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Zinc selenide engineered nanostructures: insights into modification strategies, and multifunctional applications in environmental remediation, gas sensing, energy storage, and antimicrobial activity

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Zinc selenide (ZnSe), an outstanding and admirable photocatalytic material from the II–VI group, exhibits a direct energy band gap of 2.67 eV. This rising contender has sparked considerable attention owing to its distinctive physicochemical characteristics and extensive multifunctional potential. This article commences with a comprehensive and systematic exploration of the intrinsic novel attributes of ZnSe nanostructures, encompassing their structural, optical, and electronic novelties. It further summarizes the various fabrication methodologies which have been instrumental in tailoring parameters like particle size, morphology, and crystallinity to optimize functional performance across a breadth of applications. Key modification strategies, including elemental doping and heterojunction engineering, are highlighted to underscore their indispensable roles in mitigating the recombination rate while enhancing the efficiency of photoinduced charge carrier separation and migration. The discourse progresses to delineate the evolution from conventional composite architectures to advanced Z-scheme configurations, offering profound insights into their revolutionary implications. Additionally, essential characterization techniques are surveyed, elucidating the intricate correlations between structural, morphological, optical, and electronic properties and their resultant influence on functional efficacy. Furthermore, the study spotlights the recent advancements in multifaceted applications in utilizing ZnSe-based composites as potential tools for environmental applications, including the removal of hazardous heavy metals, pharmaceuticals, phenolic compounds, and other persistent organic contaminants, as well as their role in CO₂ mitigation, Cr(VI) remediation, gas sensing, advanced electrode materials in lithium-ion (LIBs), sodium-ion (SIBs), and potassium-ion batteries (PIBs), alongside antimicrobial activities. Mechanistic insights into these remediation pathways are thoroughly outlined. Subsequently, the article sketches the inherent challenges and delineates future research developments and potential avenues for material optimization, which is anticipated to facilitate further exploration and innovation in this dynamic field in the days to come.

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1. Introduction

Over the past few decades, semiconductor photocatalysts have become a central point within the field of photochemistry due to their exceptional catalytic performance and vast potential in addressing complex environmental challenges.¹ Wastewater from industrial processes contain a diverse array of hazardous organic and inorganic contaminants, significantly compromising the quality of water.² The majority of wastewater pollutants are substances with a high resistance to biological breakdown, such as pharmaceuticals, heavy metals, dyes, cosmetics, and pesticides.^{3–5} A number of physicochemical procedures, such as adsorption, microfiltration, ultrafiltration,

reverse osmosis, and advanced oxidation processes, have been proposed as means of wastewater purification.⁶ One such method that has recently come up as an eco-friendly solution to the issue of wastewater treatment is the advanced oxidation process.^{7,8} Over the past few years, nanostructured semiconductors have been the topic of meticulous research, not only to gain a better understanding of their underlying properties, but also to create practical applications in electrical and optoelectronic devices.⁹ Additionally, their photocatalytic capabilities hold enormous promise, especially for solar fuel generation and environmental pollution control.^{10,11} The photocatalytic process, employing semiconductors as photocatalysts, is designed to generate reactive species responsible for the breakdown of organic pollutants into non-hazardous by-products. At its core, photocatalysis entails the excitation of electron–hole pairs upon appropriate light irradiation. These

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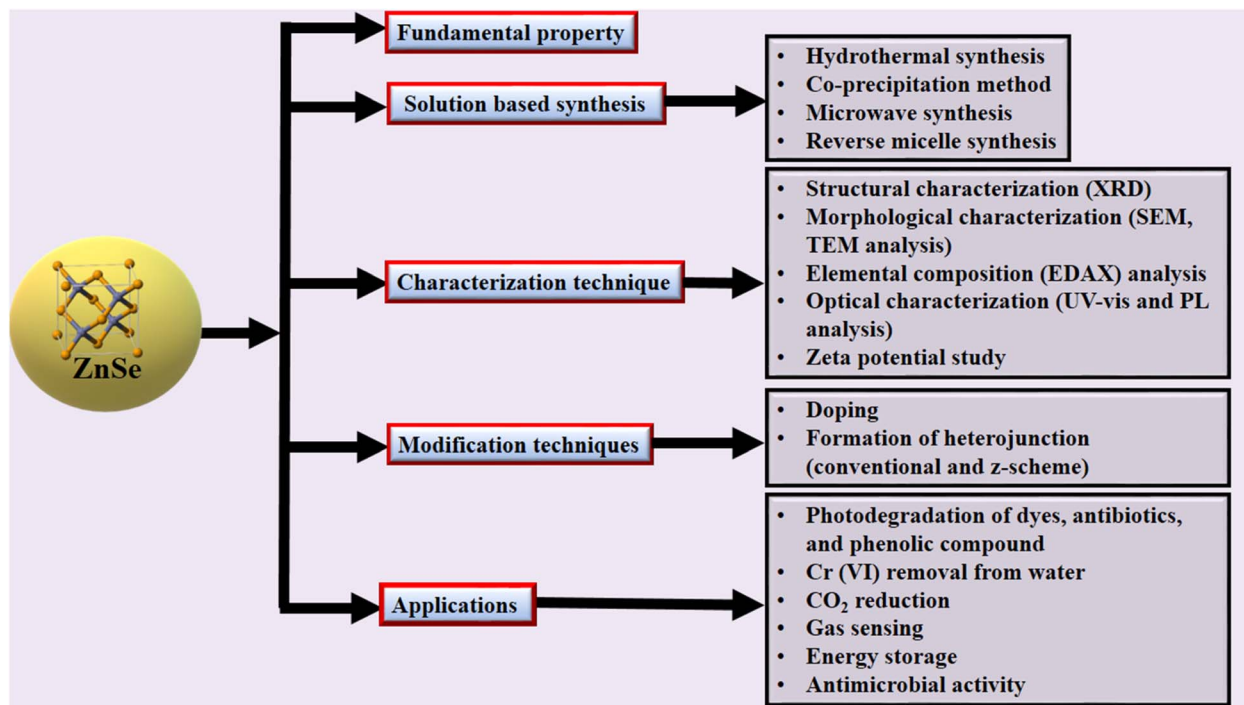


Fig. 1 Overview and summary of the review (self-produced).

charge carriers subsequently move toward the semiconductor surface, driving redox reactions critical for the origination of reactive oxygen species (ROS), such as $\cdot\text{OH}$, $\cdot\text{O}_2$, and $\cdot\text{OOH}$, which play a pivotal role in the pollutant breakdown process into simpler molecules such as CO_2 and H_2O .^{9,12}

Numerous semiconductors and earth-abundant photocatalysts have been reported over the years. However, limitations, including a wide bandgap (3.2 eV), absorption of ultraviolet light, and weak photocatalytic response in visible light, reduce their effectiveness.^{13,14} It has been reported that the high band gap of nanoscale TiO_2 (3.2 eV) and ZnO (3.37 eV) powder allows them to absorb light in the ultraviolet region, which accounts for 3–5% of the total electromagnetic spectrum.^{15–17} Nevertheless, because of their high rate of electron–hole recombination and low doping content, their visible-light catalytic efficiency is relatively poor. Recently, catalysts based on Ag_3PO_4 ,^{18,19} BiVO_4 ,^{20,21} and semiconductor heterostructures have been developed for the visible-light degradation of organic contaminants with exceptional photocatalytic efficacy.²² Unfortunately, their substantial cost and possible heavy metal contamination still hinder their practical usage in field applications. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), a metal-free material, has recently garnered much attention in the realm of visible-light photocatalysis.^{23,24} However, to boost its catalytic performance, it is still necessary to couple it with other photoactive materials. Thus, it is imperative to create novel visible-light photocatalysts of the aforementioned properties to address the growing demand for environmental remediation.

Recently ZnSe has gained significant attraction due to its tunable optical and electronic behavior, chemical stability and potential for recyclability.^{25–28} Additionally, it absorbs light in the

visible-light region, making them a promising visible-light photocatalyst.²⁹ Zinc selenide, featuring a direct band gap of 2.70 eV (460 nm) at room temperature, stands as a pivotal II–VI semiconductor, opening the door to advancements in short-wavelength photoelectronics, including cutting-edge photodetectors,^{30,31} biomedical sensors,³² blue laser diodes,³³ LEDs,³⁴ solar cells,²⁸ and photocatalysts.^{29,35} Additionally, it can also serve as electrodes in lithium ion batteries,³⁶ sodium ion batteries,³⁷ potassium ion batteries,³⁸ and toxic gas sensors.³⁹

ZnSe nanocage structures have demonstrated strong interaction energies with CO_2 molecules, making them suitable candidates for the development of sensitive gas sensors capable of detecting hazardous gases such as CO_2 and SO_2 .⁴⁰ While a wide range of materials have been investigated for CO_2 photoreduction,^{41–43} zinc chalcogenides, especially ZnSe stand out due to their suitable bandgap and strong visible-light absorption, which enable efficient charge generation and utilization.⁴⁴ Also, ZnSe is considered a very promising anode material because of its strong electrochemical activity and reliable performance across different energy storage systems.⁴⁵ It is also chemically stable, non-hygroscopic, remains highly pure, and has a dense structure, which further contribute to its ease of processing and applicability.⁴⁶ In LIBs, ZnSe undergoes a conversion process where reduced Zn reacts with Li^+ to form LiZn , supplying additional capacity to the battery.⁴⁵ Additionally, bacterial infections represent a significant and growing threat to human health, compelling researchers to explore cutting-edge strategies and materials to address diseases caused by pathogenic strains, antibiotic resistance, and genetic mutations. The formation of bacterial biofilms further complicates this issue, leading to critical implications in both medical

and industrial sectors. Selenide materials, with their ability to release ions at the surface, exhibit potent antibacterial properties by inducing cell wall disruption, making them a promising candidate for mitigating these challenges.^{47,48}

This review article offers a detailed and systematic exploration of the recent advancements, spotlighting the distinctive structural, optical, and electronic attributes of ZnSe nanostructures. It summarizes the fabrication methodologies that have been instrumental in precisely tailoring critical parameters—such as particle size, morphology, and crystallinity, to optimize performance across diverse functional domains. The discussion accentuates pivotal modification strategies, notably elemental doping and heterojunction engineering, which are indispensable for suppressing charge carrier recombination and enhancing the efficiency of photoinduced charge separation and migration. Furthermore, the article surveys essential characterization techniques, elucidating the intricate correlations between structural, morphological, optical, and electronic properties and their influence on functional efficacy. Despite the escalating interest in photocatalytic materials, there remains a noticeable paucity of comprehensive studies dedicated specifically to ZnSe photocatalysts, as evidenced by Scopus analyses and earlier reports.^{44,49} Addressing this critical gap, the review assembles the compelling advantages of ZnSe across a spectrum of multifaceted applications, encompassing not only the degradation of textile dyes but also the comparatively underexplored breakdown of antibiotics and phenolic contaminants, removal of Cr(VI), and CO₂ mitigation. Additionally, it highlights the burgeoning roles of ZnSe in gas sensing, particularly for NO₂, NH₃, and acetone, and as an anode material in Li⁺, Na⁺, and K⁺ ion batteries, thereby highlighting its expanding significance within environmental and energy technology landscapes (Fig. 1). By seamlessly integrating discussions on photocatalysis, sensing, and energy storage, this review offers a timely and holistic perspective on ZnSe as a versatile platform for sustainable technological solutions. Mechanistic insights into these remediation pathways are comprehensively outlined. The article concludes by delineating inherent challenges and mapping out future research directions and strategic avenues for material optimization, anticipated to

drive continued innovation and deeper exploration within this dynamic field.

2. Fundamental properties of ZnSe

ZnSe is a binary octet semiconductor. Fig. 2(a and b) displays two allotropes of ZnSe: the hexagonal wurtzite (W) and the cubic zinc blende (ZB) structures.⁴⁴ The dihedral configuration of the fourth interatomic bond determines the variation among them. In contrast to W's ABABAB arrangement, ZB's coordination number is 4, and Zn and Se are aligned in an ABCABC fashion. W structure's lattice parameters are $a = b = 3.98 \text{ \AA}$, $c = 6.53 \text{ \AA}$ (space group = $P6_3mc$), while the experimental calculated parameters of ZB are $a = b = c = 5.68 \text{ \AA}$ (space group = $F\bar{4}3m$).⁴⁹ The lattice parameters of the W structure, as computed by Dai *et al.*,⁵⁰ are $a = b = 4.005$, $c = 6.657$, which slightly exceeds the experimental result. ZnSe shows the so-called W-ZB polytypism due to an insignificant variation in total energy between the ZB and the W structure (5.3 meV per atom) despite ZB being the low-temperature ground state structure.⁵¹ At ambient temperature, the bulk band gap E_g of cubic ZnSe is 2.7 eV (460 nm).⁴⁴

ZnSe exhibits large-scale property variations owing to minute variations in atom configurations. Acharya *et al.* discovered that a distinct shift in the ZnSe nanorods' polarization-dependent optical characteristics coincided with the lattice configuration transition from W to ZB. Unlike the random rods, the aligned rods display polarization at a right angle to their long axis.⁵³

An essential part of understanding the optoelectronic properties of nanoscale optoelectronics is nanostructures rather than differences in atomic patterns. Reiss unveiled that a significant relationship exists as a function of the ZnSe bandgap and its radius (r) (Fig. 2(c))⁵² through the application of the Brus formula. Their research also highlighted the remarkable size-induced optoelectronic behavior of ZnSe nanocrystals.^{52,54} Moreover, their findings suggested that the optical behavior of ZnSe thin sheets is strongly influenced by thickness variations, which are determined by the deposition method.⁵⁵

In a study by Yu *et al.*, first-principles calculations grounded in density functional theory (DFT) were carried out to explore the electronic and optical characteristics of zinc blende (ZB)

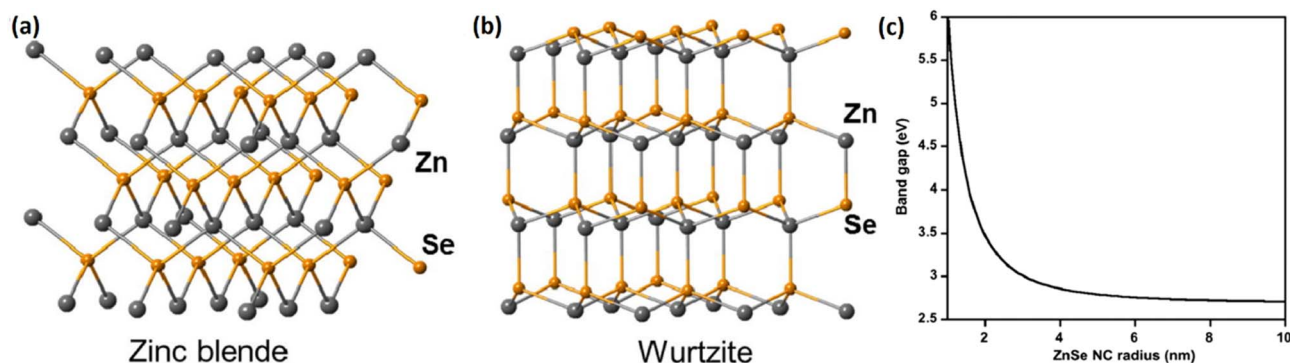


Fig. 2 Schematic representation of (a) zinc blende, (b) wurtzite crystal structures (reproduced from ref. 44); and (c) ZnSe NCs' band gap and size are correlated (reproduced from ref. 52). "This figure has been reproduced from ref. 44 with permission from Elsevier, copyright 2016". "This figure has been reproduced from ref. 52 with permission from Royal Society of Chemistry, copyright 2007".



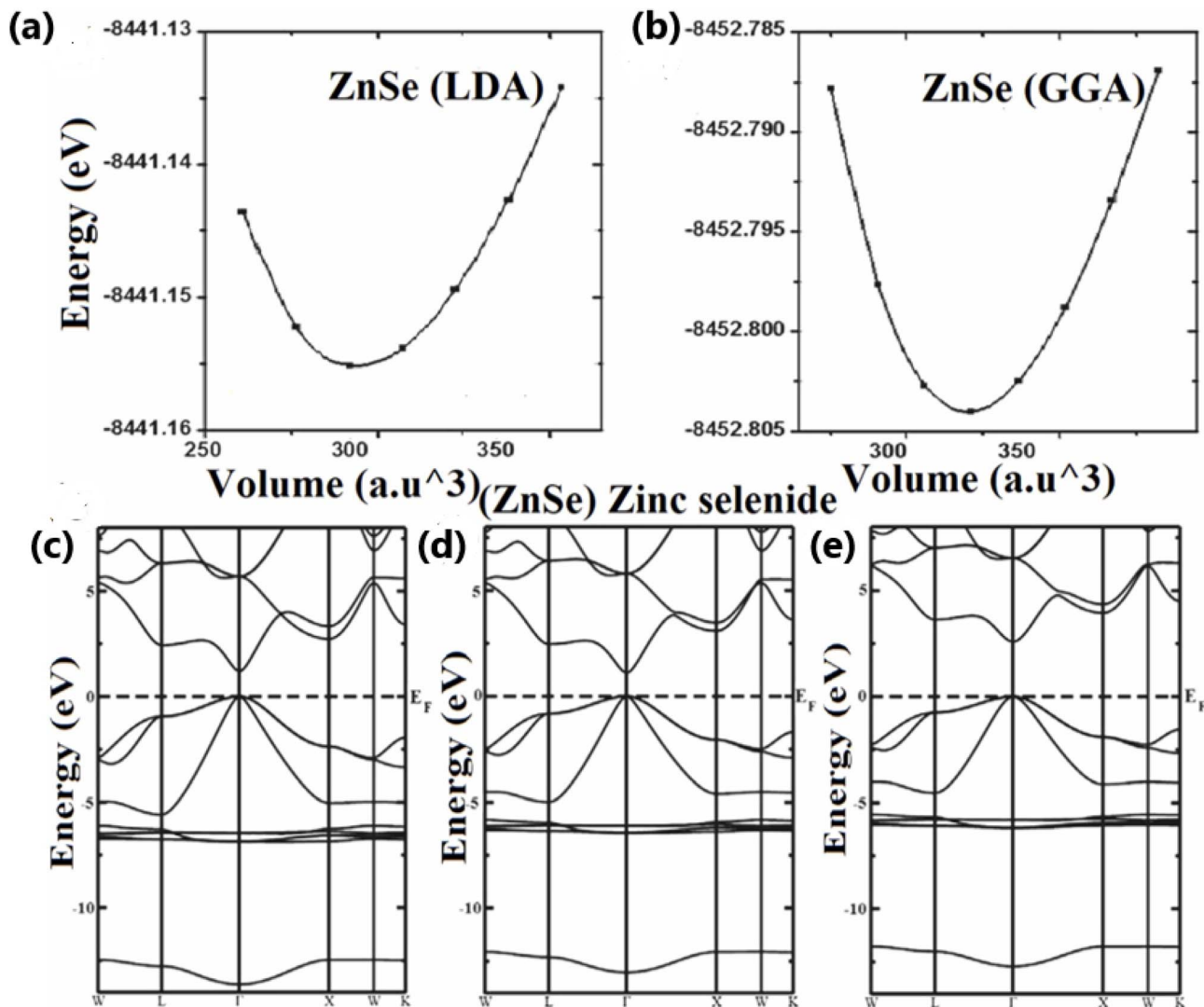


Fig. 3 Energy versus volume curve for ZnSe by utilizing (a) LDA and (b) GGA; band illustration of ZnSe by utilizing (c) LDA, (d) GGA, and (e) mBJ-GGA (reproduced from ref. 57). "This figure has been reproduced from ref. 57 with permission from Springer Nature, copyright 2017".

ZnSe.⁵⁶ Similarly, Kabita and Sharma investigated the structural and electronic properties of ZnSe using generalized gradient approximation (GGA), local density approximation (LDA), and the modified Becke–Johnson potential (mBJ-GGA) (Fig. 3).⁵⁷ The resulting structural parameters from these calculations aligned well with earlier literature, validating their use for subsequent electronic structure analysis.⁵⁷ Across all three computational methods, the valence band maximum (VBM) and conduction band minimum (CBM) were consistently located inside the Brillouin zone, Γ point, clearly indicating the direct bandgap nature of ZnSe. Notably, two key observations emerged: the upward shift of the conduction band (CB) and the corresponding broadening of the bandgap. The calculated bandgaps were 1.12 eV and 1.05 eV using the GGA and LDA methods, respectively. In contrast, the mBJ-GGA approach yielded a significantly improved bandgap of 2.5 eV, closely aligning with the experimental value of 2.7 eV. The slight discrepancy between the mBJ-GGA and experimental results can be attributed to the fact that the DFT calculations were conducted at

absolute zero, whereas the experimental measurements were performed at room temperature. As shown in Fig. 3, the lower energy bands in the LDA calculations are primarily influenced by the Se atom's s-states around 3.12 eV, with this contribution shifting to higher energies in the GGA and further in the mBJ-GGA results, following the trend LDA < GGA < mBJ-GGA. In the valence band region, the Zn d-orbitals exhibit a strong presence in LDA, contributing approximately 34.94 eV, which decreases under GGA and increases again with the mBJ-GGA approach. These variations underscore the superior capability of the mBJ-GGA functional in accurately representing the electronic states, thus offering a more reliable depiction of ZnSe's band structure compared to GGA and LDA.⁵⁷

3. Solution-based synthesis of ZnSe

The synthesis of ZnSe nanomaterials can be achieved through hydrothermal, co-precipitation, microwave-assisted, and reverse osmosis methods, each with distinct advantages and



Fig. 4 Schematic representation of a hydrothermal method for the synthesis of zinc selenides (reproduced from ref. 60).

limitations. The hydrothermal method utilizes high temperature and pressure in an autoclave, producing highly crystalline ZnSe with precise control over size and morphology, though it requires expensive equipment and significant energy input. In contrast, the co-precipitation method is simpler and more economical, involving the reaction of zinc and selenium precursors at room or mild temperatures, albeit with potentially lower crystallinity. The microwave-assisted method offers rapid and uniform heating, significantly reducing reaction times while enhancing energy efficiency, often resulting in ZnSe with superior purity and uniformity. Although less commonly used for ZnSe synthesis, the reverse osmosis method serves primarily for purification or separation rather than direct production, limiting its applicability. The selection of the synthesis method is governed by factors such as cost, scalability, and the desired material properties.

3.1. Hydrothermal synthesis

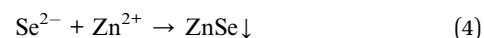
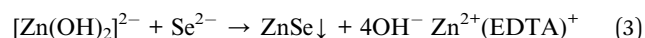
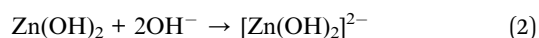
When it comes to synthesizing nanomaterials, the hydrothermal approach reigns supreme. The hydrothermal method provides several advantages for nanomaterial synthesis, yielding particles with uniform size distribution, ultra-fine dimensions, and high crystallinity. Additionally, it generates relatively low waste, making it an environmentally friendly approach.⁵⁸ However, the method has limitations, such as the inability to monitor crystal growth in real-time and the high cost of the required equipment.⁵⁹ The process usually begins with dissolving the metal and selenide salts in water and then moving the mixture to a sealed autoclave. Here, the nanocrystals are grown under high temperatures and pressure. Fig. 4 shows a hydrothermal procedure used to synthesize transition metal selenides.⁶⁰

Reports of ZnSe synthesis by hydrothermal methods date back to the 1970s. The initial hydrothermal synthesis of ZnSe crystals from OH[−] solutions with or without Li⁺ was accomplished in 1970 by Kolb and Laudise.⁶¹ Prior to 2008, a limited number of studies had been conducted on the synthesis of ZnSe. In 2008, Cao *et al.* explored the photocatalytic activity of 3D flower-like ZnSe nanostructures under UV light that were synthesized by hydrothermal treatment.²⁹ Compared to P25 and ZnSe microspheres, the ZnSe nanostructures synthesized by Cao demonstrated superior photocatalytic activity.

Subsequently, ZnSe/Cu nanocrystals were fabricated at a temperature of 160 °C for 50 min utilizing NaHSe, Zn(NO₃)₂, and Cu(NO₃)₂.⁶² The pH was maintained using NaOH, and the solution was stabilized with 3-mercaptopropionic acid.

