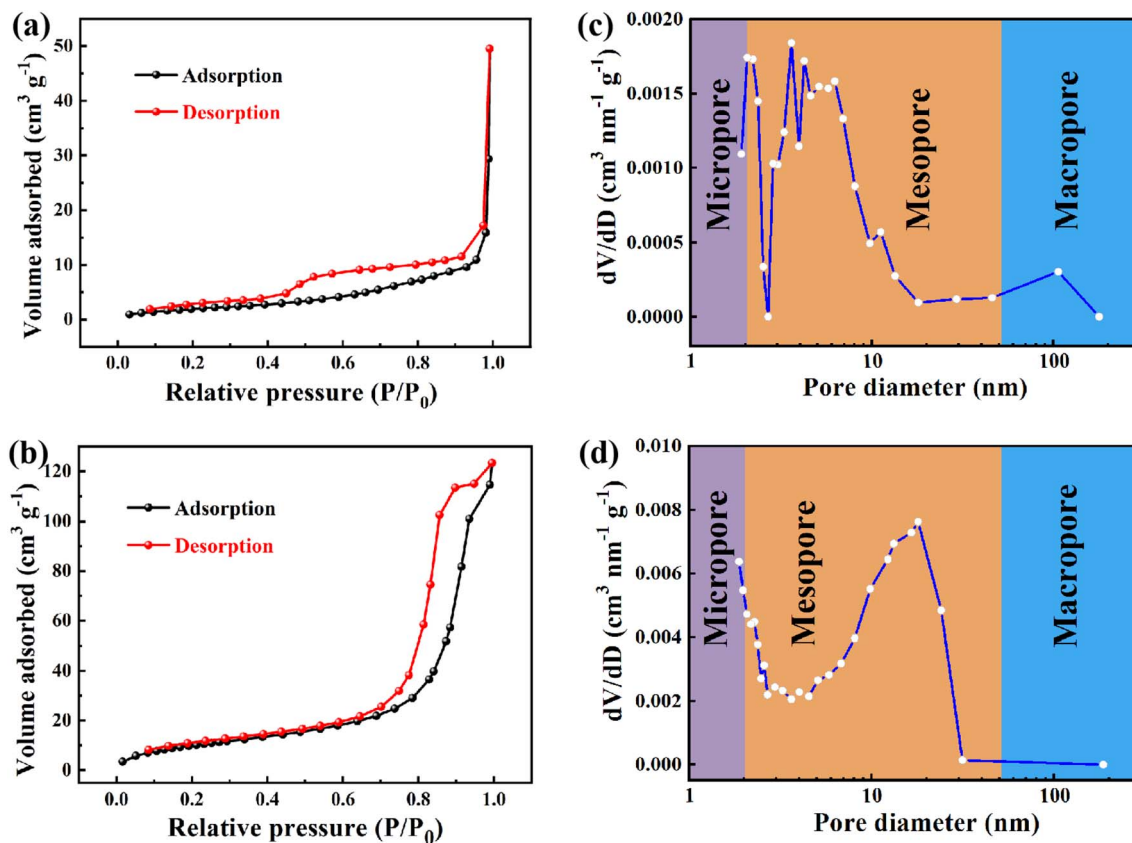


Fig. 8 (a and b)  $N_2$  adsorption/desorption isotherms and (c and d) the corresponding pore-size distribution curves of  $Ga_2Se_3$  nanoparticles and  $Ga_{1.6}Cr_{0.4}Se_3$  nanosheets.

## 4. Conclusion

In summary, we have successfully synthesized  $Ga_2Se_3$  nanoparticles and  $Ga_{2-x}Cr_xSe_3$  nanosheets using high temperature organic liquid phase method. The optical band gaps of  $Ga_{2-x}Cr_xSe_3$  can be continuously adjusted in the range of 2.23 to 2.80 eV with changing the annealing temperature (150–300 °C) and introduction of different Cr doping concentrations. The magnetic study results indicate that moderate Cr doping ( $x < 0.4$ ) induces a transition in  $Ga_2Se_3$  from paramagnetic to ferromagnetic behavior, with a magnetization intensity reaching 18.0  $emu\ g^{-1}$  at 40 kOe. Besides, photoelectrochemical studies reveal that  $Ga_{1.6}Cr_{0.4}Se_3$  nanosheets exhibit superior hydrogen evolution performance compared to  $Ga_2Se_3$  nanoparticles. Therefore, the dual modulation of bandgap and magnetic properties through Cr doping presents a promising avenue for the development of high-performance opto-electromagnetic devices.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of interest

There is no conflict to declare.