Later, the influence of temperature on the synthesis of ZnSe microspheres was demonstrated by Duan.⁶³ It was observed that the crystallinity of the material improved with the rise in the reaction temperature, and the intensity of the diffraction peaks increased. According to the study, 180 °C was found to be the ideal temperature of achieving highly crystalline ZnSe nanostructures, fabricated using zinc nitrate and sodium selenite, together with hydrazine and NaOH for 4 hours. In contrast to this study, higher temperatures were employed by Sobhani *et al.* to synthesize ZnSe nanospheres using the metal salt, SeCl₄, and N₂H₄.^{62–64}

Additionally, Bu *et al.* investigated the mechanism of the fabrication of ZnSe micrograsses and microspheres that involved 36 hours at 190 °C (eqn (1)–(4)).⁶⁵ The microspheres were grown on graphene oxide sheets, and their various morphologies were created by varying the NaOH and EDTA concentrations.



Interestingly, utilization of a fresh Se source enabled reactions to proceed at reduced temperatures and in shorter time-scales than those reported earlier.⁶⁶ ZnSe was fabricated using ZnCl₂ and Na₂SeSO₃ at 150 °C for 6 hours. Additionally, a nanohybrid comprising zinc selenide and smectites was developed. The round-shaped nanoparticles with diameters less than 5 nm in this nanohybrid developed in the interlayer gap of smectites.

3.2. Co-precipitation method

Zinc selenide (ZnSe) nanoparticles are commonly synthesized using the co-precipitation approach. The co-precipitation method is recognised for its simplicity, low cost, and rapid



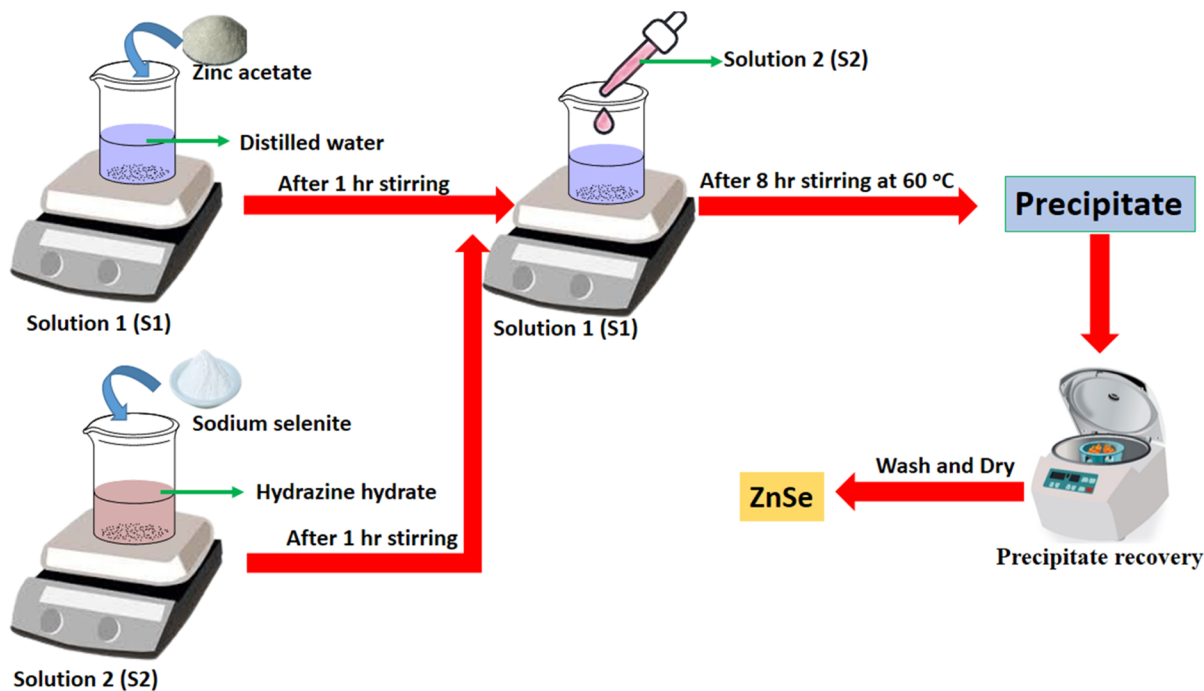


Fig. 5 Schematic representation of co-precipitation method for the synthesis of ZnSe (self-produced).

synthesis, making it suitable for large-scale industrial production. It enables the formation of high-purity nanomaterials through an environmentally friendly route, avoiding hazardous solvents and extreme conditions.⁶⁷ Nevertheless, this method provides limited control over nanoparticle size and uniformity, and the crystallinity of the products is generally lower than that achieved *via* hydrothermal synthesis.⁶⁸ The underlying principle of co-precipitation involves the simultaneous precipitation of

two or more ionic species from a solution to form a compound, which allows the straightforward fabrication of nanomaterials. ZnSe nanoparticles were produced by co-precipitating zinc ions (Zn^{2+}) and selenium ions (Se^{2-}) as outlined in Fig. 5.

ZnSe nanoparticles were synthesized by Ahamad and his team by utilizing polyvinylpyrrolidone (PVP) as a capping agent in a straightforward, affordable co-precipitation method using zinc chloride and sodium selenide.⁶⁹ Studies have demonstrated the effect of Zn/Se molar ratios on the shape and photocatalytic potential of ZnSe nanostructures through a series of controlled tests with varying concentrations of selenium anions.⁷⁰ It was observed that the sample having a 1 : 0.6 Zn/Se ratio displayed nanobelts (NBs) as its morphology. Similarly, other sources such as $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and selenium powders, with thiourea ($\text{CH}_4\text{N}_2\text{S}$) as the surfactant agent was employed by Sanchez-Martinez *et al.*⁷¹ During the same period, Beena *et al.* synthesized ZnSe nanoparticles *via* a two-step procedure.⁷² Step one involved dissolving zinc acetate in deionized water with constant magnetic agitation and adding 2-mercaptoethanol. In contrast, sodium borohydride (NaBH_4), selenium powder, and deionized water were used to prepare sodium hydrogen selenide (NaSeH), which was continuously stirred. The solutions of zinc and selenium were then mixed, stirred, and heated to 100 °C while keeping a pH of 10 using NaOH solution. The second phase reactions were conducted at 100 °C for over 24 hours, yielding a white-yellowish precipitate, which was washed and heated in a vacuum at 80 °C for 48 hours. Finally, the collected sample was heated using several temperature ranges, including 200 °C, 400 °C, 600 °C, and 800 °C.⁷² A modified co-precipitation approach was reported by Gupta *et al.* by employing zinc sulphate and selenium powder as sources of zinc and selenium, respectively, at 60 °C for 8 hours with the use of

Table 1 Summary of the synthesis of ZnSe using different approaches

Catalyst	Synthetic approach	Morphology	Ref.
ZnSe	Hydrothermal	Hollow-sphere	95
		Nano sphere	96
		Spherical	97
		Hollow microspheres	98
		Rose-like nanoflowers and microspheres	99
		Zinc-blende crystalline structure	100
		Grass-like	101
		Sphere	102
		Spherical	71
		Nanorods	103
		Single-phase nanocrystal	104
ZnSe	Coprecipitation	Quasi-spherical	72
		Spherical	73
		Nanorods	105
		Nanorods	106
		Spherical shape	78
ZnSe	Microwave	QDs	79
		Cubic	93
ZnSe	Reverse micelle	QDs	94



hydrazine hydrate and ethylenediamine as reacting agent.⁷³ The resulting black precipitate was cleaned and dried in an open environment for 5 hours at 100 °C.

3.3. Microwave synthesis

Microwave synthesis is a fast and energy-efficient method for producing versatile semiconductor material. It offers rapid and uniform heating, high reaction efficiency, and the ability to control particle size and morphology by adjusting reaction conditions. The homogeneous heating minimizes thermal gradients, facilitating consistent nucleation and growth and producing nanomaterials with uniform size distribution.⁷⁴ However, this method has limitations, including safety concerns, and low reproducibility of the synthesis procedures.⁷⁵ In this process, zinc precursors, such as zinc salts, react with selenium sources, like selenium powder or selenides, in an appropriate solvent. The reaction mixture is subjected to microwave irradiation, which heats the system rapidly and evenly, facilitating the formation of ZnSe in a significantly shorter time compared to conventional heating methods.^{76,77} This rapid heating accelerates the nucleation and growth of ZnSe crystals, resulting in high-purity products with controlled particle size and morphology. The advantages of microwave synthesis include reduced reaction times (often minutes instead of hours), improved energy efficiency, and better reproducibility, making it an ideal technique for producing ZnSe for applications in optoelectronics, solar cells, and infrared devices.

Shakir and co-workers were the first to synthesize ZnSe nanoparticles using a microwave heating method.⁷⁸ Water-soluble glutathione-capped ZnSe quantum dots were synthesized through microwave irradiation by dissolving $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and glutathione (GSH) in 50 mL of deionized water, with the addition of Na_2SeO_3 and excess NaBH_4 while stirring continuously.⁷⁹ After a few minutes, the pH of the solution was carefully elevated to 10 using NaOH. The mixture was then exposed to microwave irradiation (300 W) and refluxed at 100 °C for 60 min. After the solution was cooled to ambient temperature, the quantum dots (QDs) were precipitated with 2-propanol and re-dissolved in deionized water. This purification process was carried out for three cycles, and the final ZnSe QDs were dried under vacuum.

3.4. Reverse micelle synthesis

When a surface active substance is added in a mixture of aqueous and organic phases, reverse micelles are formed.⁸⁰ Drug delivery,^{81,82} micro-reactors,⁸³ and general detergents⁸⁴ are just a few of the possible and practical uses for these micelle systems. The preparation of nanoparticles to create hybrid materials comprising polymers and inorganic components is an additional advancement in the approaches.⁸⁵ Particles with regulated morphology and structure have been created using various techniques; however, the employment of reverse micelles appears to be particularly well-suited for nanoscale particle size customization.^{86,87} It is also well known that the composition of the reverse micelles significantly influences the

final size and shape of the nanocrystals.⁸⁸ Reverse micelle synthesis provides control over particle size and ensure uniformity in both concentration and morphology.⁸⁹ However, one of the major drawbacks of this methods is the requirements of costly chemicals or specifically designed surfactants.^{90–92} It has been utilized to fabricate semiconductor nanostructures, and several copolymer reverse micelles serving as models for the preparation of inorganic nanoparticles.^{90–92}

ZnSe nanoparticles, synthesized by reverse micelle approach, was first reported by Quinlan *et al.* utilizing an ion exchange process.⁹³ The method begins with the addition of sodium dioctyl sulfosuccinate salt (AOT) to heptane in a reaction vessel, forming reverse micelles while being continuously stirred. After forming reverse micelles, $\text{Zn}(\text{ClO}_4)_2$ was injected into the reaction vessel, followed by the addition of Na_2Se solution to the mixture initiating the reaction of ZnSe. Furthermore, a gas-contacting method for synthesizing ZnSe nanocrystals was described by Karanikolos *et al.*⁹⁴ The hydrogen selenide gas was bubbled into a microemulsion of formamide/poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)/*n*-heptane using this method. The gas then diffused into the center of the reverse micelles and reacted with the diethylzinc to produce ZnSe.⁹⁴ Table 1 summarizes the synthesis of ZnSe using different synthetic approaches.

4. Characterization of ZnSe

The characterization of ZnSe nanomaterials is vital for gaining insights into their structural, compositional, surface, and optical characteristics. This section explores the essential analytical methods such as XRD, SEM, TEM, EDAX, UV-visible (UV-vis) Spectroscopy, and Photoluminescence (PL) Spectroscopy, each providing valuable insights into the unique attributes of ZnSe nanomaterials.

4.1. Structural characterization

4.1.1. X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) serves as a vital tool for characterizing ZnSe nanomaterials, offering detailed information about their crystalline structure, phase composition, and crystallite size. ZnSe typically crystallizes in cubic (zinc blende) or hexagonal (wurtzite) forms, each displaying unique diffraction patterns. The XRD patterns of ZnSe nanoparticles synthesized *via* the chemical bath deposition technique exhibited distinct peaks at 27.8°, 45.7°, and 54.3°, which corresponded to the (111), (220), and (311) planes of the cubic ZnSe phase (Fig. 6(a)).¹⁰⁷ The samples were labeled as A for 0.2 M, B for 0.5 M, and C for 1 M concentration of zinc acetate, respectively. These peaks proved the formation of single-phase cubic ZnSe, with no additional phases or impurities present. The broadening of the (111), (220), and (311) diffraction peaks is evidence of nanoparticle formation. On the other hand, the ZnSe NPs synthesized using a straightforward co-precipitation method, followed by annealing at different temperatures, revealed a cubic (face-centered) crystal structure consistent with JCPDS file No. 88-2345.¹⁰⁸ The XRD pattern in Fig. 6(b) displayed peaks at 27°, 45°, 53°, 65°, and 72°



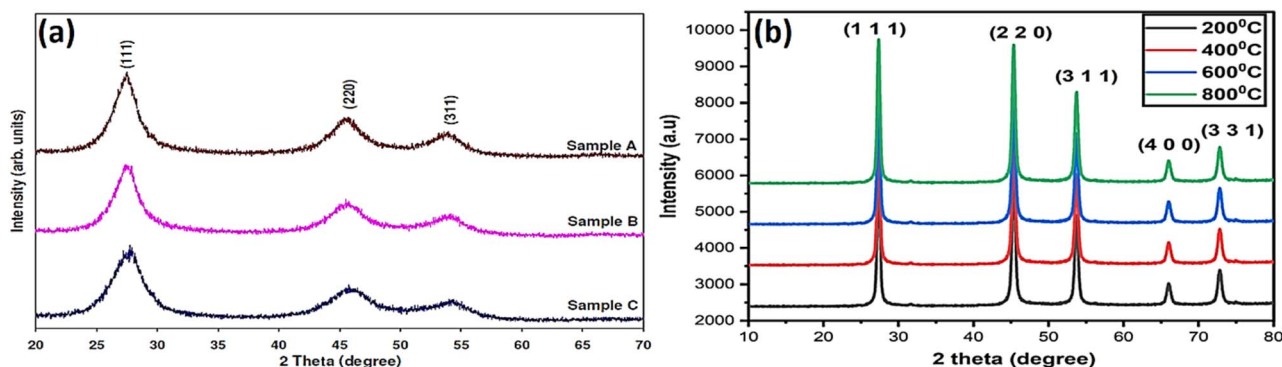


Fig. 6 XRD patterns of the synthesized ZnSe nanoparticles synthesized via (a) chemical bath deposition method (reproduced from ref. 107) and (b) co-precipitation method followed by calcination at various temperatures (reproduced from ref. 108). "This figure has been reproduced from ref. 107 with permission from AIP Publishing, copyright 2014". "This figure has been reproduced from ref. 108 with permission from Springer Nature, copyright 2021".

corresponding to the (111), (220), (311), (400), and (331) lattice planes. As the annealing temperature rises, the intensity of the peaks progressively intensifies, and the particle size increases, suggesting enhanced crystallinity and structural ordering of the ZnSe NPs.

4.2. Morphological characterization

4.2.1. Scanning electron microscopy (SEM). SEM is highly effective for studying ZnSe nanomaterials, as it generates high-resolution images that reveal detailed surface characteristics. SEM enables precise surface morphology analysis, capturing the texture, shape, and structure of particles, along with their

size, which is crucial for predicting the efficacy of the material in different applications. The interaction of the electron beam with the atoms on the ZnSe surface produces signals, forming a detailed image of the material's topography, essentially mapping the "landscape" down to minute features. For instance, the SEM micrograph of ZnSe NPs, synthesized by Sharma *et al.*, highlights a combination of nanorods and spherical particles (Fig. 7(a)).¹⁰⁷ The nanorods measured between 400 nm and 3 μm in length, with diameters ranging from 50 to 100 nm. At higher magnification, it is evident that the larger spherical particles consist of agglomerated nanoparticles, each measuring under 10 nm (Fig. 7(b)). Similarly, Fig. 7(c) and (d) depict the SEM images of ZnSe microdisks at

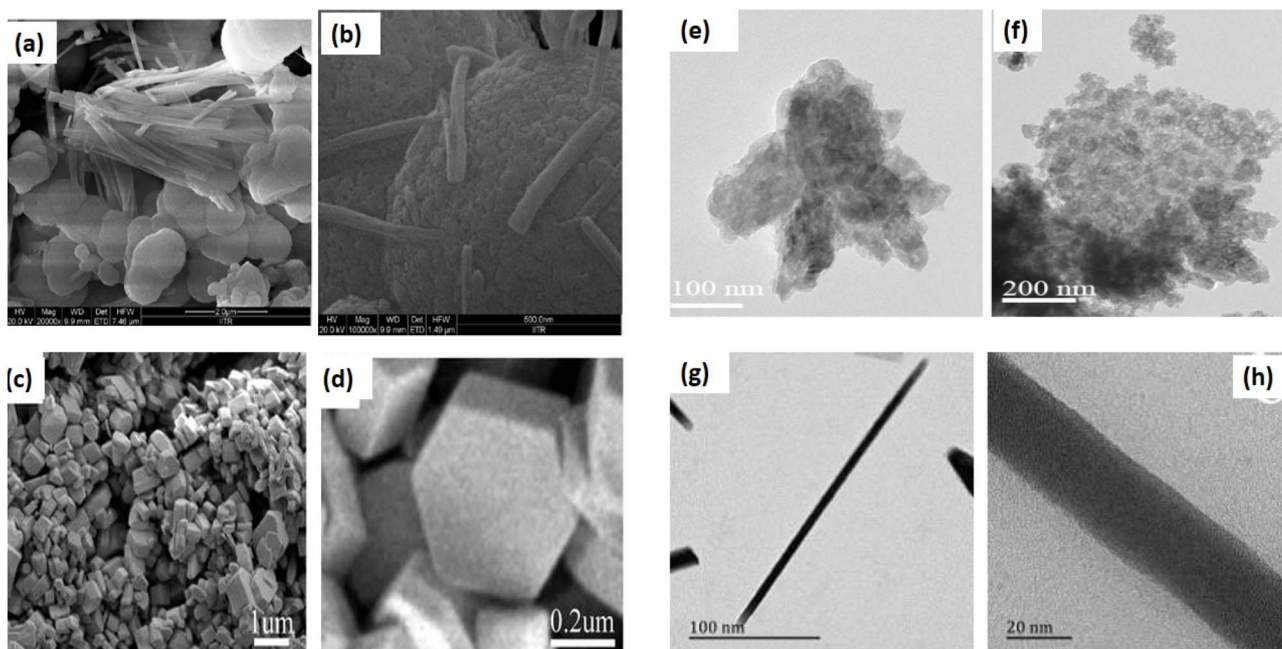


Fig. 7 (a and b) SEM image of the as-synthesized ZnSe nanoparticles (reproduced from ref. 107); (c and d) SEM images of ZnSe microdisks (reproduced from ref. 109); (e and f) HRTEM images of the sample calcined at 800 $^{\circ}\text{C}$ (reproduced from ref. 108); (g) TEM, and (h) HRTEM images of the as-synthesized ZnSe nanoflowers (reproduced from ref. 110). "This figure has been reproduced from ref. 108 with permission from Springer Nature, copyright 2021". "This figure has been reproduced from ref. 109 with permission from Springer Nature, copyright 2016". "This figure has been reproduced from ref. 110 with permission from Elsevier, copyright 2016".

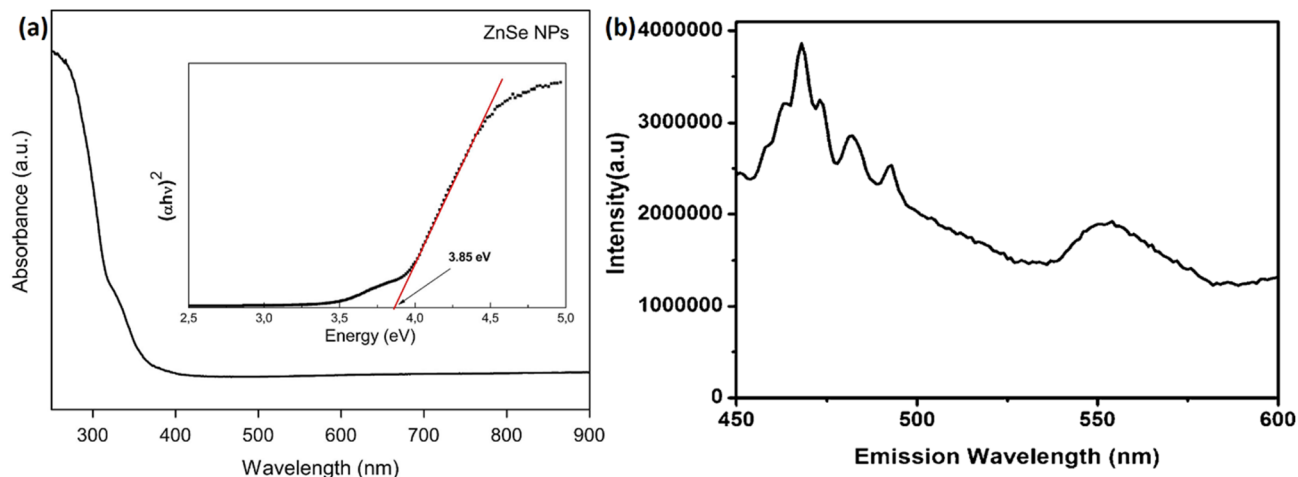


Fig. 8 (a) Absorbance spectrum and the band gap energy plot (inset) (reproduced from ref. 111), and (b) PL spectrum of the as-synthesized ZnSe NPs (reproduced from ref. 110). "This figure has been reproduced from ref. 111 with permission from Elsevier, copyright 2017". "This figure has been reproduced from ref. 110 with permission from Elsevier, copyright 2016".

low and high magnifications, respectively, as reported by Li *et al.*¹⁰⁹ The microdisks, synthesized through a solvothermal approach followed by annealing in an argon atmosphere, exhibit uniform morphology with diameters ranging from 0.4 to 0.6 μm and thicknesses between 0.1 and 0.4 μm .

4.2.2. Transmission electron microscopy (TEM). TEM provides a comprehensive analysis of the morphology and size distribution of ZnSe nanoparticles, allowing the observation of their overall shape, surface characteristics, and particle dimensions. On the other hand, high-resolution TEM (HRTEM) offers a more detailed view by revealing the lattice fringes within the nanoparticles, which gives valuable insights into their atomic-level structure, including the arrangement and spacing of atoms in the crystal lattice. For instance, the TEM images, displayed in Fig. 7(e) and (f), of ZnSe NPs synthesized at 800 $^{\circ}\text{C}$ were captured at two different magnifications.¹⁰⁸ The nanoparticles exhibit a predominantly quasi-spherical shape with some variations, suggesting a large surface area that could enhance their catalytic and biological properties. The particle size observed is approximately 30 nm, consistent with the calculated crystallite size, further confirming the synthesis conditions. Meanwhile, ZnSe nanoflowers consisted of radially aligned ZnSe nanorods with smooth surfaces, as shown in the TEM images (Fig. 7(g) and (h)).¹¹⁰ These nanorods were straight, long, and smooth. The HRTEM image revealed a d -spacing of approximately 3.3 \AA , which matches the interplanar spacing of the cubic ZnSe (111) planes.

4.3. Elemental composition

4.3.1. Energy dispersive X-ray analysis (EDAX). EDAX is a vital tool for analyzing ZnSe nanomaterials, primarily used to confirm their elemental composition and purity. It detects the presence of zinc (Zn) and selenium (Se), ensuring their correct stoichiometric ratio, which is crucial for maintaining the desired properties of ZnSe. Additionally, EDAX helps identify any impurities or contaminants introduced during synthesis

and provides insights into the uniformity of elemental distribution across the sample. By complementing structural and morphological analyses, EDAX ensures the chemical accuracy and quality of ZnSe nanomaterials, making it an indispensable technique in material characterization. For instance, the EDAX analysis of the ZnSe NPs synthesized by Sharma *et al.* reveals that both the nanorods and spherical nanoparticles consist of approximately 49 atomic percent zinc and 51 atomic percent selenium, demonstrating their nearly ideal stoichiometry and high chemical purity.¹⁰⁷

4.4. Optical characterization

4.4.1. UV-visible spectroscopy. UV-vis spectroscopy is widely used to study the optical properties of ZnSe NPs, particularly for determining their band gap energy by analyzing the absorption edge. It also reveals size-dependent effects like quantum confinement and provides data on absorbance and transmittance, making it valuable for applications in optoelectronics. For instance, ZnSe NPs synthesized by Mosquera *et al.* using a top-down approach involving ultrasound at low temperatures displays an optical absorption edge around 320 nm (3.87 eV), attributed to the first exciton absorption caused by the $1S^e-1S_{2/3}^h$ transition (Fig. 8(a)).¹¹¹ Compared to the bulk ZnSe with band edge at 2.7 eV, the absorption edge exhibits a blue shift ($\Delta E_g = 1.17$ eV). The direct band gap (E_g) was calculated using the relationship between the absorption coefficient (α) and photon energy ($h\nu$). By extrapolating the linear section of the $(\alpha h\nu)^2$ versus $h\nu$ plot to $\alpha = 0$, the band gap was found to be 3.87 eV, further confirming the blue shift. This shift towards higher energy is attributed to the quantum size effect of the ZnSe nanocrystals.

4.4.2. Photoluminescence (PL) spectroscopy. PL spectroscopy is used to analyze the optical properties of ZnSe NPs, helping to determine their band gap and identify defects or impurities. It reveals size-dependent changes in emission, such as quantum confinement effects, and assesses material quality



by the sharpness of the emission peaks. For instance, the PL spectrum of ZnSe nanoflowers in Fig. 8(b) exhibited strong light emission at ambient temperature when excited at 211 nm.¹¹⁰ Four peaks were observed at 468 nm (2.65 eV), 484 nm (2.56 eV), 494 nm (2.51 eV), and 554 nm (2.24 eV). The 468 nm peak was attributed to bulk band emission, while the others were associated with self-activated luminescence due to defects such as zinc vacancies or surface emission.¹¹⁰

4.5. Zeta potential analysis

Zeta potential studies are conducted in order to determine the charge stability of nanoparticles, predict their interactions with surfaces, and quantify the charges present in a material.¹¹² It represents the electrical charge on the surface of nanoparticles in a dispersion, which originates from the adsorption of ions from the surrounding medium.^{113,114} Zeta potential can be positive or negative and plays a key role in determining the stability of nanofluids and colloidal systems.^{115,116} A higher absolute value indicates better dispersion and stability, while a lower value suggests a higher likelihood of particle clumping or settling.¹¹⁷ Zeta potential measurement is especially valuable for studying nanoparticle dispersions. ZnSe nanoparticles usually have a negative zeta potential, often falling between -30 mV and -57 mV. For example, ZnSe nanocrystals synthesized by Mir *et al.* using an aqueous method exhibited a zeta potential of -30 mV.¹¹⁸ Similarly, Atef *et al.* reported that ZnSe

nanoparticles coated with green seaweed (*Ulva fasciata*, ZnSe-Uf) against *Leishmania major* (*L. major*) had zeta potentials ranging from -35.6 mV to -57.9 mV.¹¹⁹

5. Surface modification techniques

ZnSe is a dual metal-semiconductor that possesses remarkable photo-electronic capabilities and a direct bandgap of 2.67 eV. It also has an excitation binding energy of 21 meV.^{120,121} Considering its favorable photocatalytic capabilities, it has been considered as a potential photocatalyst demonstrating extensive usability in photocatalysis, including the removal of heavy metal ions, the generation of hydrogen, the reduction of CO₂, and the degradation of contaminants.^{49,122} Despite these benefits, ZnSe has an unstable structure, and due to its narrow E_g (2.7 eV), it possesses a high rate of charge carrier recombination during photocatalysis.⁷⁰ However, to overcome these constraints it requires some improvements. Certain modifications can be made to its structure to maximize its photocatalytic potential and broaden the range of applications for photocatalytic processes. The creation of heterojunctions and doping are two features of ZnSe enhancement techniques. These modification strategies minimize the band gap by incorporating dopant materials and significantly reduce the electron-hole pair recombination rate. This can be achieved by promoting charge carrier separation and improving migration efficiency through the development of heterojunctions. In the following

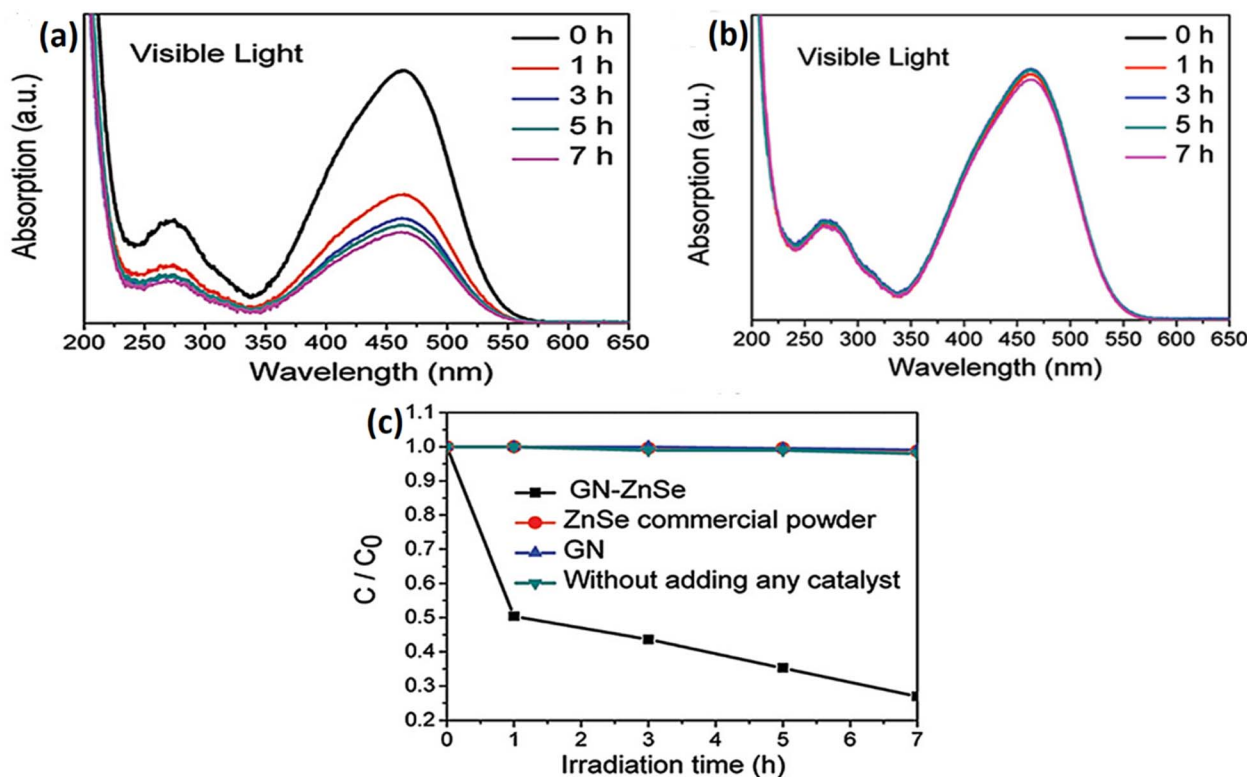


Fig. 9 UV-visible spectra for methyl orange solution in the presence of (a) GN-ZnSe composite, and (b) commercial ZnSe powder under visible light, and (c) Photobleaching curves of methyl orange under visible light in water using photocatalysts (reproduced from ref. 124). "This figure has been reproduced from ref. 124 with permission from American Chemical Society, copyright 2012".

section, doping and various heterojunctions, as well as their photocatalytic enhancements, are described.

5.1. Doping

The process of doping is a method that enhances charge carrier separations and minimizes the rate of photoinduced charge carrier recombination. This is accomplished by increasing the number of vacancies that are generated. Doping in semiconductors is an effective way of improving the efficiency of photocatalysts.¹²³ To narrow the bandgap and boost light absorption efficiency of ZnSe, various dopants are introduced into its lattice structure. This has sparked significant interest among researchers in exploring the doping of ZnSe photocatalysts with transition and non-transition metal ions, aiming to extend their light absorption into the visible spectrum. For instance, Chen *et al.* utilized a catalyst-free technique for the fabrication of N-doped graphene/ZnSe (GN-ZnSe) hybrid.¹²⁴ They found that these composites displayed remarkable

photocatalytic efficiency in degrading methyl orange (MO) dye alongside optimized electrochemical behavior for oxygen reduction. Specifically, the GN-ZnSe hybrid bleached 71.50% of MO dye in 7 hours of UV-vis irradiation, as shown in Fig. 9(a). On the other hand, commercial ZnSe did not demonstrate any MO bleaching results Fig. 9(b). After 8 hours on GN-ZnSe composite, 30.72% of the dye had been consumed, but on commercial ZnSe, just 7.84% had been used.

Also, Kim and colleagues investigated the photocatalytic efficiency of Er and Yb doped ZnSe microspheres to degrade MO.¹²⁵ Similarly, Cu-doped ZnSe NPs were investigated for the photodegradation of MO and found it to be 87%.¹²⁶ Table 2 summarizes the various previous reported doped ZnSe nanoparticles along with their synthetic method.

Studies have described the use of a first-principle study to scientifically investigate the effects of metal and non-metal doping on ZnSe monolayer.¹²⁷ The electromagnetic characteristics of doped ultrathin tetragonal ZnSe monolayers were

Table 2 Summary of ZnSe nanoparticles doped with various dopants

Catalyst	Dopant(s)	Synthesis method	Ref.
ZnSe	Nd	Hydrothermal	129
	Fe	Microemulsion-mediated hydrothermal	130
	Cu	Hydrothermal	131
	Ag	Hydrothermal	132
	Co ²⁺	Hydrothermal	133
	La	Hydrothermal	134
	Ni, Cr, Co, and Ti	Co-precipitation	135
	Fe	Co-precipitation	136
	Sr	Co-precipitation	137
	Ni	Co-precipitation	138
	Cr ³⁺	Co-precipitation	139

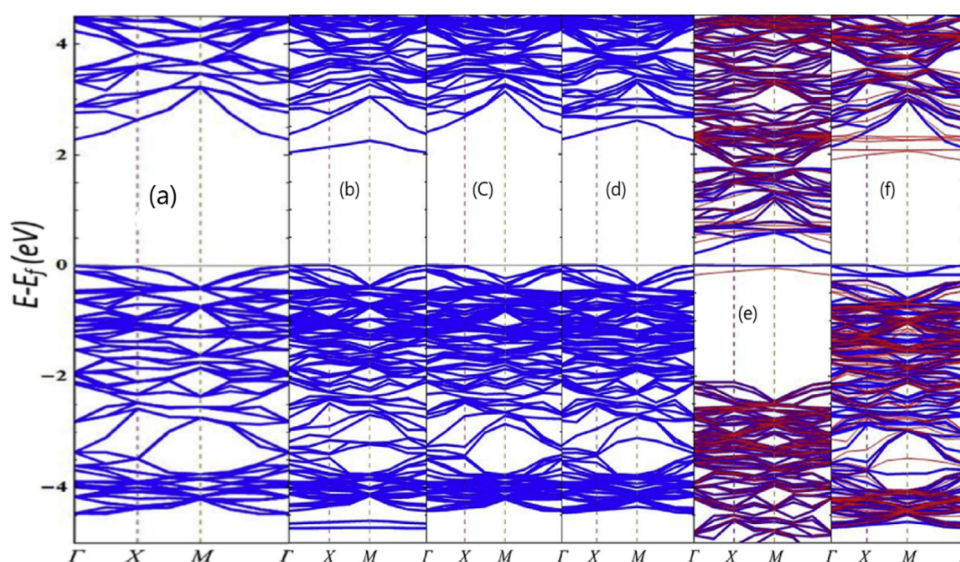


Fig. 10 (a) Band structure of undoped ZnSe monolayer, band alignments of (b) F-, (c) Ca-, (d) Sc-, (e) Ti-, and (f) Mn-doped monolayer of ZnSe. The spin-up and spin-down channels are denoted by the blue and red lines, respectively, for spin-polarized calculations (reproduced from ref. 127). "This figure has been reproduced from ref. 127 with permission from Elsevier, copyright 2017".



explored by utilizing atoms of various metals and metalloids (K to As). It was observed that only the F atom was thermodynamically advantageous in replacing the Se site in both Se-rich and Zn-rich environments. In contrast, the Ca and Sc atoms were more beneficial in replacing the Zn site. Additionally, only in a Se-rich environment, atoms of Ti and Mn replaced only zinc sites. It was also observed that the pristine tetragonal ZnSe monolayer had a straight E_g of 2.28 eV from Γ to Γ at the PBE level (Fig. 10(a)).¹²⁷ This discovery was in agreement with the other estimated value, which was 2.22 eV.¹²⁸ Furthermore, in conditions with excess Zn and/or Se, F, Ca, Sc, Ti, and Mn atoms were the only ones thermodynamically favoured to replace Se or Zn sites (Fig. 10(b–f)).

5.2. Formation of heterojunctions

When semiconductors with different band structures come together, a heterojunction forms, opening up a world of possibilities for band alignments. Conventional, p–n and Z-scheme heterojunction photocatalysts are the three main varieties of semiconductor-based heterojunctions.^{140,141}

5.2.1. Conventional heterojunction photocatalysts. The heterojunction photocatalysts belonging to these classes can be broadly classified into type-I, type-II, and type-III. Compared to semiconductor B, semiconductor A has a higher CB and a lower VB for a type-I heterojunction photocatalyst (Fig. 11(a)).^{142,143} Thus, in semiconductor B, holes and electrons collect at the VB and CB levels under light exposure, respectively. Therefore, in a type-I heterojunction photocatalyst, the decoupling of electron–hole pairs is significantly restricted, as both charge

carriers are confined within the same semiconductor.¹⁴⁴ Furthermore, a redox reaction occurs mostly on the semiconductor, which has a decreased redox potential. This leads to a considerable decline in the heterojunction photocatalyst's overall redox performance.¹⁴⁵ On the other hand, the CB and VB values of semiconductor A are higher than those of semiconductor B in the type-II heterojunction photocatalyst (Fig. 11(b)).¹⁴³ Consequently, photoinduced electrons will go to semiconductor B, while photoinduced holes will migrate to semiconductor A when the semiconductor is exposed to light. This will result in the decoupling of electron–hole pairs.^{146,147} As shown in Fig. 11(c),¹⁴³ the arrangement of the type-III heterojunction photocatalyst closely resembles that of the type-II heterojunction. However, the enhanced staggered gap prevents bandgap overlap, limiting electron–hole migration in the type-III heterojunction and diminishing its efficiency under visible light.^{148,149} Therefore, of the heterojunctions discussed, the type-II heterojunction is evidently the most practical for boosting photocatalytic performance, as its structure enables effective spatial separation of electron–hole pairs.

In 2011, three unique type II three-dimensional ZnO/ZnSe heterostructures (H1, H2, and H3) were fabricated by Cho *et al.* using a process of solution-based surface modification method and employed them for the degradation of orange-II dye by the illumination of visible light.¹⁵⁰ The feasible fabrication mechanism can be outlined as follows (eqn (5)–(8)):

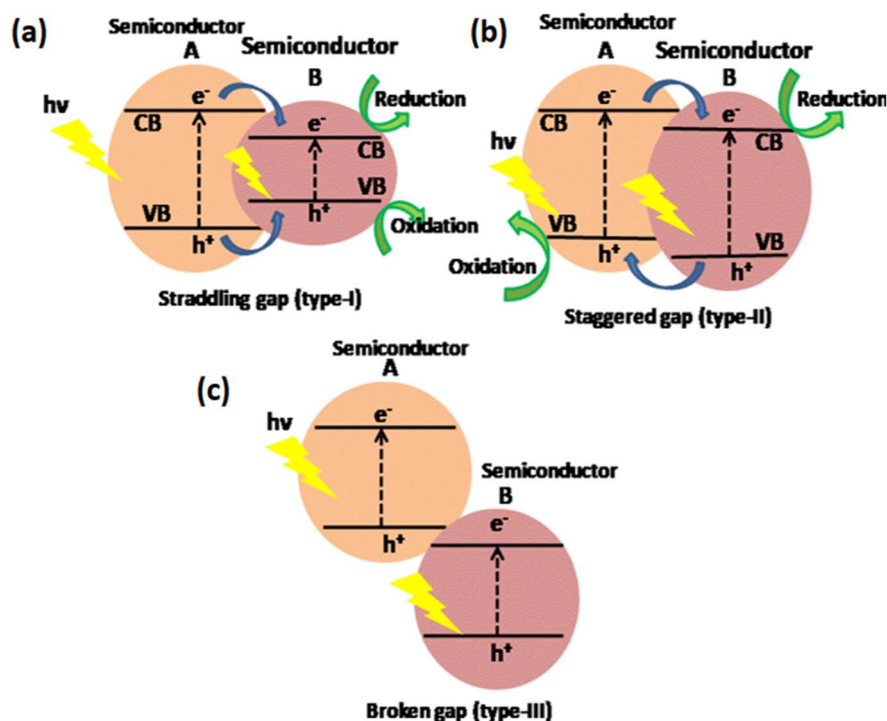
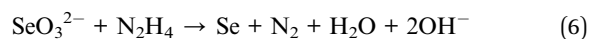
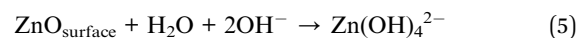


Fig. 11 Diagram showing the separation of electron–hole pair in three types of conventional heterojunction photocatalysts: (a) Type-I, (b) Type-II, and (c) Type-III (reproduced from ref. 143).



Fig. 12(a) depicts the UV-vis absorption spectra of three-dimensional ZnO nanostructures (S1, S2, and S3) that were utilized as reaction substrates, as well as 3D ZnO/ZnSe heterostructures (H1, H2, and H3) that were produced as a result of surface modification reactions.¹⁵⁰ The 3D ZnO/ZnSe heterostructures and 3D ZnO nanostructures showed markedly different optical absorption characteristics, according to the spectra. The 3D ZnO nanostructures (S1, S2, S3) demonstrated

strong UV absorption in the vicinity of the visible range, typical of ZnO with a broad bandgap. In contrast, the 3D ZnO/ZnSe heterostructures (H1, H2, H3) shows absorption peak in both the UV and visible regions. Again, type-II ZnSe/g-C₃N₄ heterojunctions were synthesized through ultrasonication and evaluated for PEC water splitting.¹⁵¹ When compared to 0.5 ZG, 1 ZG photocatalyst, and pristine g-C₃N₄, the absorption spectra of the as-prepared 0.05 ZG photocatalyst exhibited a greater degree of visible light absorption (400–500 nm), which is indicated in Fig. 12(b). Further, the Tauc plot demonstrated that the E_g was reduced from 2.76 eV to 2.60 eV for the 0.05 ZG photocatalyst in

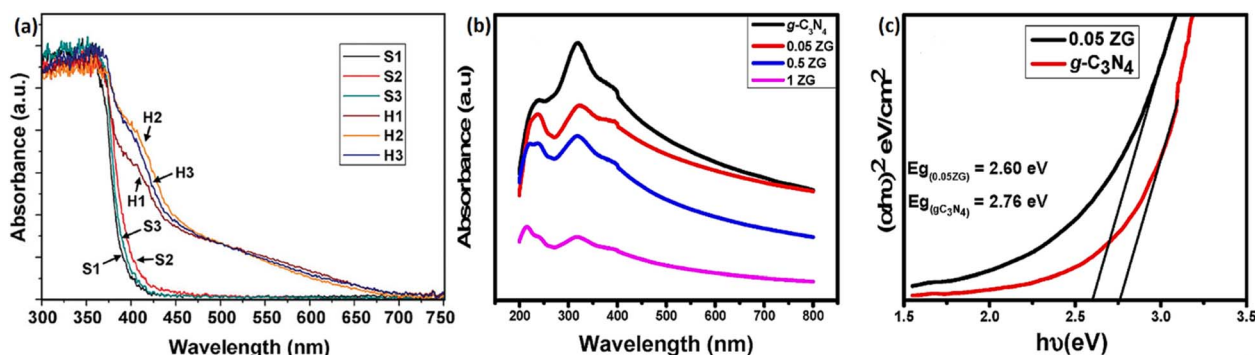


Fig. 12 (a) UV-vis absorption spectra of 3D superstructures (reproduced from ref. 150); (b) UV-visible absorption spectra of g-C₃N₄ and its heterostructures, and (c) Tauc plot of g-C₃N₄ and 0.05 ZG heterostructure for the determination of E_g (reproduced from ref. 151). "This figure has been reproduced from ref. 150 with permission from American Chemical Society, copyright 2011". "This figure has been reproduced from ref. 151 with permission from Elsevier, copyright 2021".

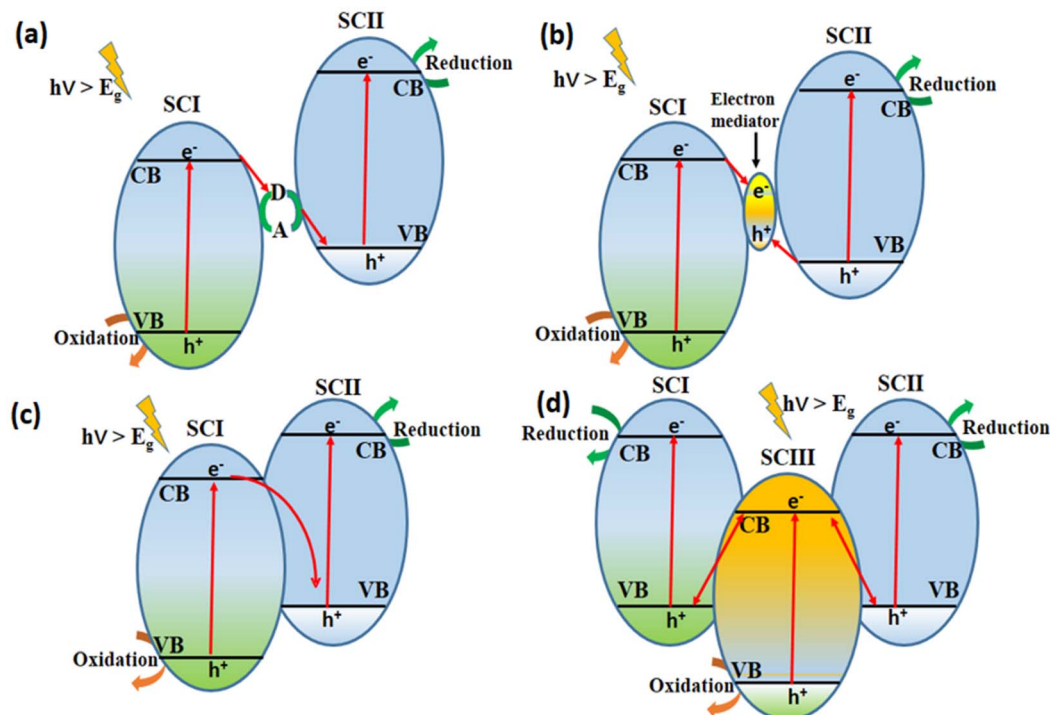


Fig. 13 A schematic overview of charge carrier migration in Z-scheme heterojunction photocatalysts when exposed to visible light: (a) conventional, (b) all-solid-state (ASS), (c) direct Z-scheme heterojunction, and (d) dual direct Z-scheme (reproduced from ref. 143).



comparison to the pristine $g\text{-C}_3\text{N}_4$ (2.76 eV) (Fig. 12(c)), reflecting the successful formation of type-II heterostructure.