## Acknowledgements

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## References

- 1 H. Kim, D. Monllor-Satoca, W. Kim and W. Choi, *Energy Environ. Sci.*, 2015, **8**, 247–257.
- 2 Q. Deng, X. Li, H. Si, J. Hong, S. Wang, Q. Feng, C. X. Hu, S. Wang, H. L. Zhang, K. Suenaga and H. Xu, *Adv. Funct. Mater.*, 2020, **30**, 2003264.
- 3 Z. Dai, L. Liu and Z. Zhang, *Adv. Mater.*, 2019, **31**, 1805417.
- 4 Q. Lv and R. Lv, *Carbon*, 2019, **145**, 240–250.
- 5 M. Kapilashrami, Y. Zhang, Y. S. Liu, A. Hagfeldt and J. Guo, *Chem. Rev.*, 2014, **114**, 9662–9707.
- 6 J. H. Clark, M. S. Dyer and R. G. Palgrave, *J. Am. Chem. Soc.*, 2011, **133**, 1016–1032.
- 7 S. Dai, X. Yan, C. R. Ward, J. C. Hower, L. Zhao, X. Wang, L. Zhao, D. Ren, and R. B. Finkelman, *Coal Geology of China*, Area Studies, London, 2020.
- 8 Z. Lu, G. P. Neupane, G. Jia, H. Zhao, D. Qi, Y. Du, Y. Lu and Z. Yin, *Adv. Funct. Mater.*, 2020, **30**, 2001127.

- 9 K. Xu, L. Yin, Y. Huang, T. A. Shifa, J. Chu, F. Wang, R. Cheng, Z. Wang and J. He, *Nanoscale*, 2016, **8**, 16802–16818.
- 10 X. Li, L. Li and M. Wu, *Mater. Today Phys.*, 2020, **15**, 100229.
- 11 N. Balakrishnan, Z. R. Kudrynskiy, M. W. Fay, G. W. Mudd, S. A. Svatek, O. Makarovskiy, Z. D. Kovalyuk, L. Eaves, P. H. Beton and A. Patanè, *Adv. Opt. Mater.*, 2014, **2**, 1064–1069.
- 12 H. Cai, Y. Gu, Y. C. Lin, Y. Yu, D. B. Geohegan and K. Xiao, *Appl. Phys. Rev.*, 2019, **6**, 041312.
- 13 C. H. Ho, X. R. Lai, C. A. Chuang, W. L. Kuo and K. K. Tiong, *Adv. Photonics Res.*, 2021, **2**, 2000110.
- 14 W. Xue, Q. Jiang, F. Wang, R. He, R. Pang, H. Yang, P. Wang, R. Yang, Z. Zhong, T. Zhai and X. Xu, *Small*, 2022, **18**, 2105599.
- 15 G. Y. Huang, N. M. Abdul-Jabbar and B. D. Wirth, *J. Phys.: Condens. Matter*, 2013, **25**, 225503.
- 16 M. Isik and N. M. Gasanly, *Vacuum*, 2020, **179**, 109501.
- 17 C. H. Ho, *ACS Omega*, 2020, **5**, 18527–18534.
- 18 C. A. Chuang, M. H. Lin, B. X. Yeh and C. H. Ho, *RSC Adv.*, 2018, **8**, 2733–2739.
- 19 A. Ravagli, C. Craig, G. A. Alzaidy, P. Bastock and D. W. Hewak, *Adv. Mater.*, 2017, **29**, 1606329.
- 20 G. Y. Huang, N. M. Abdul-Jabbar and B. D. Wirth, *Acta Mater.*, 2014, **71**, 349–369.
- 21 K. George, C. H. de Groot, C. Gurnani, A. L. Hector, R. Huang, M. Jura, W. Levason and G. Reid, *Chem. Mater.*, 2013, **25**, 1829–1836.
- 22 C. S. Jung, F. Shojaei, K. Park, J. Y. Oh, H. S. Im, D. M. Jang, J. Park and H. S. Kang, *ACS Nano*, 2015, **9**, 9585–9593.
- 23 T. Zhang, Y. Li, Y. Zhang, Q. Feng, J. Ning, C. Zhang, J. Zhang and Y. Hao, *J. Alloys Compd.*, 2021, **859**, 157810.
- 24 C. V. Ramana, D. Das, G. Gutierrez, F. S. Manciu and V. Shutthanandan, *J. Mater. Sci.*, 2022, **57**, 11170–11188.
- 25 H. Yang, Y. Wu, L. Y. Hu, J. J. Wang, F. Wang and X. H. Xu, *Rare Met.*, 2023, **42**, 189–197.
- 26 C. Kim, K. Kurosaki, M. Ishimaru, H. Muta and S. Yamanaka, *J. Electron. Mater.*, 2011, **40**, 999–1004.
- 27 D. Sun, S. Xu, L. Zhang, Z. Chen, Y. Ge, N. Wang, X. Liang, C. Wei, Y. Zhao and X. Zhang, *J. Semicond.*, 2015, **36**, 044009.
- 28 J. I. Pankove, *Optical Processes in Semiconductors*, Courier Corporation, 1975.
- 29 C. E. P. Villegas, A. R. Rocha and A. Marini, *Nano Lett.*, 2016, **16**, 5095–5101.
- 30 C. Yu, Z. Chen, J. J. Wang, W. Pfenninger, N. Vockic, J. T. Kenney and K. Shum, *J. Appl. Phys.*, 2011, **110**, 063526.
- 31 H. Yang, F. Wang, H. Zhang, L. Guo, L. Hu, L. Wang, D. J. Xue and X. Xu, *J. Am. Chem. Soc.*, 2020, **142**, 4438–4444.