5.2.2. Z-scheme heterojunction photocatalysts. The Z-scheme is an effective photocatalytic system that enhances the decoupling and transfer of photoinduced charge carriers, serving as an alternative to traditional heterojunctions.¹⁵² A Z-scheme photocatalytic system can be distinguished as direct or indirect based on the presence of an electron mediator within the system. One of the components of a Z-scheme heterojunction photocatalyst is a reduction semiconductor with an elevated CB position (SC II), and the other component is an oxidation semiconductor with a reduced VB position (SC I). The presence of an electron mediator can sometimes be found, which ultimately results in an indirect Z-scheme photocatalyst. In 1979, Bard *et al.* presented the theory of Z-scheme heterojunction, which was influenced by the process of photosynthesis in plants.¹⁵³ The first applications of the Z-scheme heterojunction were in liquid-phase photocatalytic processes. Without significant direct contact, the redox mediator functions as an acceptor–donor pair at the semiconductor interface. As shown in Fig. 13(a),¹⁴³ the redox mediator acts as both a donor and an acceptor during light exposure, facilitating the transport of photoinduced electrons from the CB of SC I to the VB of SC II.¹⁵⁴ Consequently, oxidation and reduction reactions can occur successfully within this heterojunction system due to the accumulation of photoinduced holes in the VB of SC I and the accumulation of electrons in the CB of SC II.¹⁴⁵ Despite this, this system is confronted with several difficulties. For example, standard Z-scheme photocatalysts usually function in the liquid phase, which necessitates the exact control of the pH of the reaction environment. In addition, they frequently display poor charge transfer rates, which makes it difficult for them to be utilized in practical applications involving the degradation of contaminants. In addition, a great number of liquid-phase redox mediators are unstable and prone to deactivation, which leads to a decrease in the overall effectiveness of photocatalysis.¹⁵⁵

In light of the constraints of liquid-phase Z-scheme heterojunction photocatalysts, researchers are seeking alternatives to boost the efficiency of indirect Z-scheme systems. In 2006, a novel Z-scheme photocatalyst was proposed, using an electron

solid conductor and noble metal Au as an electron mediator instead of traditional redox couples, integrating CdS and TiO_2 and paving the way for all-solid-state (ASS) Z-scheme photocatalysts.¹⁵⁶ In this system, light energy greater than the semiconductors' band gaps excites electrons in SC I, generating holes in the VB. These electrons then move to the VB of SC II *via* conducting materials at the semiconductor interface (Fig. 13(b)),¹⁴³ maintaining redox capability and effective separation of the photoinduced carriers.¹⁵⁷ However, ASS Z-scheme semiconductor photocatalysts typically rely on rare and expensive electron mediators, and many experience a shielding effect, significantly limiting their long-term practical applicability.¹⁵⁸

Research on direct Z-scheme photocatalysts began seven years after the proposal of the ASS Z-scheme heterojunction photocatalyst.¹⁵⁹ Direct Z-scheme photocatalysts, in contrast to traditional liquid-phase and ASS Z-scheme heterostructures, involve two semiconductors that are in close contact with one another (Fig. 13(c)).¹⁴³ This eliminates the requirement for an electron mediator. Notably, they successfully minimized backward reactions and light shielding effects without needing mediators while combining the advantages of indirect Z-scheme heterojunctions, such as effective decoupling of electron–hole pair and optimal redox potential.^{160–162} Additionally, the development of an internal electric field at the interfaces of the direct Z-scheme system compensates for mediators, speeding up the recombination of charge carriers with lower redox potentials while preserving those with higher capabilities. Typically, the staggered band arrangement of two semiconductors results in an internal electric field only when both semiconductors have different work functions.¹⁶³

Dual Z-scheme heterojunction photocatalytic systems with three semiconductors have recently attracted interest due to their distinct band alignment, charge transfer routes, and redox site locations. In a standard double Z-scheme heterojunction, charge carriers from the intermediate semiconductor (SC III) dissipate as they transfer from nearby semiconductors, leaving the outer semiconductors (SC I and SC II) to drive redox reactions, while SC III also contributes to oxidation or reduction (Fig. 13(d)).¹⁴³ In certain situations, electrons and holes on the intermediate semiconductor are depleted, leaving the peripheral semiconductors' charge carriers solely responsible for

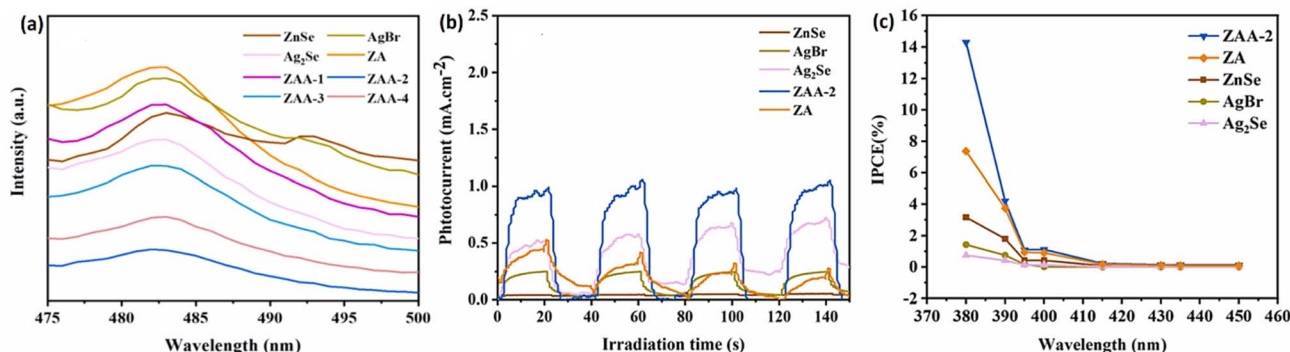


Fig. 14 (a) Photoluminescence spectra, (b) photocurrent response, and (c) IPCE of various fabricated samples (reproduced from ref. 165). "This figure has been reproduced from ref. 165 with permission from Elsevier, copyright 2023".

redox reactions.¹⁶⁴ For instance, Liang *et al.* fabricated a series ZnSe/Ag₂Se/AgBr (ZAA) heterojunction by depositing ZnSe on the surface of AgBr, with the *in situ* generation of Ag₂Se between the two components using a hydrothermal method and the resulting samples were labelled as ZAA-1, ZAA-2, ZAA-3, and ZAA-4, corresponding to ZnSe amounts of 0.15 g, 0.2 g, 0.25 g, and 0.3 g, respectively.¹⁶⁵ ZAA-2 displayed the lowest PL intensity at an excitation wavelength of 395 nm, indicating that it had the most efficient carrier separation (Fig. 14(a)). Additionally, the highest photocurrent response displayed by ZAA-2 under multiple on-off irradiations revealed efficient transport of photo-generated carriers (Fig. 14(b)). The incident photon-to-electron conversion (IPCE) efficiency, with ZAA-2 (14.30%) and ZA (7.37%) outperformed other materials (Fig. 14(c)). These findings demonstrate the superior light conversion efficiency of ZAA-2, where AgBr acts as a hole trap, ZnSe serves as an electron collector, and Ag₂Se functions as an electron-buffer mediator, enabling effective separation and directional transfer of electrons and holes.

Despite extensive research, high efficiency in heterojunction photocatalysts remains elusive. Traditional type I/II systems are limited by ineffective suppression of charge carrier recombination and decreasing redox capabilities, hindering their broader use. In contrast, Z-scheme heterostructured photocatalysts enable efficient charge transfer and strong redox capabilities. However, conventional Z-scheme photocatalysts suffer from reduced light absorption because of redox ion mediators. In ASS Z-scheme photocatalysts, the scarce metal mediator can compete with the semiconductors for light absorption. Therefore, direct Z-scheme heterostructured photocatalysts are regarded as the most favourable heterojunction systems available till date.

6. Applications of ZnSe

ZnSe displays significant activity in environmental remediation due to its photocatalytic properties, enabling it to effectively break down pollutants in both aqueous medium and air. It serves as a catalyst in sustainable processes, such as water splitting and hydrogen generation. Additionally, ZnSe facilitates advanced oxidation processes (AOPs) in wastewater treatment, allowing for the targeted degradation of persistent organic chemicals like pesticides, herbicides, and pharmaceutical residues, textile dyes that are difficult to eliminate using conventional approaches. In the field of microbiology, ZnSe nanoparticles have gained attention as effective antimicrobial agents capable of inhibiting the growth of various bacteria, fungi, and viruses. This makes them valuable for developing disinfectants and antimicrobial coatings for medical devices and surfaces.

6.1. Photodegradation of pollutants

Rapid population growth and economic expansion have escalated water pollution, making it a critical global challenge. The rise in agricultural, industrial, and domestic activities has led to substantial degradation of river and groundwater quality, with

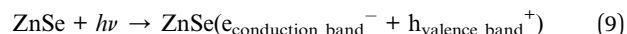
toxic wastes contaminating these vital resources. These harmful pollutants pose serious threats to human health and disrupt the balance and integrity of ecosystems.^{166,167} Significant sources of water contamination include heavy metal ions, dyes, phenols, polychlorinated biphenyls (PCBs), pharmaceutical residues, pesticides, and various non-natural compounds.^{168–170}

Currently, a diverse set of methods ranging from physical and chemical to biological and hybrid techniques are being explored for the breakdown and mineralization of contaminants. Among the various methods, photocatalysis is notably promising and crucial due to its impressive efficiency, energy-saving advantages, gentle reaction conditions, and minimal generation of other pollutants. Consequently, it has attracted considerable interest from researchers in the scientific field.^{171,172} Photocatalysis is a mechanism that accelerates the occurrence of a photoreaction through the use of a catalyst. The process works simply: when a photon with sufficient energy to meet or exceed the bandgap energy hits the catalyst, it produces a pair of charge carriers. This energy conversion triggers the generation of electrons and holes.¹⁷³ The electrons and holes generated by light interact with oxygen (O₂), water (H₂O), and hydroxyl groups, resulting in the production of reactive oxygen species (ROS) such as hydroxyl radicals ([•]OH) and superoxide radical anions (O₂^{•−}), both of which have powerful oxidative capabilities.¹⁷⁴ After fluorine, these hydroxyl radicals exhibit the second-highest oxidation potential, measured at 2.8 eV.¹⁷⁴ These highly reactive species rapidly interact with organic molecules, with rate constants generally falling between 10⁶ and 10⁹ mol L^{−1} s^{−1}.¹⁷⁵ They initiate a cascade of reactions with contaminants on the photocatalyst's surface, leading to the effective degradation of organic pollutants.¹⁷⁶

According to Herrmann,¹⁷⁷ heterogeneous photocatalytic processes involve five distinct steps, specifically:

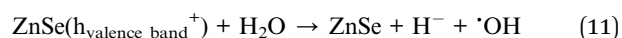
(i) Transfer of reactants to the catalyst surface, (ii) adsorption of one or more reactants, (iii) reaction of adsorbed reactants, (iv) desorption of products, and (v) diffusion of products away from the catalyst surface.

In the context of using ZnSe as a photocatalyst, the mechanism of heterogeneous photocatalysis can be described as follows:

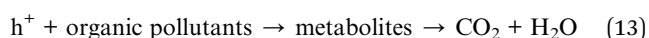
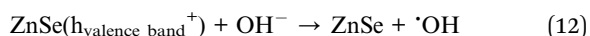


Here, $\text{e}_{\text{conduction band}}^-$ and $\text{h}_{\text{valence band}}^+$ serve as reducing and oxidizing agents, respectively. The oxidation and reduction of pollutants are as follows (eqn 10–18):

Oxidative reaction:



This reaction proceeds with the neutralization of the OH[−] ion into [•]OH by the h⁺:



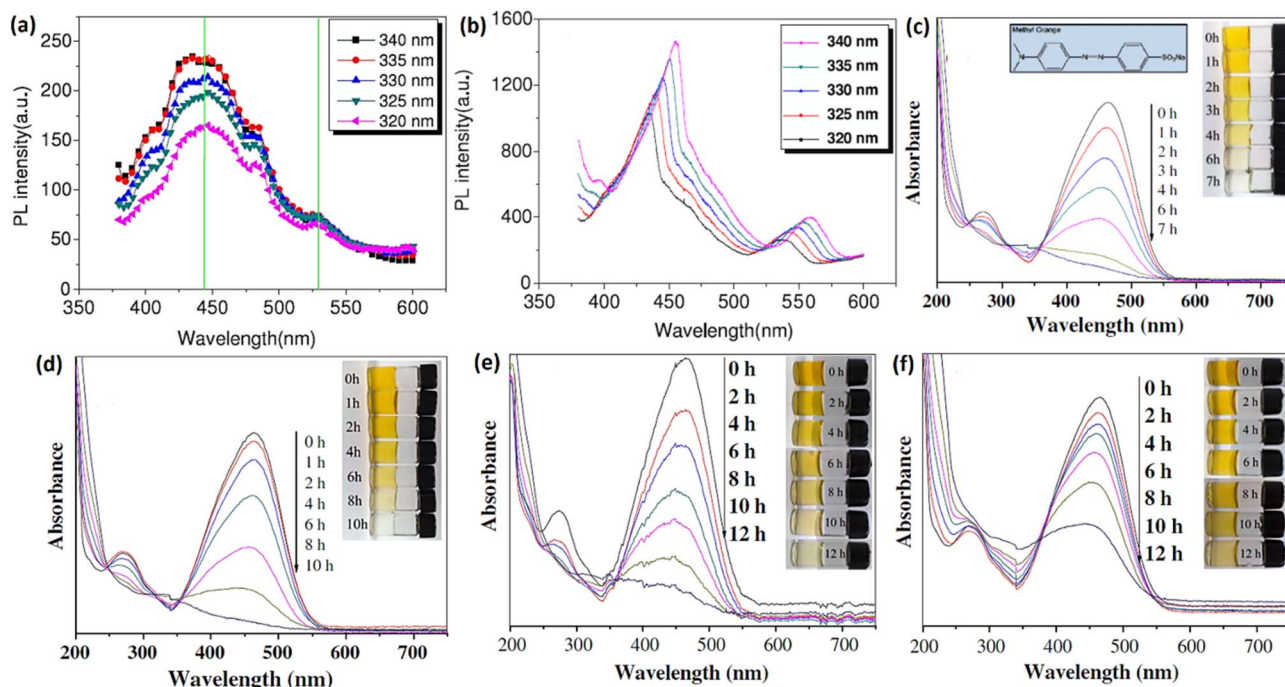
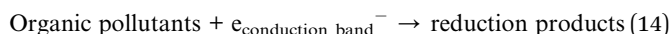
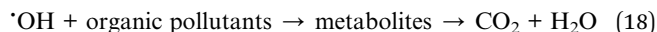
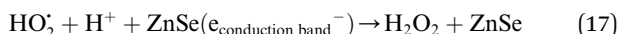
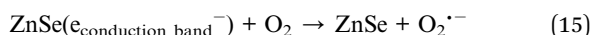


Fig. 15 Photoluminescence (PL) spectra of (a) ZnSe microspheres, and (b) commercially available ZnSe powder; temporal UV-visible absorption spectral shifts and related colour variations (insets) observed in MO solutions in the presence of (c) ZnSe microspheres, and (d) commercial ZnSe powder under UV light irradiation, temporal UV-visible absorption spectral shifts and related colour variations (insets) observed in MO solutions in the presence of (e) ZnSe microspheres, and (f) commercial ZnSe powder under visible light irradiation (reproduced from ref. 25). "This figure has been reproduced from ref. 25 with permission from IOP Publishing, copyright 2010".

Reductive reaction:



In this process, $\text{O}_2^{\cdot-}$ is generated by the electron in the following manner:



Within the outlined steps, the formation of hydroxyl radicals ($\cdot\text{OH}$) and superoxide anion radicals ($\text{O}_2^{\cdot-}$) is pivotal in driving the photocatalytic oxidation reaction.^{178,179}

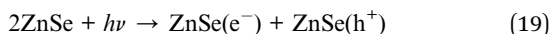
6.1.1. Photodegradation of dyes. Water serves as the most critical resource for life, yet nearly 80% of the world's population now faces water supply and security issues due to rapid industrialization, urbanization, and lack of awareness.¹⁸⁰ Wastewater contaminated with dyes, mainly from industries like textiles, paper, food processing, paints, and cosmetics, is a major source of water pollution.¹⁸¹ These dyes harm aquatic life with toxic effects and block sunlight, disrupting underwater ecosystems.¹⁸² Azo dyes, commonly applied in textile production, carry severe toxic and carcinogenic risks for both humans and animals.¹⁸³ Consequently, it is crucial to eliminate dye

residues because of their toxic nature and their significant harm to human health and environmental well-being. These residues can lead to serious health issues and disrupt ecosystems, making their removal a priority. For instance, ZnSe microspheres synthesized by Cao *et al.* via a surfactant-free solvothermal method using selenophene ($\text{C}_4\text{H}_4\text{Se}$) and ZnCl_2 were evaluated for the photocatalytic degradation of the azo dye MO under ultraviolet (UV) and visible light.²⁵ Fig. 15(a) and (b) illustrates the photoluminescence (PL) emission spectra for ZnSe microspheres and commercial ZnSe powder. The photocatalytic performance of the ZnSe microspheres was assessed by the degradation of MO dye in a 5×10^{-5} M aqueous solution under UV light for varying time periods (Fig. 15(c) and (d)), with the degradation process monitored using MO's characteristic absorption at $\lambda = 462$ nm. Control analyses showed negligible degradation of MO without UV light or ZnSe microspheres. In a comparative study, the synthesized ZnSe microspheres achieved about 94% MO degradation after 7 hours, changing the color from orange to transparent, while commercial ZnSe powder required 10 hours to reach 95.1% degradation. These results indicated that ZnSe microspheres reveal intrinsic photocatalytic behaviour under UV light. On the other hand, the photocatalytic performance of the synthesized ZnSe microspheres and commercial powder were assessed for degrading MO dye under visible light (Fig. 15(e) and (f)). The ZnSe microspheres achieved around 94.3% MO degradation within 12 hours, while the commercial ZnSe powder reached approximately 60.6% degradation in the same period. When subjected

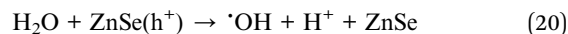
to UV or visible light, the excitation of ZnSe microspheres and commercial powder generated conduction-band electrons and valence-band holes. The notable variations in photocatalytic behaviour between the synthesized ZnSe microspheres and commercial ZnSe powder were due to the greater number of available surface active sites in the microspheres and the larger surface area, which improved the electron-hole separation efficiency in the ZnSe microspheres.^{25,184}

The mechanism of photodegradation of MO dye can be shown by the following equations:

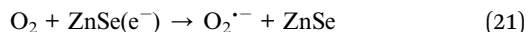
The ZnSe microspheres absorb UV or visible light having energy $h\nu$ equal to or greater than the bandgap energy (E_g), producing electron (e^-) and hole (h^+) pairs.



The absorbed H_2O on the surface of ZnSe microspheres captures the holes, producing highly reactive hydroxyl radicals ($\cdot\text{OH}$), as shown in eqn (20).



In this process, O_2 functions as an electron acceptor from the conduction band, resulting in the formation of a superoxide anion radical ($\text{O}_2^{\cdot-}$), which then reacts with protons to yield $\cdot\text{OOH}$, as depicted in eqn (21) and (22).



The $\cdot\text{OH}$ radical may also arise from the trapped electron (e^-) subsequent to the creation of the $\cdot\text{OOH}$ radical, as outlined in eqn (23) and (24):

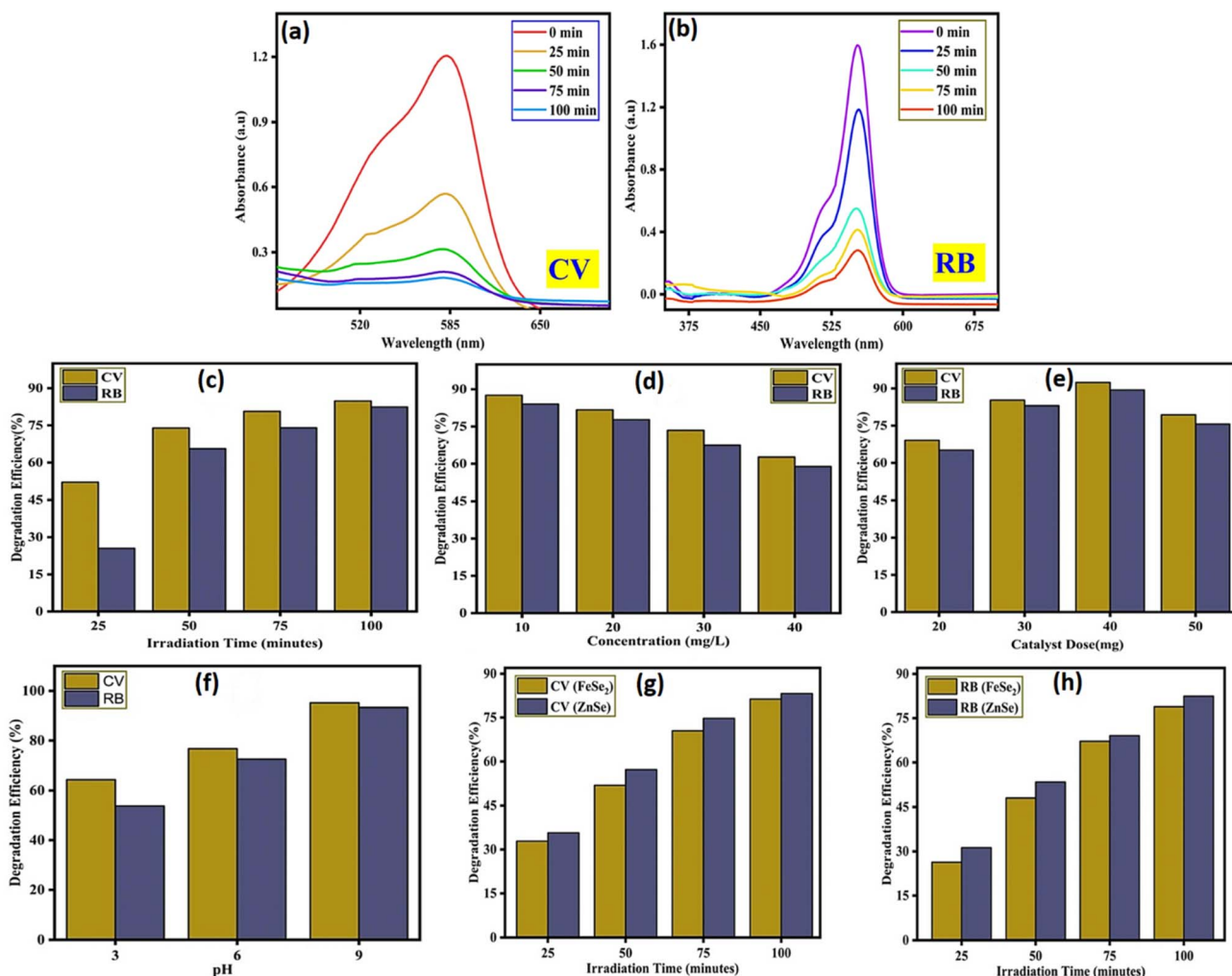
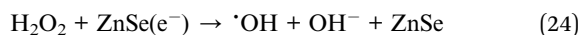
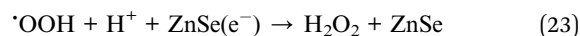


Fig. 16 Time-dependent UV-vis absorbance spectra of (a) CV, and (b) RB; effect of operational parameters on dye degradation using ZS/FS nanocomposite: (c) irradiation time, (d) initial dye concentration, (e) catalyst dose, and (f) solution pH; (g and h) comparison of degradation efficiencies of individual ZnSe (ZS) and FeSe₂ (FS) (reproduced from ref. 189). "This figure has been reproduced from ref. 189 with permission from Springer Nature, copyright 2024".



Table 3 Previously reported ZnSe-based photocatalysts for the photodegradation of organic contaminants

Catalyst	Target contaminant	Source	Degradation efficiency, time	Ref.
ZnSe	MO	UV light	94% in 7 h	25
ZnSe	AY 17	UV light	44% in 150 min	190
CuSe/ZnSe	MO	Visible light	100% in 90 min	191
	MB		96% in 60 min	
ZnSe	MO	Visible light	100% in 5 h	192
ZnSe/TiO ₂	MB	Visible light	47% in 150 min	193
	MO		31% in 150 min	
	RhB		40% in 150 min	
ZnSe	MO	Simulated sunlight (100 mW cm ⁻²)	96% in 9 h	194
Cu-doped ZnSe	MB	Visible light	98.09% in 180 min	195
ZnTe/ZnSe	CR	UV-vis solar illumination	94% in 65 min	196
ZnSe/rGO	MV	Visible light	94% in 3 h	197
CS/ZnSe	Tartrazine	Sunlight	98% in 3 h	198
	SY		97% in 3 h	
CoNi ₂ O ₄ /ZnSe	MB	Visible light	92% in 2 h	199
Fe ₃ O ₄ /rGO/ZnSe/TiO ₂	MB	UV irradiation	100% in 40 min	200
ZnIn ₂ S ₄ /ZnSe	TC	Visible light	80% in 60 min	201
	OTC		74% in 60 min	
RGO-ZnSe	Norfloxacin	Simulated solar light	83.5% in 40 min	202
ZnSe-Ag/g-C ₃ N ₄	Ceftriaxone sodium	Visible light	89.24% in 90 min	203
MoO ₃ /ZnSe	Ciprofloxacin hydrochloride	Visible light	80% in 180 min	204
MoS ₂ /ZnSe	Levofloxacin	Visible light	73.2% in 2 h	205
ZnO/ZnSe/CdSe/MoS ₂	Amoxicillin	UV-visible	100% in 30 min	206

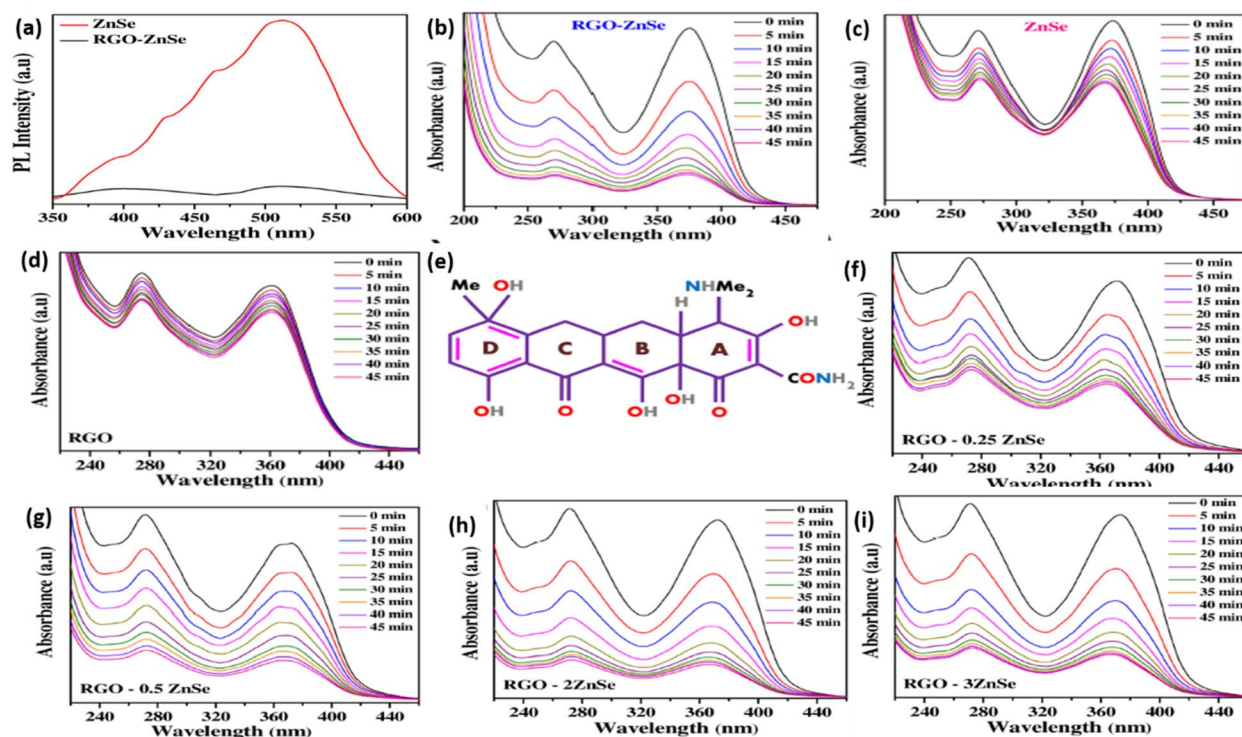
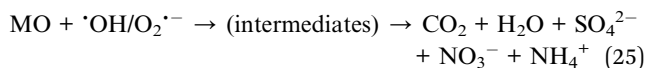


Fig. 17 (a) PL spectra of RGO-ZnSe and controlled ZnSe; UV-visible absorption spectra of an aqueous solution of tetracycline containing (b) RGO-ZnSe, (c) controlled-ZnSe, (d) controlled RGO; (e) structure of tetracycline; UV-visible absorption spectra of an aqueous solution of tetracycline containing (f) RGO-0.25 ZnSe, (g) RGO-0.5 ZnSe, (h) RGO-2 ZnSe, and (i) RGO-3 ZnSe over distinct intervals of simulated solar light illumination (reproduced from ref. 212). "This figure has been reproduced from ref. 212 with permission from John Wiley and Sons, copyright 2018".



These radicals, including $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$, possess exceptionally strong oxidizing capabilities, and can effectively degrade the MO dye.¹⁸⁵ Oxidative cleavage of azo dyes, including MO, is typically attributed to the subsequent attacks by $\cdot\text{OH}$ radicals.¹⁸⁶ Following the addition of $\cdot\text{OH}$ radicals to the aromatic group of MO, the carbon atom linked to the azo bond undergoes a transformation, resulting in the opening of the hydroxylated ring and ultimately producing CO_2 gas, H_2O , SO_4^{2-} , NO_3^- and NH_4^+ through a series of oxidation steps, as illustrated below.¹⁸⁷



The ZnSe/graphene nanocomposites, fabricated by Hsieh *et al.*, were assessed for the photocatalytic degradation of MB dye under visible-light irradiation achieving a degradation efficiency of 99.6% after 6 hours.¹⁸⁸ Recently, Bhat *et al.* synthesized a ZnSe/FeSe₂ (ZS/FS) heterostructure *via* a simple one-pot hydrothermal method and investigated its photocatalytic performance toward crystal violet (CV) and Rhodamine B (RB) under UV-visible light.¹⁸⁹ As shown in Fig. 16(a) and (b), the dye absorption intensity decreased with increasing irradiation time, achieving maximum degradation at 100 min–84.87% for CV and 82.43% for RB (Fig. 16(c)).

Fig. 16(d) shows that lower dye concentrations favoured degradation; for instance, 87.62% of 10 mg per L CV and 84.09% of 10 mg per L RB were degraded, while only 62.73% and 58.90% degradation were observed at 40 mg L⁻¹, respectively. Catalyst dose optimization indicated that 40 mg was the optimal amount, resulting in maximum degradation of 92.43% for CV and 89.39% for RB (Fig. 16(e)). Beyond this dose, efficiency declined due to increased turbidity and reduced photon absorption. Additionally, the effect of pH (3–9) on dye degradation was studied, with optimal performance observed at pH 9, where 95.23% of CV and 93.35% of RB were degraded (Fig. 16(f)). The enhancement at higher pH is attributed to increased OH⁻ availability, promoting active radical generation. Comparative studies revealed that the ZS/FS heterostructure outperformed individual ZnSe and FeSe₂, which showed lower efficiencies–ZnSe: 83.19% (CV), 82.44% (RB); FeSe₂: 81.33% (CV), 78.89% (RB)–likely due to faster charge recombination in the pristine materials (Fig. 16(g and h)). Table 3 summarizes the photodegradation of various dyes using ZnSe based photocatalysts.

6.1.2. Photodegradation of antibiotics. As chemotherapeutic agents, antibiotics act to inhibit and eliminate bacterial infections. Since Fleming's breakthrough discovery of penicillin in 1928, they have saved millions of lives.²⁰⁷ Approximately 250 different antibiotics are utilized in both human and veterinary medicine.²⁰⁸ However, improper antibiotic use has led to their continuous release into the water from industries, households, farms, and fisheries, making them significant emerging contaminants (ECs). Their complex structures, like β -lactam rings, tetracyclic nuclei, and lactone rings, give them long half-lives and resist microbial degradation, posing health risks. For instance, sulfadiazine, ofloxacin, tetracycline, and erythromycin have half-lives of 25.7, 11.1, 4.15, and 4.22 days, respectively.²⁰⁹

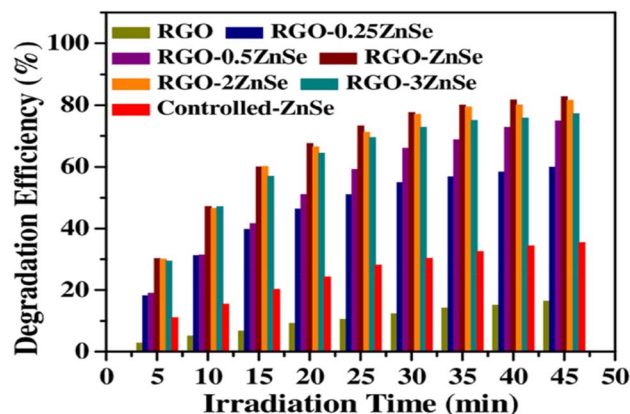
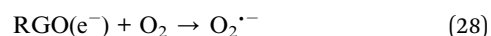
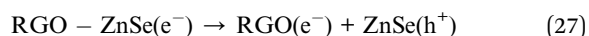
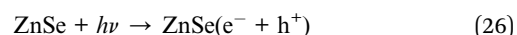


Fig. 18 Comparison of the degradation efficiency of all the fabricated RGO–ZnSe composites with varying ZnSe to RGO ratios (reproduced from ref. 212). "reproduced from ref. 212 with permission from [John Wiley and Sons], copyright [2018]".

This means antibiotics can travel long distances in rivers before their concentration decreases by half. Ongoing releases have lasting ecotoxic effects on wildlife, promote antibiotic-resistant genes (ARG) and bacteria (ARB), and can disrupt fish reproduction. Consequently, it is urgent to remove antibiotics from water sources.^{210,211} For instance, RGO–ZnSe nanocomposites were fabricated *via* a one-step solvothermal reaction, evaluating their photocatalytic performance for tetracycline (TC) degradation under simulated solar light irradiation.²¹² The PL spectra of ZnSe and RGO–ZnSe nanocomposite, excited at 300 nm, reveal a significant quenching effect due to robust interfacial interactions between ZnSe and RGO at ambient temperature (Fig. 17(a)). This pronounced reduction in PL intensity highlights an efficient charge transfer process, making RGO–ZnSe a compelling candidate for advanced photocatalytic applications. The photocatalytic behaviour was assessed with a UV-vis spectrophotometer. Fig. 17(b) shows the UV-vis absorption spectra of TC solution degraded by RGO–ZnSe for 0–45 min at 5-min intervals. Comparable data for controlled ZnSe and RGO photocatalysts are shown in Fig. 17(c) and (d), with the TC structure depicted in Fig. 17(e). The effectiveness of the RGO–ZnSe composite in photodegrading aqueous TC solutions was tested at varying ZnSe to RGO ratios (RGO0.25ZnSe, RGO–0.50ZnSe, RGO–2ZnSe, RGO–3ZnSe) under uniform experimental conditions, with the UV-vis spectra presented in Fig. 17(f–i). The degradation efficacy of all the fabricated RGO–ZnSe composites is illustrated in Fig. 18, with the RGO–ZnSe demonstrating the highest photocatalytic behaviour, outperforming RGO and all other tested ratios, including controlled-ZnSe.

The mechanism of the degradation of TC is explained below (eqn (26)–(33)):²¹²



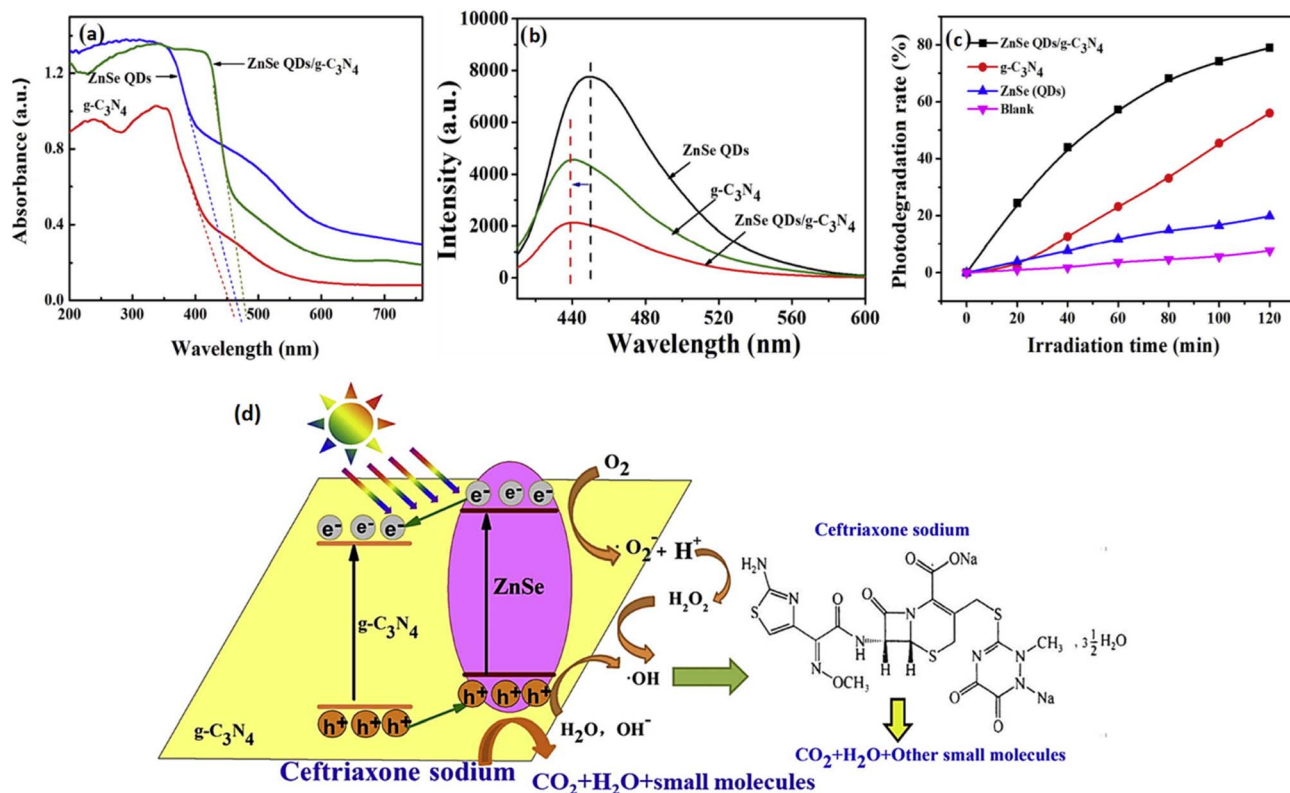
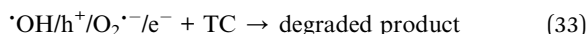
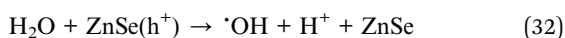
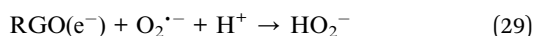


Fig. 19 (a) UV-vis diffused absorption spectra, (b) photoluminescence spectra, (c) photocatalytic performance; (d) possible degradation mechanism of ceftriaxone sodium using ZnSe QDs/g-C₃N₄ composite (reproduced from ref. 213). "This figure has been reproduced from ref. 213 with permission from Elsevier, copyright 2018".



Under the influence of visible light, excitons formed in ZnSe dissociate into electrons (e^-) and holes (h^+). Without RGO, most of these charges quickly recombined, limiting reactivity. However, the close contact between ZnSe NPs and RGO enabled the transfer of excited electrons to RGO, enhancing charge separation and reducing recombination. This process also led to the formation of hydroxyl radicals ($\cdot\text{OH}$) from photoexcited holes in the valence band. The excited electrons moved freely along the conductive network of RGO. When O_2 was adsorbed onto the RGO surfaces, the electrons reacted with O_2 , resulting in the formation of superoxide anion radical ($\text{O}_2^{\cdot-}$). The TC molecules can be broken down into degradation products by the highly reactive species $\cdot\text{OH}$, h^+ , $\text{O}_2^{\cdot-}$, and e^- , due to their strong reactivity.

Similarly, Zhao *et al.* synthesized a ZnSe QDs/g-C₃N₄ composite and investigated its photocatalytic efficiency for degrading Ceftriaxone sodium in water under visible light.²¹³

The DRS absorption edges of pure g-C₃N₄ and ZnSe QDs were observed at 454 nm and 466 nm, respectively, while the ZnSe QDs/g-C₃N₄ composite exhibited a red-shifted absorption at 475 nm, indicating improved visible light harvesting characteristics (Fig. 19(a)). Moreover, the composite showed the lowest photoluminescence intensity among all samples, suggesting superior charge carrier separation and enhanced photocatalytic performance (Fig. 19(b)). The ZnSe QDs/g-C₃N₄ composite exhibited a significantly higher degradation rate of ceftriaxone sodium compared to pure g-C₃N₄ and ZnSe QDs, confirming its superior photocatalytic activity (Fig. 19(c)). The proposed mechanism for the degradation of ceftriaxone sodium using the ZnSe QDs/g-C₃N₄ composite is illustrated in Fig. 19(d). Under visible light irradiation, photogenerated electrons (e^-) in the conduction band (CB) of ZnSe QDs transfer to the CB of g-C₃N₄, while holes (h^+) are excited from the valence band (VB) of g-C₃N₄ to the VB of ZnSe QDs. In this heterojunction, g-C₃N₄ serves as an electron acceptor, effectively suppressing the recombination of photogenerated e^-/h^+ pairs. The transferred electrons react with O_2 to form $\text{O}_2^{\cdot-}$ radicals which further interact with H^+ to generate additional $\text{O}_2^{\cdot-}$. Concurrently, the holes accumulated in the VB of ZnSe QDs oxidize H_2O and OH^- to produce $\cdot\text{OH}$ radicals. These reactive species synergistically degrade Ceftriaxone sodium into CO_2 , H_2O , and other smaller molecules. The proposed degradation pathway is as follows (eqn (34)–(37)):²¹³



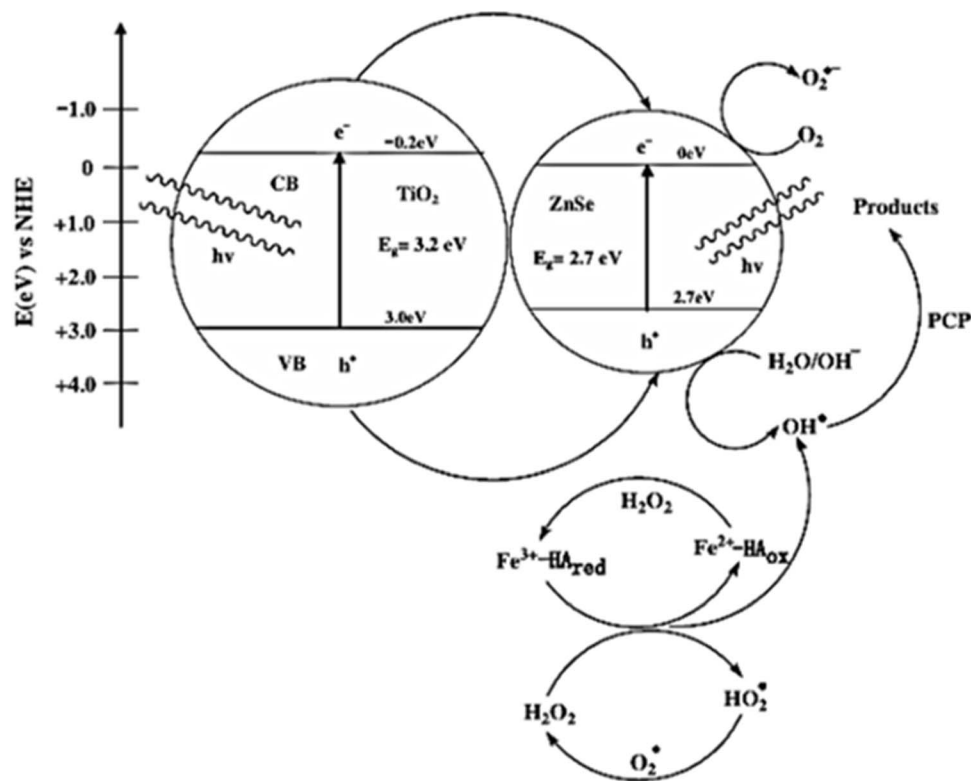


Fig. 20 Illustration of electron and hole transfer in the ZnSe sensitized TiO_2 NTAs and mechanism of photocatalysis degradation with support of the photo-Fenton system (reproduced from ref. 121). "This figure has been reproduced from ref. 121 with permission from Elsevier, copyright 2013".

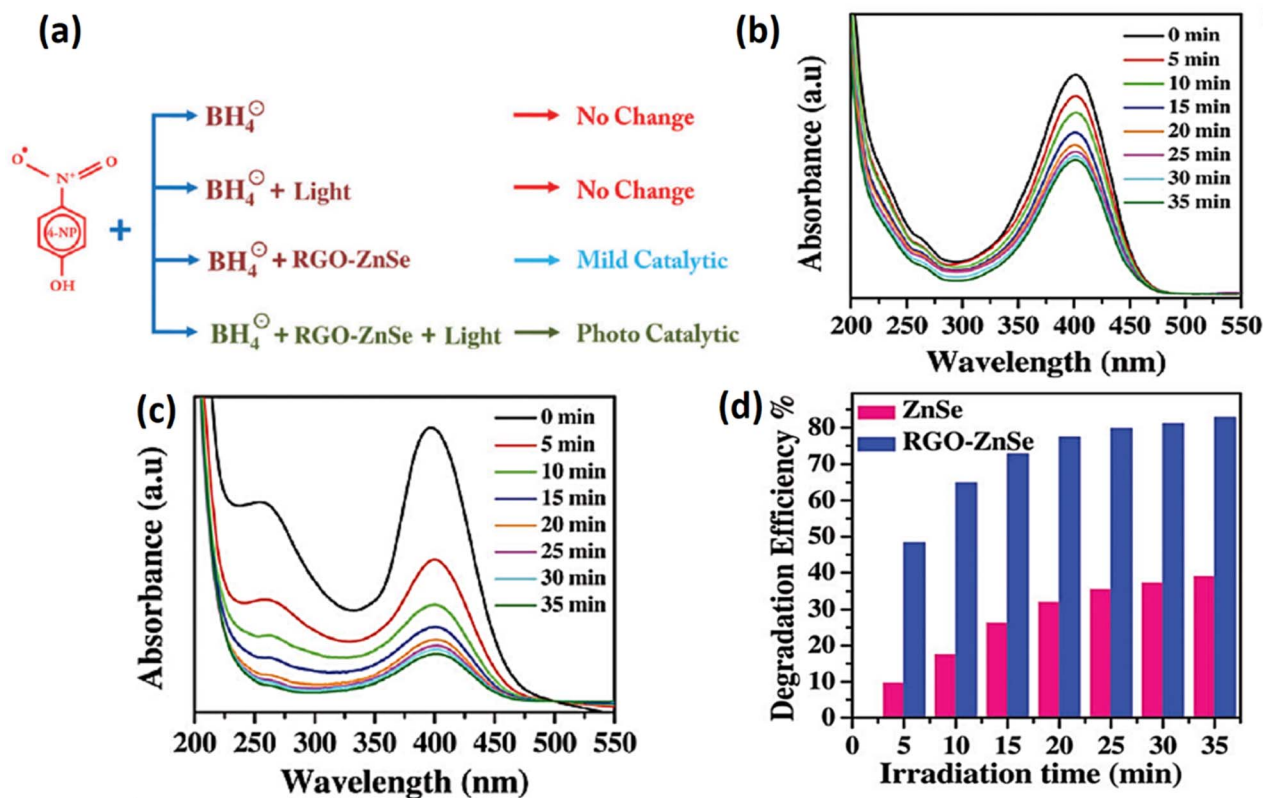


Fig. 21 (a) Schematic presentation of different reaction conditions for the possible reduction of 4-NP. UV-vis absorption spectra of 4-NP and NaBH_4 aqueous with (b) controlled ZnSe and (c) RGO-ZnSe composite for varying times of simulated solar light illumination, (d) comparison of photodegradation efficiency as a function of time for controlled ZnSe and the RGO-ZnSe composite (reproduced from ref. 219).

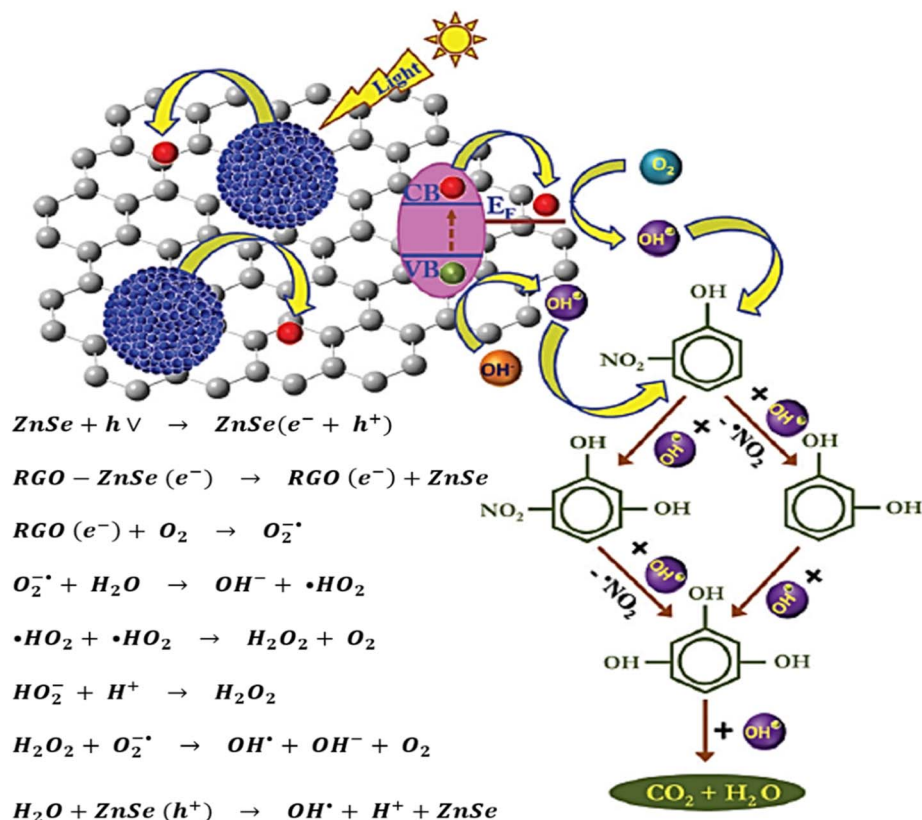
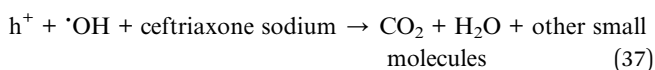
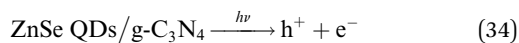


Fig. 22 Mechanism of photocatalytic 4-NP degradation using RGO-ZnSe composite (reproduced from ref. 219).



Recently, Liu *et al.* synthesized a novel 3D/3D S-scheme ZnSe/NiMoO₄ heterostructure *via* a hydrothermal method, with 15% ZnSe identified as the optimal composition.²¹⁴ The photocatalytic performance was evaluated against tetracycline under visible light irradiation using a 300 W Xe lamp equipped with a UV cut-off filter ($\lambda < 400$ nm). NiMoO₄ exhibited the lowest activity, attributed to its weak absorption in the visible region and fast recombination of photogenerated charge carriers. Notably, all ZnSe/NiMoO₄ composites showed a substantial improvement in photocatalytic activity, with the 15% ZnSe/NiMoO₄ sample delivering the highest degradation efficiency under the same experimental conditions. The progressive decline in the absorption peaks at 357 and 275 nm, along with noticeable peak shifts, suggests the gradual degradation of tetracycline, involving the breakdown of aromatic structures and formation of intermediate compounds. Table 3

summarizes the previously reported ZnSe-based photocatalysts utilized for the photodegradation of various antibiotics.

6.1.3. Photodegradation of phenolic compounds. Among the diverse array of contaminants, the widespread presence of phenolic compounds in wastewater and their associated environmental risks have raised serious public health concerns.²¹⁵ Phenols and their derivatives are recognized for their strong resistance to biodegradation and high toxicity. These compounds are continuously released into aquatic systems through numerous human activities. Furthermore, the structural diversity, high toxicity, and environmental persistence of these compounds can severely impact ecosystem integrity and endanger human health through the contamination of surface and groundwater sources. As a result, the efficient removal of phenolic compounds from wastewater effluents has emerged as a significant challenge, essential for mitigating pollution risks and promoting the safe reuse of treated water.²¹⁶ The photocatalytic performance of the WO₃-ZnSe nanostructures was evaluated through the degradation of phenol under UV-visible light irradiation, with nearly 93% degradation achieved within 105 min.²¹⁷ The degradation mechanism can be described in two main steps: initially, highly reactive species such as free radicals are generated. In the second step, these radicals oxidize the phenol molecules adsorbed on the catalyst surface. The catalyst, surrounded by hydroxyl groups, becomes negatively charged when dispersed in the phenol solution. Due to electrostatic interaction, phenol-being weakly acidic, is readily



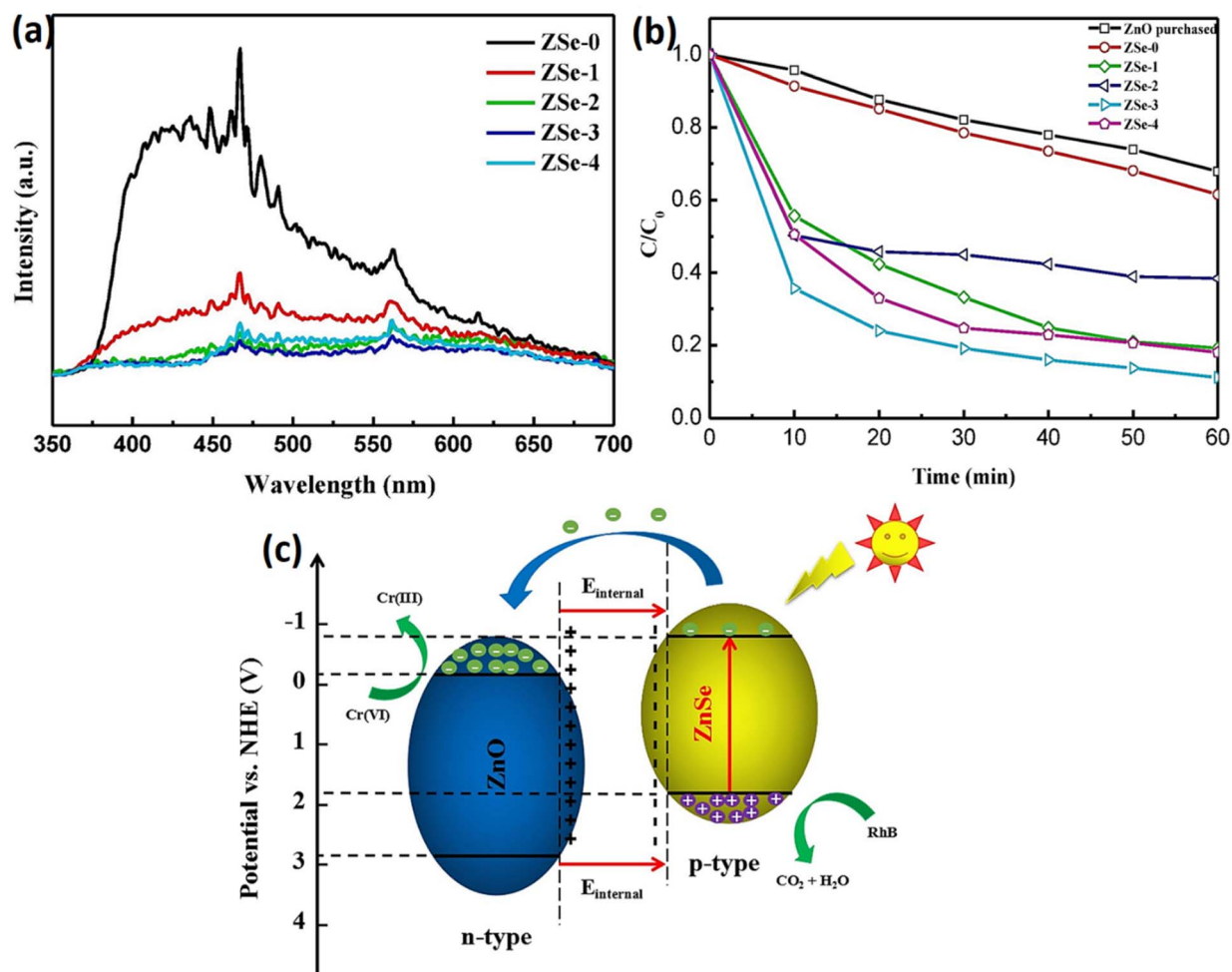


Fig. 23 (a) PL spectra of pure ZnO and ZnO/ZnSe composites at room temperature under 325 nm excitation, (b) time-dependent changes in C/C_0 of Cr(VI) using different photocatalysts under visible light exposure, and (c) proposed photocatalytic degradation pathways of Cr(VI) using ZnO/ZnSe composite (reproduced from ref. 225). "This figure has been reproduced from ref. 225 with permission from Elsevier, copyright 2021".

adsorbed onto the catalyst surface. Upon exposure to light, photons with energy equal to or greater than the bandgap excite the catalyst, resulting in the formation of electron-hole pairs. The excited electrons migrate to the CB, while holes remain in the VB. The holes oxidize the adsorbed hydroxyl groups, forming highly reactive $\cdot\text{OH}$ radicals. Simultaneously, the CB electrons reduce molecular oxygen to $\text{O}_2^{\cdot-}$ radicals, which further interact with water to produce H_2O_2 . However, Kumar *et al.* previously reported a ZnSe- WO_3 nano-hetero-assembly supported by Gum ghatti for the effective photodegradation of a phenolic derivative, bisphenol A (BPA).²¹⁸ The designed Z-scheme photocatalyst exhibited superior visible light absorption and efficient charge separation, with gum ghatti serving as both a super-adsorbent and a charge carrier reservoir. BPA degradation was investigated under three different experimental conditions, achieving an impressive 99.5% degradation within just 45 minutes through the synergistic action of photocatalysis, adsorption, and ozonation. This nano-hetero-assembly demonstrated high surface area, excellent stability, and minimized charge carrier recombination.

In a related study, ThanhThuy *et al.* synthesized a ZnSe/TiO₂ nanotube array (NTAs) photocatalyst *via* pulse electrodeposition of ZnSe nanoparticles onto TiO₂ NTAs and demonstrated its application in the photo-Fenton-assisted degradation of pentachlorophenol (PCP).¹²¹ The enhanced degradation is attributed to the HA-mediated photosensitized generation of H_2O_2 and $\text{O}_2^{\cdot-}$ radicals under AM 1.5G illumination. After 80 min of irradiation, PCP removal efficiencies were recorded at 93.2%, 68.9%, and 60.2% for H_2O_2 concentrations of 150 μM , 75 μM , and 40 μM , respectively. Extending the irradiation time to 2 hours improved the degradation to 99% and 79.9% for H_2O_2 concentrations of 75 μM and 40 μM , respectively. These findings confirm the critical role of H_2O_2 in generating $\cdot\text{OH}$ radicals, which significantly enhance the oxidative degradation of PCP in the ZnSe/TiO₂ photocatalytic system. The decline in efficiency at higher initial concentrations of PCP is attributed to increased optical density, which limits light penetration and photon absorption at the catalyst surface. Additionally, elevated PCP levels reduce the availability of active sites due to competitive adsorption, thereby diminishing the generation of $\cdot\text{OH}$ radicals.



and other reactive species essential for effective degradation. Furthermore, Fig. 20 illustrates the proposed mechanism of charge transfer in the ZnSe-sensitized TiO₂ NTAs, highlighting the photocatalytic degradation pathway facilitated by the synergistic action of the photo-Fenton process.

Similarly, ZnSe-decorated RGO was utilized in the photocatalytic degradation of 4-nitrophenol (4-NP) (Fig. 21(a)).²¹⁹ While a progressive decline in the 4-NP absorption peak was observed in the UV-vis absorbance spectra with increasing irradiation time, the absence of a characteristic aminophenol peak (~295 nm) confirms that the degradation proceeds *via* an oxidative rather than a reductive pathway for both catalysts (Fig. 21(b) and (c)). Notably, the RGO-ZnSe composite achieved approximately 85% degradation of 4-NP within 35 min, significantly outperforming the pristine ZnSe (35%) and RGO (24%) under identical conditions (Fig. 21(d)). Upon illumination, both ZnSe and RGO components in the composite generate excitons. These excitons in ZnSe undergo diffusion and separation at the RGO/ZnSe interface, where efficient electron transfer from ZnSe

to RGO occurs, leaving behind holes in the semiconductor matrix. The spatially separated electron-hole pairs in the RGO-ZnSe system effectively initiate the formation of 'OH radicals, which are pivotal in driving the photocatalytic degradation process. A comprehensive schematic representation of the 'OH generation pathway and the proposed mechanism underpinning the elevated activity of the RGO-ZnSe composite is presented in Fig. 22.

6.2. Removal of Cr(vi) from aqueous medium

With rapid global industrialization, environmental issues have become more severe, with heavy metal pollutants such as Pb, Cd, Cr, As, and Hg posing significant threats to human health.²²⁰ Among these, hexavalent chromium [Cr(vi)] is especially toxic, known for its carcinogenic, mutagenic, and irreversible harmful effects on living organisms. Consequently, the reduction of Cr(vi) to the less toxic and more stable trivalent chromium [Cr(III)] has garnered significant attention.²²¹ Therefore, developing an economical, sustainable, and highly

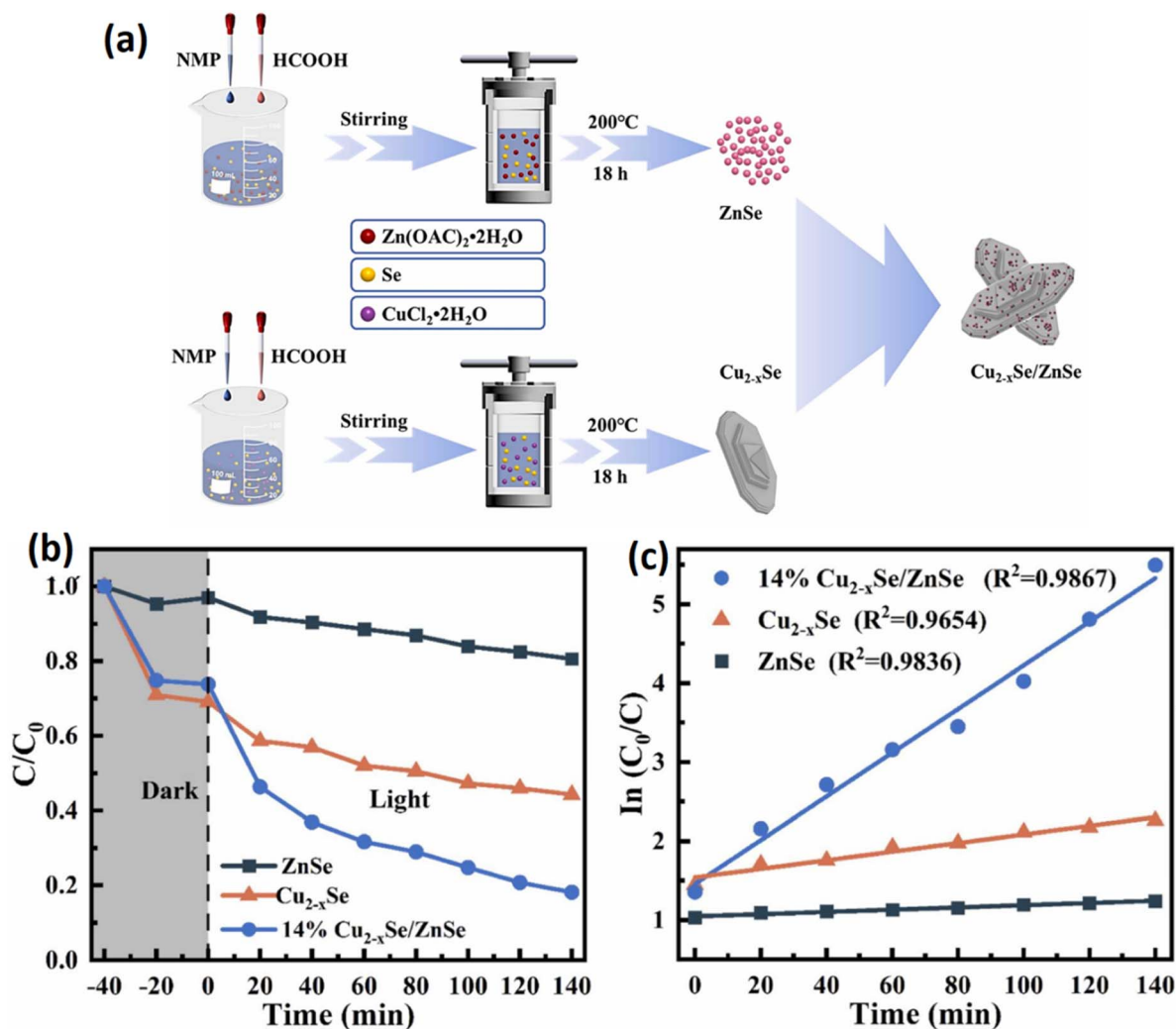


Fig. 24 (a) Synthetic scheme of Cu_{2-x}Se/ZnSe composite; photocatalytic Cr(vi) reduction studies: (b) comparison of activities of individual materials and 14% Cu_{2-x}Se/ZnSe composite, and (c) kinetic analysis (reproduced from ref. 226). "This figure has been reproduced from ref. 226 with permission from Elsevier, copyright 2025".

Table 4 Summary of Cr(vi) photoreduction using ZnSe-based materials

Catalyst	Synthetic method	Source	Efficiency	Ref.
MoSe ₂ /ZnO/ZnSe	Hydrothermal	Visible light	100%	227
ZnO/ZnSe	Two-step hydrothermal and ion-exchange	Visible light	88.8%	225
14% Cu _{2-x} Se/ZnSe	Solvothermal	—	82%	226
ZnS/ZnSe/MoSe ₂	Solvothermal and ion-exchange	Visible light	96%	221
3% ZnSe/TiO ₂	Solution-based synthesis	Visible light	83%	222

efficient method for Cr(vi) removal from wastewater is of utmost importance. Photocatalysis has recently emerged as an effective and environmentally friendly approach for reducing highly toxic Cr(vi) ions to the less toxic Cr(III), and further to insoluble Cr(OH)₃, through photoinduced electrons in the CB. Among various semiconductor materials, transition metal chalcogenides have gained attention due to their abundance and suitable band gaps, enabling efficient visible-light-driven photocatalysis.²²² Notably, ZnSe exhibits excellent physicochemical properties that are highly dependent on its particle size, morphology, and synthesis method.^{223,224} Zhang *et al.* successfully synthesized a ZnSe/ZnO p–n heterojunction *via* a combination of hydrothermal and ion exchange methods, significantly enhancing the photocatalytic reduction of Cr(vi).²²⁵ PL analysis revealed that the ZSe-3 composite exhibited the lowest PL intensity, indicating superior charge carrier separation compared to pure ZnO, which showed the highest PL intensity (350–700 nm) (Fig. 23(a)).

As shown in Fig. 23(b), ZSe-3 demonstrated the highest photocatalytic activity, achieving 88.8% Cr(vi) reduction within 60 min, outperforming ZSe-1 and ZSe-2. In contrast, bare ZnO and commercial ZnO showed significantly lower efficiencies, with Cr(vi) reduction rates of only 38.5% and 32.1%, respectively. The enhanced performance of the ZnSe/ZnO nanocomposite is attributed to the favourable band alignment between ZnSe and ZnO. Upon visible-light irradiation, electrons in the CB of ZnSe, which possesses a more negative potential than ZnO, transfer to the CB of ZnO, while h⁺ migrate from the VB of ZnO to that of ZnSe. This effective charge separation facilitates the reduction of Cr(vi) to Cr(III), as supported by the CB potential of ZnO being sufficiently negative (Fig. 23(c)).

In a recent study, Yu *et al.* fabricated a novel p–n heterojunction photocatalyst by integrating ZnSe nanoparticles onto Cu_{2-x}Se nanoplates, effectively generating a built-in electric field that promotes rapid charge carrier separation and minimizes recombination (Fig. 24(a)).²²⁶ This synergistic interaction significantly enhanced the photocatalytic performance, with the 14% Cu_{2-x}Se/ZnSe composite exhibiting superior activity compared to other formulations. Under identical conditions, the individual components ZnSe and Cu_{2-x}Se displayed relatively low Cr(vi) removal efficiencies of 19% and 56%, respectively, after 140 min of irradiation. Notably, the 14% Cu_{2-x}Se/ZnSe heterostructure exhibited a marked enhancement in photocatalytic activity, reaching a Cr(vi) reduction efficiency of 82% under identical experimental conditions (Fig. 24(b) and (c)). Further, Qiu *et al.* successfully fabricated ZnS/ZnSe/MoSe₂

(ZZM) nanocomposites incorporating dual type-II heterojunctions through a combination of solvothermal synthesis and ion exchange techniques, for the first time.²²¹ The Cr(vi) reduction performance of the ZZM photocatalysts was assessed under visible light illumination, achieving a Cr(vi) removal rate of 96%. The improved photocatalytic activity can be assigned to the dual heterostructures, which effectively promoted the separation and migration of photogenerated charge carriers. Meanwhile, the extended light response range and the increased specific surface area also contribute to the improvement of the photocatalytic efficiency. A comparative overview of Cr(vi) photoreduction using various ZnSe-based photocatalysts is presented in Table 4.

6.3. Reduction of CO₂

As modern lifestyles progress, energy consumption is expected to reach 25–27 TW, surpassing 80% of available fossil fuel reserves. This heavy reliance will deplete resources and emit large amounts of CO₂, disrupting ecological carbon balance.²²⁸ The increasing emissions are causing severe environmental issues, like melting polar ice caps and rising sea levels. To counter this, researchers are working on capturing and converting CO₂ into useful fuels. Carbon capture and storage (CCS) methods offer a promising solution, including the catalytic hydrogenation of CO₂ into compounds like formate/formic acid, methanol or dimethyl ether.²²⁹ While significant efforts have gone into developing heterogeneous electrocatalysts to valorize CO₂, achieving efficient and selective electroreduction remains challenging due to high overpotentials and the formation of multiple intermediates.²³⁰ In contrast, photoreduction processes present a promising alternative for improving selectivity and efficiency. Extensive research on photocatalysts has led to advanced strategies for CO₂ photoreduction, with early studies using TiO₂ semiconductors in aqueous suspension successfully producing formaldehyde, formic acid, methanol, and methane.²³¹

Various materials have been explored for CO₂ photoreduction, with numerous novel materials being thoroughly investigated.^{41–43} Among these, zinc chalcogenide-based catalysts stand out as promising candidates for CO₂ photoreduction. Zinc chalcogenides, particularly ZnSe, are promising for CO₂ photoreduction due to their visible-light responsiveness, with bandgaps of 2.7 eV.⁴⁴ Unlike ZnO and ZnS, which require UV light, these materials have conduction band potentials negative enough to reduce CO₂ efficiently, matching the redox potentials of typical CO₂ reduction products (–0.24 to –0.61 V *vs.* NHE).²³² Although ZnSe



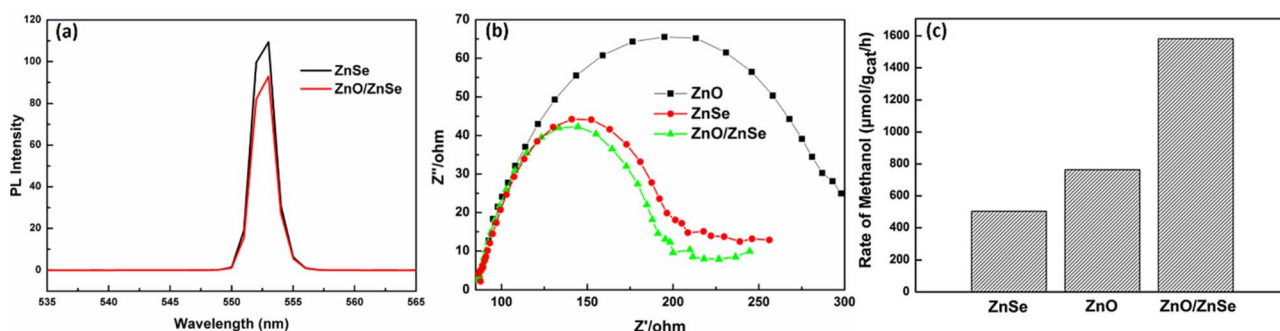


Fig. 25 (a) The PL spectra for both pure ZnSe and the 3 wt% ZnO/ZnSe composite, (b) EIS analysis of ZnO, ZnSe, and 3 wt% ZnO/ZnSe composite electrodes, and (c) the photocatalytic reduction of CO₂ to methanol using pure ZnO, ZnSe, and 3 wt% ZnO/ZnSe composite materials (reproduced from ref. 233). "This figure has been reproduced from ref. 233 with permission from Elsevier, copyright 2018".

demonstrates promising potential for CO₂ photocatalytic reduction, its overall photocatalytic efficiency remains low because of rapid electron-hole recombination. This recombination process limits the availability of charge carriers needed for effective CO₂ reduction, thereby hindering performance. To overcome this limitation and enhance its photocatalytic activity, modifications to the pure ZnSe structure are essential, such as preparation of heterojunction, defects, and morphology, allowing for modulation of their photocatalytic performance.^{129,233} For instance, in 2018, Zhang *et al.* synthesized ZnO/ZnSe composites *via* a solvothermal

technique, enabling the photocatalytic reduction of CO₂ into methanol.²³³ The PL spectra showed that the 3 wt% ZnO/ZnSe composite has the highest electron-hole separation efficiency, suppressing recombination and maximizing methanol production (Fig. 25(a)). The EIS Nyquist plot in Fig. 25(b), with its smallest arc size for the 3 wt% ZnO/ZnSe composite, confirms enhanced charge separation and electron transport, supporting the PL results. As depicted in Fig. 25(c), the 3 wt% ZnO/ZnSe nanohybrid demonstrated a CO₂ reduction rate to methanol of 1581.82 μmol g_{cat}⁻¹ h⁻¹, which is notably higher than the 503.88 μmol g_{cat}⁻¹ h⁻¹ and

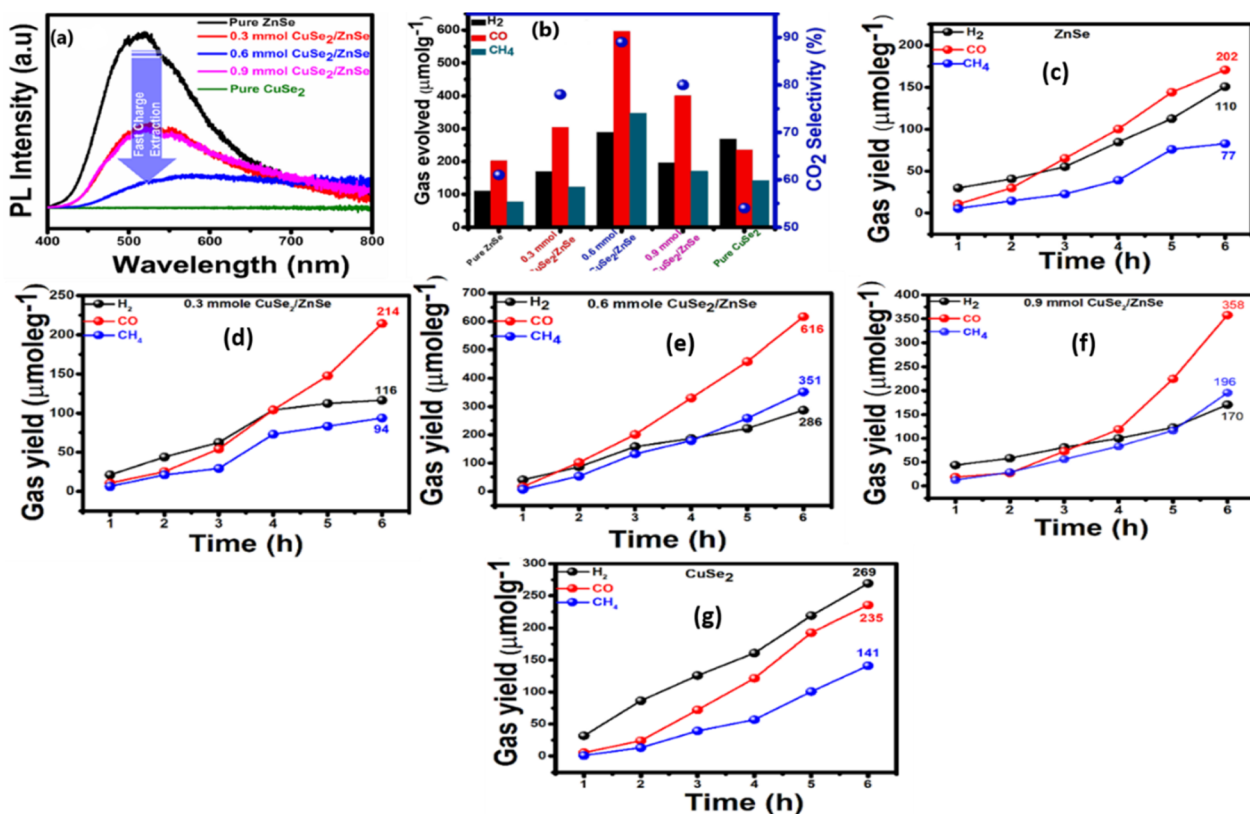


Fig. 26 (a) PL spectra, and (b) CO₂ photoreduction activities of pure ZnSe, 0.3 mmol CuSe₂/ZnSe, 0.6 mmol CuSe₂/ZnSe, 0.9 mmol CuSe₂/ZnSe, and pure CuSe₂; photoreduction of CO₂ by (c) pure ZnSe, (d) 0.3 mmol CuSe₂/ZnSe, (e) 0.6 mmol CuSe₂/ZnSe, (f) 0.9 mmol CuSe₂/ZnSe, and (g) pure CuSe₂ (reproduced from ref. 234). "This figure has been reproduced from ref. 234 with permission from Elsevier, copyright 2024".

763.9 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ observed for pristine ZnSe and ZnO, respectively.

Recently, Z-scheme $\text{CuSe}_2/\text{ZnSe}$ heterostructures were synthesized through a straightforward hydrothermal approach for the reduction of CO_2 photocatalytically under UV-visible light exposure, using different concentrations of copper(II) acetate hydrate (0.30 mmol, 0.6 mmol, and 0.9 mmol).²³⁴ The PL spectra, portrayed in Fig. 26(a), shows that all the composite photocatalysts exhibit reduced emission intensities than the pure ZnSe. The 0.6 mmol $\text{CuSe}_2/\text{ZnSe}$ photocatalyst exhibits the weakest intensity, indicating an elevated minimization in charge recombination rate and enhanced charge separation. Pure CuSe_2 , however, shows no photoemission, likely due to minimal charge carrier generation.

Fig. 26(b) shows the CO_2 photoreduction activities of the prepared photocatalysts. Pure ZnSe produced 202 $\mu\text{mol per g CO}$, 77 $\mu\text{mol per g CH}_4$, and 110 $\mu\text{mol per g H}_2$. Incorporating CuSe_2 as a co-catalyst significantly enhanced the activity, with the 0.6 mmol $\text{CuSe}_2/\text{ZnSe}$ heterostructure showing the best photocatalytic efficiency. As shown in Fig. 26(e), the photocatalytic yields of CO, CH_4 , and H_2 for 0.6 mmol $\text{CuSe}_2/\text{ZnSe}$ reached 616, 351, and 286 $\mu\text{mol g}^{-1}$ after 6 hours of irradiation. These values surpass those of pure ZnSe, 0.3 mmol $\text{CuSe}_2/\text{ZnSe}$, 0.9 mmol $\text{CuSe}_2/\text{ZnSe}$, and CuSe_2 , as shown in Fig. 26(c–g).²³⁴

6.4. Gas sensing with ZnSe-based sensors

Monitoring hazardous gases is vital not only for environmental protection but also for industrial safety and regulatory compliance. Recent advances in gas sensor technology have focused on detecting harmful species such as CO, NO_2 , and NH_3 which are widely emitted from vehicles, factories, and household materials.

NO_2 is a prominent air pollutant generated from common combustion processes, including vehicular exhaust, industrial operations, and domestic heating systems. Its detrimental impact on environmental and human health has intensified the need for efficient detection technologies.²³⁵ In this context, chemiresistive sensors have been extensively investigated to meet this need, with research focusing on optimizing their response characteristics, including enhanced selectivity, faster response times, and improved operational stability. These developments are essential to creating more effective tools for monitoring air quality.²³⁶ Despite these advancements, studies on ZnSe-based sensors remain limited. Moreover, the majority of reported ZnSe gas sensors require elevated operating temperatures, which restricts their use in low-energy applications. The performance of ZnSe nanowires in detecting NO_2 were assessed using interconnected networked ZnSe nanowire sensor system.²³⁷ The study revealed that ZnSe could serve as an effective sensing material at room temperature. When exposed to NO_2 concentrations from 50 ppb to 5 ppm, the sensor demonstrated response rates of 101–102% in dark conditions and significantly higher responses of 113–234% under UV light. The response of ZnSe nanowires to 5 ppm NO_2 significantly increased from 102% to 234% as the intensity of UV illumination rose from 0 to 1.2 mW cm^{-2} . Notably, the sensing performance of ZnSe nanowires was either surpassed or matched that of traditional metal oxide semiconductors, which typically

require elevated NO_2 concentrations and higher operating temperatures to achieve similar results. Liu *et al.* reported that a mesoporous ZnSe/ZnO heterojunction-based sensor exhibited a significantly enhanced response, about 7.3 times greater than that of pristine ZnO and ZnSe sensors, when detecting 8 ppm of NO_2 at 200 $^\circ\text{C}$.³⁹ The enhanced selectivity of the sensor toward NO_2 can be primarily ascribed to its strong molecular polarity, which facilitates more favourable interactions at the heterojunction interface compared to less polar VOCs. Furthermore, the operation at a moderate temperature of 200 $^\circ\text{C}$ favours the presence of less reactive chemisorbed O^- species, which are less likely to interact with VOCs. This contrasts with conventional ZnO-based sensors operated at over 300 $^\circ\text{C}$, where more reactive O^{2-} species dominate the surface, increasing cross-sensitivity to various gases and reducing selectivity. In another study, Liu *et al.* developed a ZnSe/ SnO_2 -based sensor that effectively detected NO_2 at concentrations as low as 2.4 ppm.²³⁸ The hybrid sensor demonstrated a markedly enhanced sensing performance, delivering a response nearly 6.94 times greater than that of pure SnO_2 . In contrast, the ZnSe sensor exhibited negligible sensitivity under the same operating temperature of 160 $^\circ\text{C}$.

Recently, Abimaheshwari *et al.* fabricated n-ZnSe/p-PANI hybrid using a straightforward hydrothermal method, followed by an evaluation of their NO_2 gas sensing capabilities.²³⁹ While pristine ZnSe required an elevated temperature of 100 $^\circ\text{C}$ to exhibit a sensing response, the ZnSe/PANI composites showed significantly enhanced performance at much lower temperature (30 $^\circ\text{C}$). Among the various formulations, the 20 wt% composite (denoted as ZnSe-P2) demonstrated an outstanding maximum response of 77% at a remarkably low temperature of 30 $^\circ\text{C}$, whereas ZnSe-P1 and ZnSe-P3 exhibited considerably lower responses of 25% and 20%, respectively, under the same conditions. Moreover, at an operating temperature of 30 $^\circ\text{C}$, the sensor recorded a response time (T_{res}) of 112 s and a recovery time (T_{rec}) of 648 s, at an operating temperature of 30 $^\circ\text{C}$. The enhanced sensing capability of the fabricated sensor is primarily attributed to the formation of a depletion region at the ZnSe/PANI interface, which facilitates efficient charge transfer and provides a greater number of active sites for gas interaction. Factors such as the operating temperature, composite composition, and nature of the target gas play crucial roles in determining the overall sensing performance. To determine the most effective operating temperature for the developed sensor, a temperature-dependent sensing study was carried out at 30 $^\circ\text{C}$, 50 $^\circ\text{C}$, and 100 $^\circ\text{C}$ using 20 ppm of NO_2 gas, as illustrated in Fig. 27(a). Pure ZnSe demonstrated its highest response of 9.4% at 100 $^\circ\text{C}$, indicating a preference for elevated temperatures. In contrast, the composite sensors achieved their peak performance at 30 $^\circ\text{C}$, highlighting a significant reduction in optimal operating temperature due to the incorporation of PANI. As the temperature exceeded the optimal point, the sensing responses of the composites began to decline. This decrease is attributed to the dominance of desorption over adsorption at elevated temperatures. Notably, incorporating PANI into the ZnSe matrix significantly enhanced the gas sensing response compared to pure ZnSe, indicating that the improved interfacial charge transfer between ZnSe and PANI



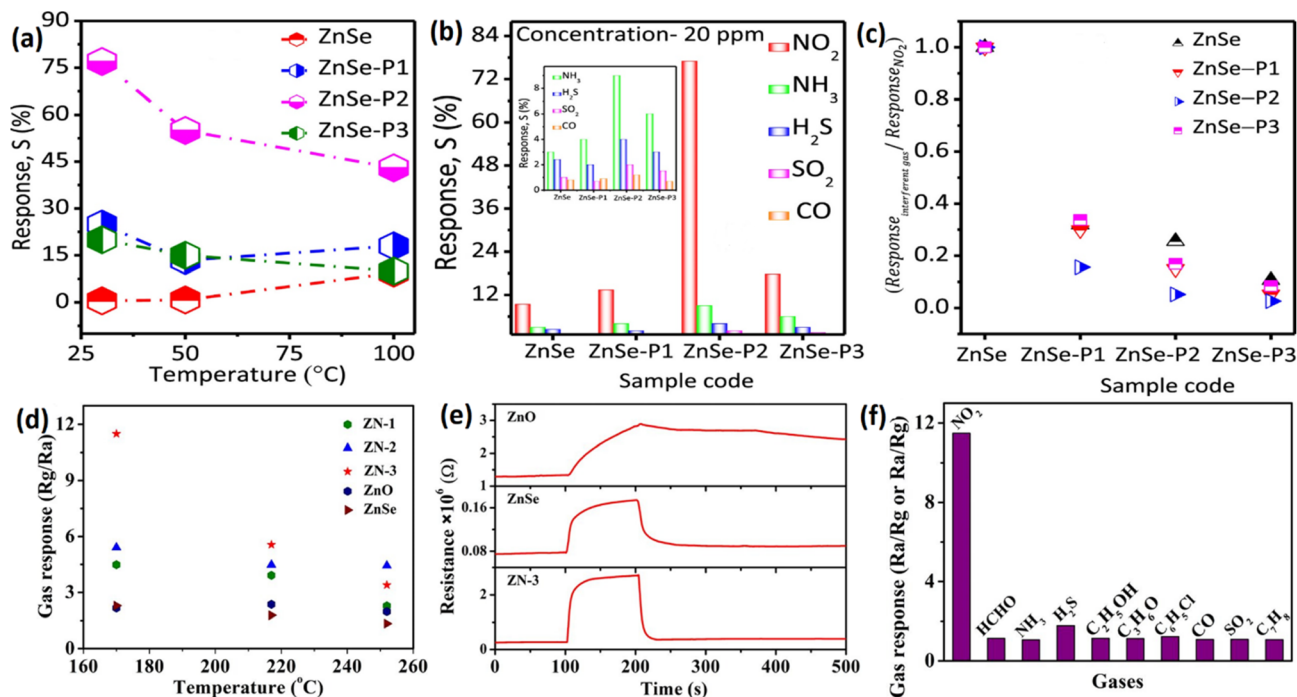


Fig. 27 (a) Sensing response as a function of operating temperature, (b) selectivity, and (c) selectivity factor of the fabricated sensors (reproduced from ref. 239); (d) comparative NO_2 sensing performance of ZnO–ZnSe variants (ZN-1, ZN-2, ZN-3) alongside pristine ZnO and ZnSe across varying temperatures, (e) response performance of ZnO, ZnSe and ZN-3 sensors toward 10 ppm NO_2 at 170 °C, and (f) response profiles of the ZN-3 sensor toward NO_2 and other common gases (reproduced from ref. 240). "This figure has been reproduced from ref. 239 with permission from Elsevier, copyright 2024". "This figure has been reproduced from ref. 240 with permission from Elsevier, copyright 2023".

contributes to the reduced optimal operating temperature of 30 °C. However, an excessive amount of PANI led to a decline in sensing performance, due to the aggregation of ZnSe particles on the surface of the PANI sheets, which decreases the effective surface area and limits the number of accessible active sites for gas adsorption, ultimately impairing sensor efficiency. To evaluate selectivity, sensing measurements were performed against various gases, including NO_2 , NH_3 , H_2S , SO_2 , and CO . As illustrated in Fig. 27(b) and (c), all sensors demonstrated the highest response toward NO_2 , confirming strong selectivity. This selective behaviour varies depending on the nature of the target gas and is governed by factors such as surface reaction dynamics, kinetic energy, and ionization energy of the analyte. NO_2 , with a relatively small kinetic diameter of 310 pm and a lower ionization energy of 9.586 eV, interacts more readily with the sensing materials, accounting for its preferential detection over other gases.

In another study, Gao *et al.* utilized a one-step, template-free hydrothermal synthesis approach to prepare ZnO–ZnSe hollow nanospheres rich in nano-heterojunctions.²⁴⁰ The gas sensing responses of ZnO, ZnSe, and ZnO–ZnSe composites were evaluated toward 10 ppm NO_2 at various operating temperatures, demonstrating optimal sensing performance at 170 °C (Fig. 27(d)). As illustrated in Fig. 27(e), the transient response profiles showed a markedly enhanced response for ZN-3, approximately 5.32 and 5.02 times greater than that of pure ZnO and ZnSe, respectively. Fig. 27(f) illustrates the selectivity analysis of the ZN-3 sensor toward NO_2 and a range of potential interfering gases. At 170 °C,

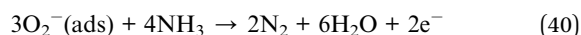
the ZnO–ZnSe composite sensor exhibited a high response of 11.49 to 10 ppm NO_2 , while significantly lower responses were recorded for formaldehyde (1.15), NH_3 (1.07), H_2S (1.79), ethanol (1.14), acetone (1.13), chlorobenzene (1.23), CO (1.09), SO_2 (1.09), and toluene (1.08) at 100 ppm each. At 10 ppm, the sensor achieved a response of 11.49 with a response time of 100 s and a recovery time of 48 s. Notably, the sensor demonstrated a detection limit as low as 100 ppb.

Besides NO_2 , ammonia (NH_3) is another widespread air pollutant, primarily originating from agricultural practices, animal husbandry, and industrial processes.²⁴¹ Exposure to high concentrations of NH_3 —either acute or prolonged—can lead to serious health complications, including respiratory distress, organ damage, and in severe cases, death. Even at lower concentrations, sustained exposure may contribute to chronic inflammatory conditions.²⁴² Therefore, developing a sensor capable of detecting ammonia at parts-per-million (ppm) levels is of critical importance. Recently, Thayil and Parne fabricated ZnSe nanostructures exhibiting spherical and flower-like morphologies by adjusting the concentration of ethylenediaminetetraacetic acid (EDTA).²⁴³ These nanostructures were utilized for NH_3 gas sensing at room temperature for the first time. Their study demonstrated that increased EDTA content promoted the formation of flower-like structures, which offer enhanced surface area, an essential factor for improving gas sensing efficiency. The improved sensing behaviour of ZnSe prepared with 2 g of EDTA is largely credited to its flower-like structure, which increases the active surface area, enhancing

gas adsorption. In the presence of air, oxygen molecules adsorb onto the ZnSe surface and capture electrons, forming ionized oxygen species (O_2^-), as described in the following reaction steps:



when NH_3 molecules come into contact with the ZnSe surface, they react with the adsorbed oxygen species, leading to electron transfer back into the ZnSe material, as illustrated in the following reaction:



The restoration of electrons to the ZnSe surface results in a measurable change in resistance, serving as the detection signal.

On the other hand, acetone is a prevalent volatile organic compound that plays a significant role in human metabolism. Monitoring acetone levels has become crucial for physicians to assess patient health. Typically, acetone concentrations in the breath of healthy adults are below 0.8 ppm, whereas in diabetic patients, these levels can rise to around 1.8 ppm due to irregular glucose metabolism.^{245,246} Therefore, accurate detection of acetone gas, particularly around the 1 ppm level, can help effectively prevent potential risks associated with acetone accumulation and enable real-time monitoring of human health. In 2022, Zhu *et al.* developed an oxygen-vacancy-rich ZnO/ZnSe heterojunction by embedding ZnSe into ZIF-8-derived ZnO, followed by an annealing process.²⁴⁴ The resulting material demonstrated superior acetone sensing capabilities, even at low concentrations. To determine the optimal operating temperature for gas sensitivity, the sensor's response to 50 ppm acetone was systematically evaluated across varying temperatures. As depicted in Fig. 28(a), the ZnO/ZnSe-2 and

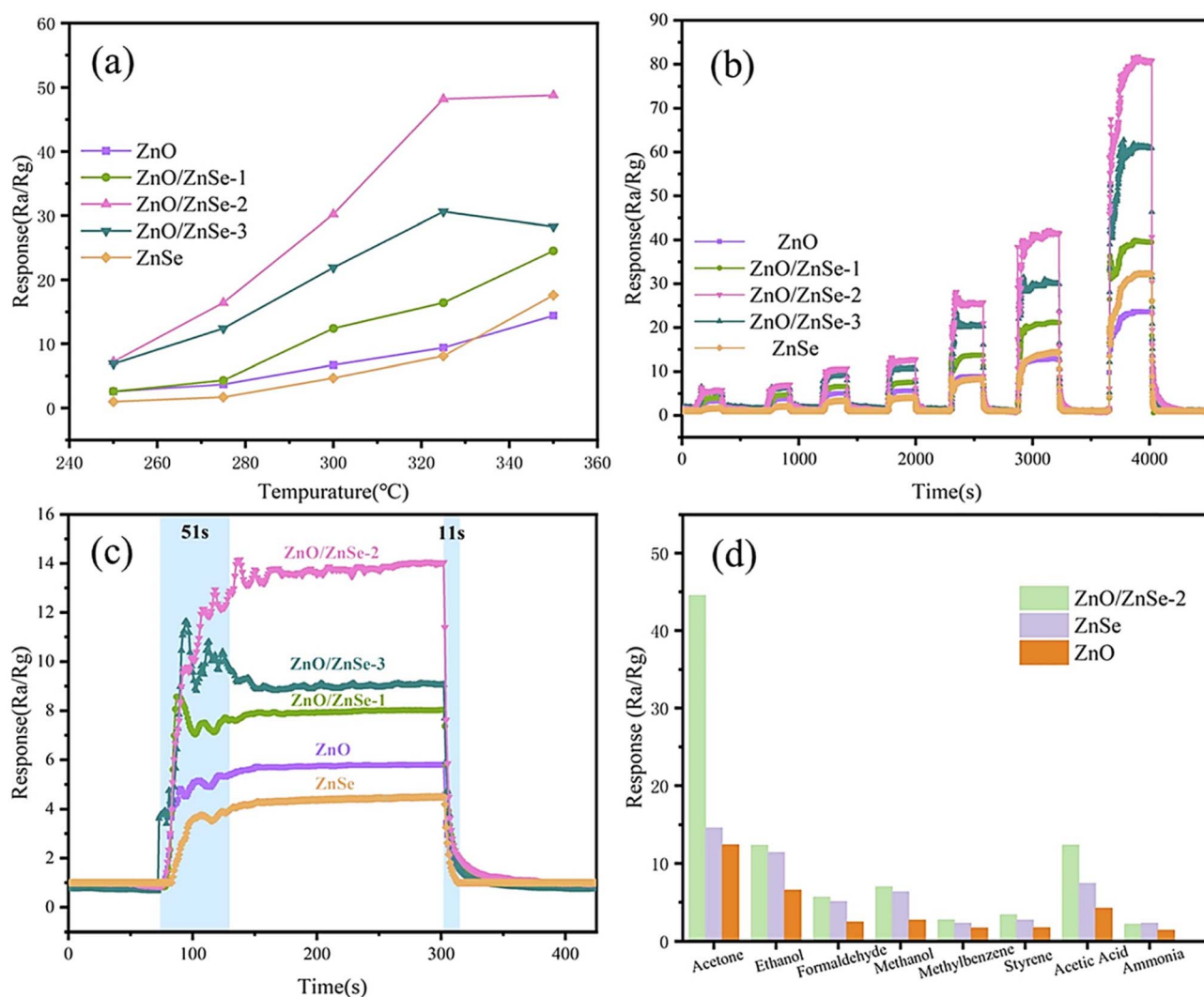


Fig. 28 (a) Sensor responses to 50 ppm acetone as a function of operating temperature, (b) real-time response curves at 325 °C for acetone concentrations ranging from 1–100 ppm, (c) dynamic response profile towards 10 ppm acetone at 325 °C, and (d) selectivity profiles of sensors toward various interfering gases at 325 °C (reproduced from ref. 244). "This figure has been reproduced from ref. 244 with permission from Elsevier, copyright 2022".



ZnO/ZnSe-3 composites demonstrated markedly superior responses around 325 °C compared to pristine ZnO and ZnSe. This enhancement confirms that the heterojunction composites significantly improve sensing performance while enabling operation at a comparatively lower temperature. To further evaluate the influence of composition on acetone sensing, dynamic response measurements were carried out for ZnO, ZnSe, and the three composite variants over a concentration range of 1–100 ppm. As shown in Fig. 28(b), ZnO/ZnSe-2 demonstrated exceptional sensitivity, with response values of 5.8, 7.2, 10.7, 12.7, 25.6, 42.3, and 80.8 corresponding to acetone concentrations of 1, 2, 5, 10, 20, 50, and 100 ppm, respectively. Notably, the composite exhibited excellent low-concentration detection, achieving a substantial response of 5.8 even at 1 ppm, underscoring its strong potential for trace-level acetone sensing in practical applications. Furthermore, the ZnO/ZnSe-2 composite exhibited rapid sensing dynamics, with a notably short response time of 51 s and an even faster recovery time of approximately 11 s, highlighting its excellent reversibility and responsiveness (Fig. 28(c)). To further examine its selectivity, the sensor was exposed to various common interfering gases (each at 50 ppm) under a constant operating temperature of 325 °C. As illustrated in Fig. 28(d), the ZnO/ZnSe-2 composite showed a significantly higher response to acetone compared to other gases, underscoring its strong selectivity and potential for reliable acetone detection in complex environmental conditions.

Apart from the above mentioned gases, other gases such as CO₂ and SO₂ are hazardous with well-documented adverse impacts on human health.²⁴⁷ CO₂, a major greenhouse gas, plays a critical role in accelerating global climate change through enhanced atmospheric warming.²⁴⁸ In contrast, SO₂ is a pungent, corrosive, and toxic gas primarily emitted from various manufacturing processes.²⁴⁹ Inhalation of SO₂ can lead to a range of serious health issues, including respiratory disorders, cardiovascular complications, and acute breathing difficulties. In a recent study, Khalil *et al.* explored the gas-sensing capabilities of ZnSe nanocages toward CO₂ and SO₂ using DFT simulations.⁴⁰ The interaction energies confirm that all isomeric configurations are thermodynamically stable, with adsorption processes characterized as exothermic. The study revealed distinct adsorption behaviours: SO₂ molecules undergo physisorption on the ZnSe nanocage surface, while CO₂ molecules exhibit chemisorption. Among the investigated configurations, the CO₂@ZnSe-A isomer was identified as the most stable, exhibiting the highest adsorption affinity toward CO₂ with a substantial interaction energy of −149.8 kcal mol^{−1}. This highlights the superior adsorption capability of the ZnSe nanocage compared to previously reported ZnSe nanotube structures.

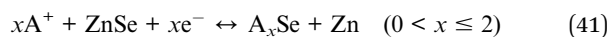
6.5. Energy storage

The rapid growth of the global economy has led to an increasing demand for energy, which is still largely met by fossil fuels such as oil, natural gas, and coal. However, these non-renewable resources are being depleted at an alarming rate. Moreover,

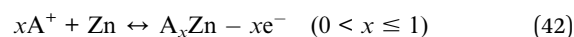
their continued use significantly contributes to environmental degradation and climate change. As a result, the shift toward sustainable and renewable energy sources has become a critical global priority.²⁵⁰ With the advancement of innovative concepts and deeper understanding in material physics and chemistry, significant progress has been achieved in cutting-edge renewable energy storage technologies, including fuel cells, batteries, and supercapacitors. Furthermore, the rising demand for electric vehicles has positioned energy storage systems, particularly lithium-ion batteries (LIBs), at the forefront of technological research and development.^{251,252} In this perspective, ZnSe has emerged as a promising material for energy storage owing to its excellent electrochemical characteristics, making it suitable for applications in supercapacitors and Li-ion batteries. As a potential high-capacity anode material for advanced Li-ion batteries, a thorough understanding of its electrochemical reaction pathways is crucial for designing efficient electrodes and enhancing overall performance. Additionally, the weaker M–S, M–Se, and M–Te bonds compared to M–O bonds in oxides enhance the kinetics of conversion reactions during charge/discharge cycles.²⁵³ *Ex situ* X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) studies have shown that during lithiation, ZnS undergoes conversion into LiZn and Li₂S, while during delithiation, it only partially reverts back to ZnS, leaving residual traces of elemental Zn and S.^{254,255} In the case of ZnSe, its lithiation–delithiation and sodiation–desodiation behaviours closely resemble those of ZnS and ZnO, indicating similar conversion-based electrochemical mechanisms.^{256,257} However, the presence of selenium enables a more complete conversion reaction during charging, with lower voltage plateau (~1.3 V and ~1.0 V), attributed to its narrower band gap, reduced bond strength, and lower electronegativity.^{258,259}

The electrochemical charge/discharge mechanism for ZnSe can be represented by the following reactions:

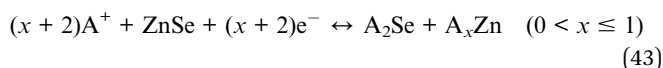
Intercalation and conversion reaction



Alloying reaction



Overall reaction



where, A = Li, Na, K.

6.5.1. Anode for Li ion batteries. Beyond its extensive use in the semiconductor industry, ZnSe has attracted significant attention for energy storage applications due to its high theoretical capacity (557 mA h g^{−1}) and superior electrical conductivity.²⁵⁸ To overcome performance limitations, extensive efforts have been directed towards engineering ZnSe nanostructures and hybridizing it with conductive carbon materials such as carbon nanoparticles, porous carbon, graphene, carbon nanotubes, and carbon nanofibers. These enhancements have been



achieved using a variety of synthesis routes, including hydrothermal synthesis, pulsed laser deposition (PLD), *in situ* pyrolysis or selenization, and solid-state or mechanical milling approaches.²⁵³ For example, using PLD, Xue *et al.* prepared highly crystalline ZnSe thin films and pioneered the investigation of its lithium storage mechanism through *ex situ* XRD and *in situ* absorbance spectroscopy.²⁶⁰ Their analysis confirmed the reversible generation and decomposition of LiZn and Li₂Se, suggesting that both alloying/dealloying and partial selenidation/reduction of nanoscale Zn take place during the lithiation process. Despite showing better cycling performance than the Zn–Se/Li system (Zn–Se is a simple Zn and Se mixture), the ZnSe/Li cell suffered from notable irreversible capacity loss and poor cycle life, likely due to the high crystallinity of the zinc alloy phase and sluggish electrochemical kinetics. ZnSe and its composites, owing to their intrinsically low potential plateau, are well-suited for operation within a narrow voltage window (*e.g.*, 0–2.0 V), which can enhance the overall energy density and voltage efficiency in full-cell configurations. For instance, a ZnSe/C nanocomposite fabricated *via* a simple solid-state synthesis exhibited excellent cycling stability, retaining a very stable capacity retention of *ca.* 437 mA h g^{−1} over 300 cycles at a current rate of 100 mA g^{−1}. In contrast, when cycled over a wider range of 0–3.0 V, a higher capacity of around 705 mA h g^{−1} was achieved.²⁵⁸

Graphene, as a single-layer carbon material, offers exceptional advantages, such as high electrical conductivity, mechanical flexibility, large surface area, and structural robustness-making it an ideal support matrix for TMCs to enhance their electrochemical performance.²⁶¹ As a notable example, Zhang *et al.* synthesized polyhedral ZnSe/reduced graphene oxide (rGO) nanocomposites (ZnSe@rGO) *via* a simple one-pot hydrothermal method, where irregularly shaped ZnSe nanoparticles (~40 nm) were uniformly anchored on graphene nanosheets.²⁶² When employed as anodes for lithium-ion batteries, these ZnSe/rGO nanocomposites demonstrated significantly enhanced electrochemical performance compared to pure ZnSe, attributed to the synergistic interaction between ZnSe and rGO. The composite delivered a high reversible capacity of 876 mA h g^{−1} at 100 mA g^{−1}, along with remarkable cycling stability and rate capability-retaining 778 mA h g^{−1} after 400 cycles at 1000 mA g^{−1}. In addition, the distinctive structure of the ZnSe/rGO nanocomposite plays a crucial role in improving performance by inhibiting ZnSe nanoparticle aggregation and preventing the restacking of graphene layers. The flexible graphene matrix serves as a conductive scaffold that facilitates rapid electron transport, buffers the volume changes of ZnSe and provides abundant accessible sites for lithium-ion storage. These synergistic effects result in enhanced electrochemical performance, highlighting the ZnSe/rGO

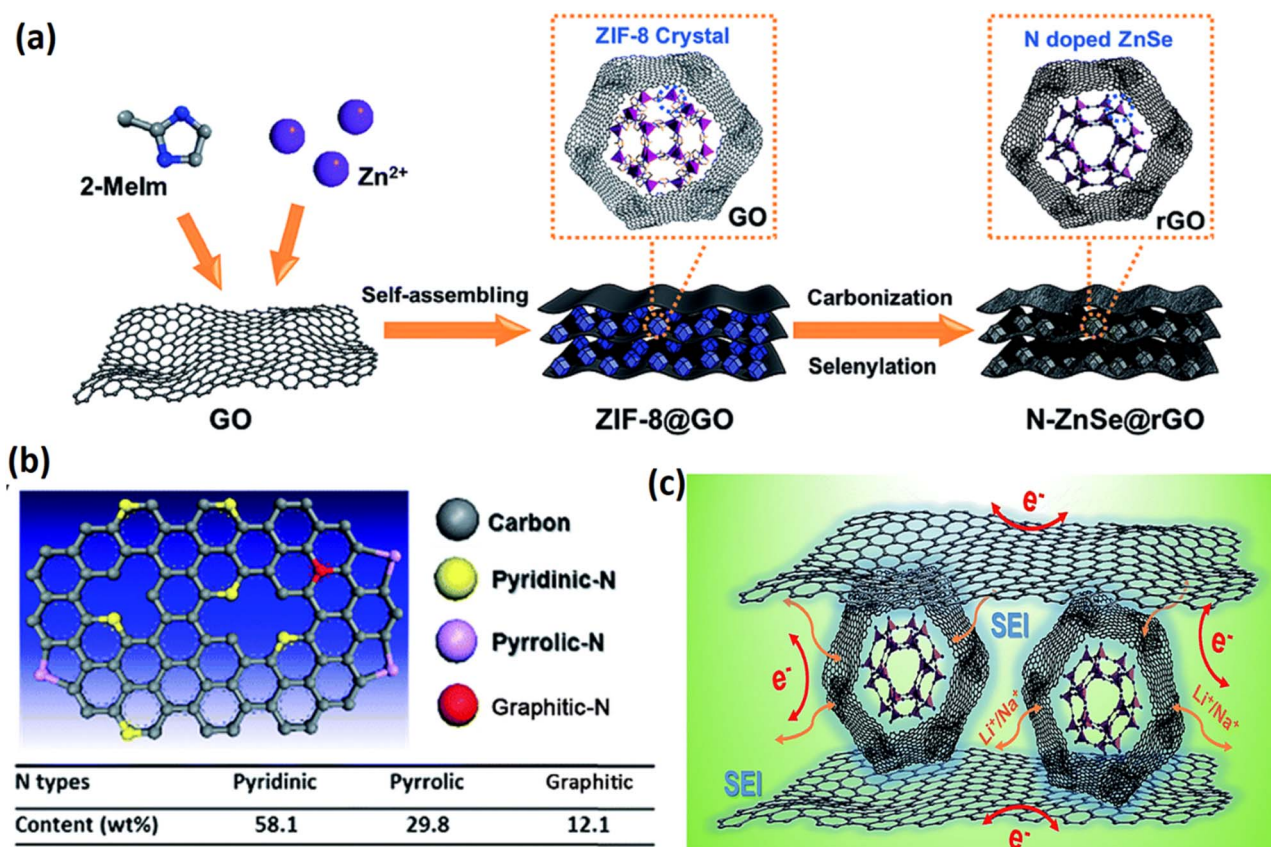


Fig. 29 (a) Schematic illustration of the preparation process of N-ZnSe@rGO, (b) graphical representation of the configurations and contents of three types of N in N-ZnSe@rGO, and (c) schematic illustration of the related mechanism of Li⁺/Na⁺ intercalation and extraction in the N-ZnSe@rGO electrode (reproduced from ref. 263).

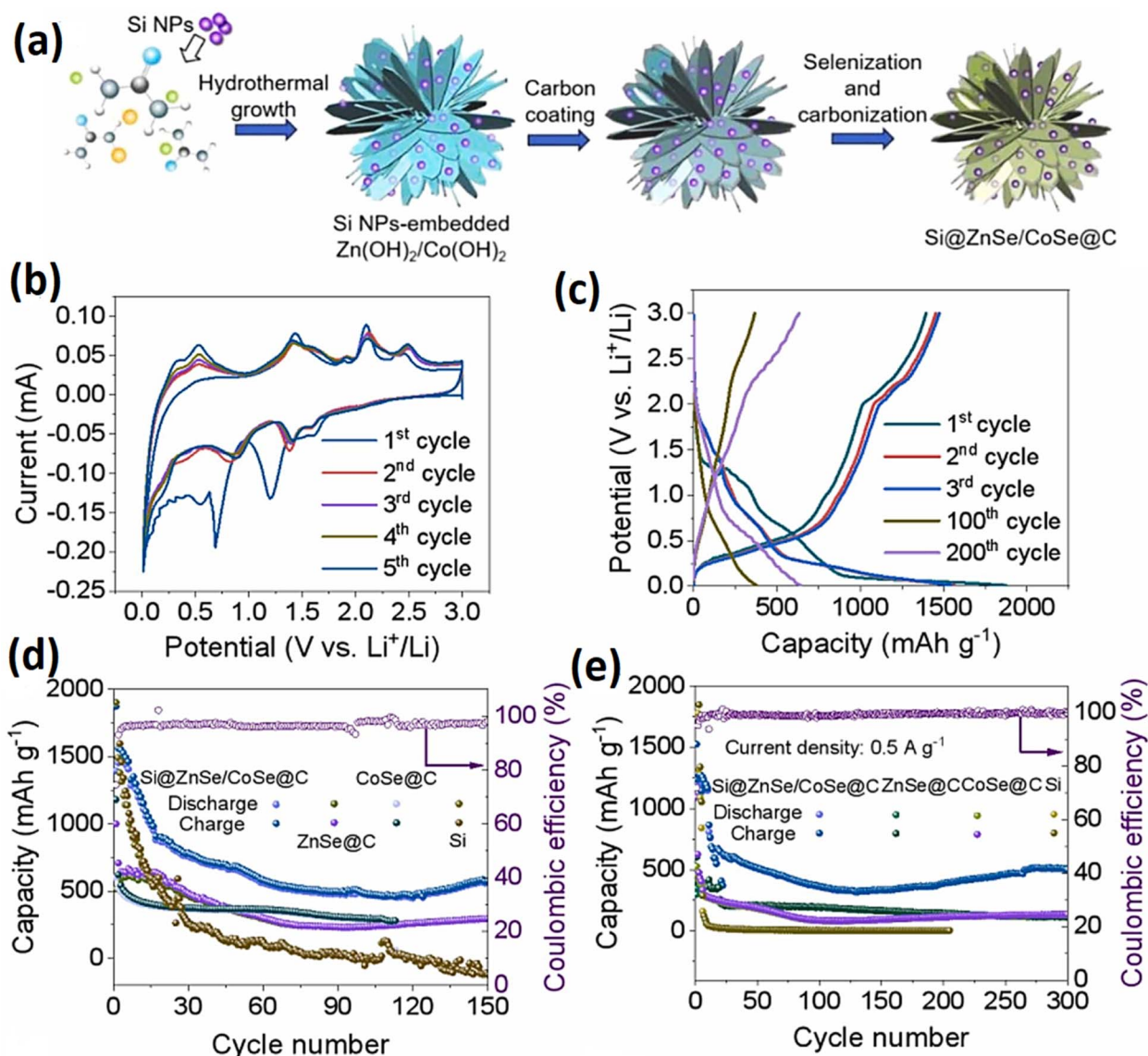


Fig. 30 (a) Illustration for the sample preparation, (b) CV profiles of Si@ZnSe/CoSe@C cycling at 0.1 mV s⁻¹, (c) charge–discharge profiles of Si@ZnSe/CoSe@C at 0.1 A g⁻¹, capacities of Si@ZnSe/CoSe@C, CoSe@C, ZnSe@C and Si at (d) 0.1 and (e) 0.5 A g⁻¹, anodes were pre-cycled at 0.1 A g⁻¹ for activation 10 cycles (reproduced from ref. 265). "This figure has been reproduced from ref. 265 with permission from Elsevier, copyright 2025".

nanocomposite as a strong candidate for high-performance anode materials in advanced lithium-ion batteries. Two years later, Liu *et al.* developed nitrogen-doped ZnSe (N-ZnSe) polyhedra encapsulated in reduced graphene oxide (rGO) composites, derived from ZIF-8 *via* a carbonization–selenylation process (Fig. 29).²⁶³ The optimized N-ZnSe@rGO composite demonstrated an exceptional capacity of 836 mA h g⁻¹ at 100 mA g⁻¹ and excellent long-term stability, retaining 464 mA h g⁻¹ at 2000 mA g⁻¹ after 1000 cycles when used as an anode in lithium-ion batteries. The N-doping of ZnSe increases the density of active sites and enhances electronic conductivity, while the rGO matrix offers a high surface area and conductive framework, facilitating charge transfer and preventing ZnSe pulverization and aggregation.

Again, Liu *et al.* synthesized nitrogen-doped carbon-encapsulated hollow ZnSe/CoSe₂ (ZnSe/CoSe₂@N-C) nanospheres through a straightforward solvothermal method followed by selenization and carbonization.²⁶⁴ The resulting nanospheres exhibited a multi-level nanoscale architecture, comprising a thin nitrogen-doped carbon shell (~12 nm) and hollow selenide cores formed by nanoscale subunits with rough surface features and abundant internal voids. The robust nitrogen-doped carbon shell, combined with the synergistic interaction between the dual metal ions (Zn and Co), significantly enhances both electron and ion transport, facilitating efficient lithium-ion insertion and extraction. As a result, the ZnSe/CoSe₂@N-C nanospheres exhibit a high reversible capacity of 1153 mA h g⁻¹ over 100 cycles at 100 mA g⁻¹ and

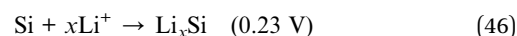
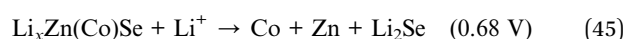
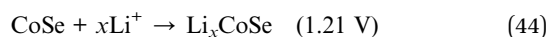
Table 5 Summary of the lithium storage performance of previously reported ZnSe-based materials

Composite	Current density (mA g ⁻¹)	Specific capacity (mA h g ⁻¹)	Cycle no.	Voltage region (V)	ICE (%)	Ref.
ZnSe/C	100	705	300	0–3	76	258
ZnSe@NC nanocubes	500	1167	500	0.01–3.0	68.8	266
ZnSe-rGO	100	876	50	0.01–3	58.6	262
	1000	778	400			
MOF-derived ZnSe/NC	1000	724.4	500	0.01–3.0	68.8	267
ZnSe ND@N-PC	600	1134	500	0.01–3.0	56.7	268
Spherical-like ZnSe	100	433	50	0.01–3.0	55.3	36
ZnSe/C hollow spheres	1000	574	800	0.01–3.0	73.9	269
	10 000	319	5000			
ZnSe-NC@CoSe ₂ -NC	200	718	600	0.005–3	67.6	270
3D ZnSe/CoSe ₂ -C composite	100/1000	807/700	100/500	0.01–3.0	69	271

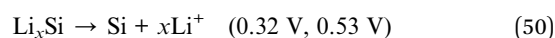
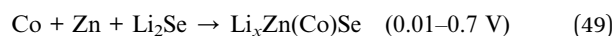
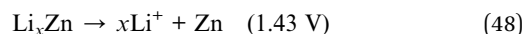
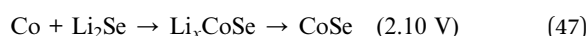
retain an impressive capacity of 966 mA h g⁻¹ after 500 cycles at a high current density of 2000 mA g⁻¹. Compared to other nitrogen-doped carbon architectures-such as hollow carbon spheres and mesoporous structures-these nanospheres demonstrate markedly superior cycling stability and capacity retention. Recently, an innovative strategy was introduced to improve the performance of lithium-ion battery anode by incorporating Si nanoparticles into a three-dimensional ZnSe/CoSe composite framework, which is further encapsulated within a carbon shell (Fig. 30(a)).²⁶⁵ In the initial scan of the cyclic voltammetry (CV) profile of the Si@ZnSe/CoSe@C composite, distinct cathodic peaks appear at 1.62, 1.21, and 0.68 V (Fig. 30(b)). The peak at 1.62 V corresponds to the initial insertion of Li⁺ ions into the composite matrix. The 1.21 V peak is attributed to the formation of Li_xZn(Co)Se and the solid electrolyte interphase (SEI) layer on the anode surface, while the 0.68 V peak is associated with the conversion reaction between Li_xZn(Co)Se and Li⁺, resulting in the generation of metallic Co, Zn, and Li₂Se. Additionally, a peak at 0.23 V is ascribed to the reduction of Si to form Li_xSi alloys. In the second scan, the cathodic peaks shift to 1.38 and 0.82 V, likely due to side reactions triggered by the initial lithiation/delithiation process. On the anodic side, a peak at 1.43 V corresponds to the multi-step dealloying of Li_xZn, while a broad peak centered at 2.10 V is indicative of the reversible selenization of Co, following the reaction: Co + Li₂Se → Li_xCoSe → CoSe. Additional peaks observed between 0.01–0.7 V are related to the electrochemical reactions among Co, Zn, and Li₂Se. Furthermore, the peaks at 0.32 and 0.53 V correspond to the transformation of Li_xSi alloys back to amorphous Si. The consistent overlap of CV curves in subsequent cycles reflects the high reversibility and stability of the electrochemical processes. Fig. 30(c) presents the cycling performance of the Si@ZnSe/CoSe@C anode at 0.1 A g⁻¹. During the initial cycle, distinct discharge plateaus appear at 0.73 and 1.31 V, while charge plateaus are observed at 2.09 and 1.36 V, consistent with the CV results. The first-cycle discharge capacity reaches 1874 mA h g⁻¹, with an initial coulombic efficiency (CE) of 74.4%. Notably, the rapid increase in CE over subsequent cycles suggests effective suppression of irreversible side reactions, minimized electrolyte decomposition, and the formation of a stable and protective SEI layer. As shown in

Fig. 30(d), the Si@ZnSe/CoSe@C anode delivers a stable specific capacity of 563 mA h g⁻¹ with a coulombic efficiency of 98.2% after 150 cycles at a current density of 0.1 A g⁻¹. Under a higher current density of 0.5 A g⁻¹, it maintains a capacity of 501 mA h g⁻¹ with an exceptional CE of 99.9% after 300 cycles (Fig. 30(e)). In contrast, ZnSe@C, CoSe@C, and pure Si electrodes exhibit significantly inferior cycling performance. The enhanced capacity and long-term stability of the Si@ZnSe/CoSe@C composite are attributed to the synergistic effect between the selenide phases and Si nanoparticles, as well as the unique 3D flower-like architecture. This robust structure effectively accommodates volume expansion during cycling by providing internal void spaces that buffer mechanical stress. The electrochemical reaction mechanisms involved in the cycling of the Si@ZnSe/CoSe@C anode are outlined below, and a comparative summary of the lithium storage performance of representative ZnSe-based materials is provided in Table 5.

Reduction process:



Oxidation process:



6.5.2. Anodes for sodium ion batteries. Sodium-ion batteries (SIBs) have emerged as highly promising candidates for large-scale energy storage systems. Transition metal chalcogenides (TMCs), known for their alloying and conversion reaction mechanisms, are extensively investigated as anode materials due to their high theoretical capacities and rich redox chemistry.²⁷² Among them, ZnSe has demonstrated notable



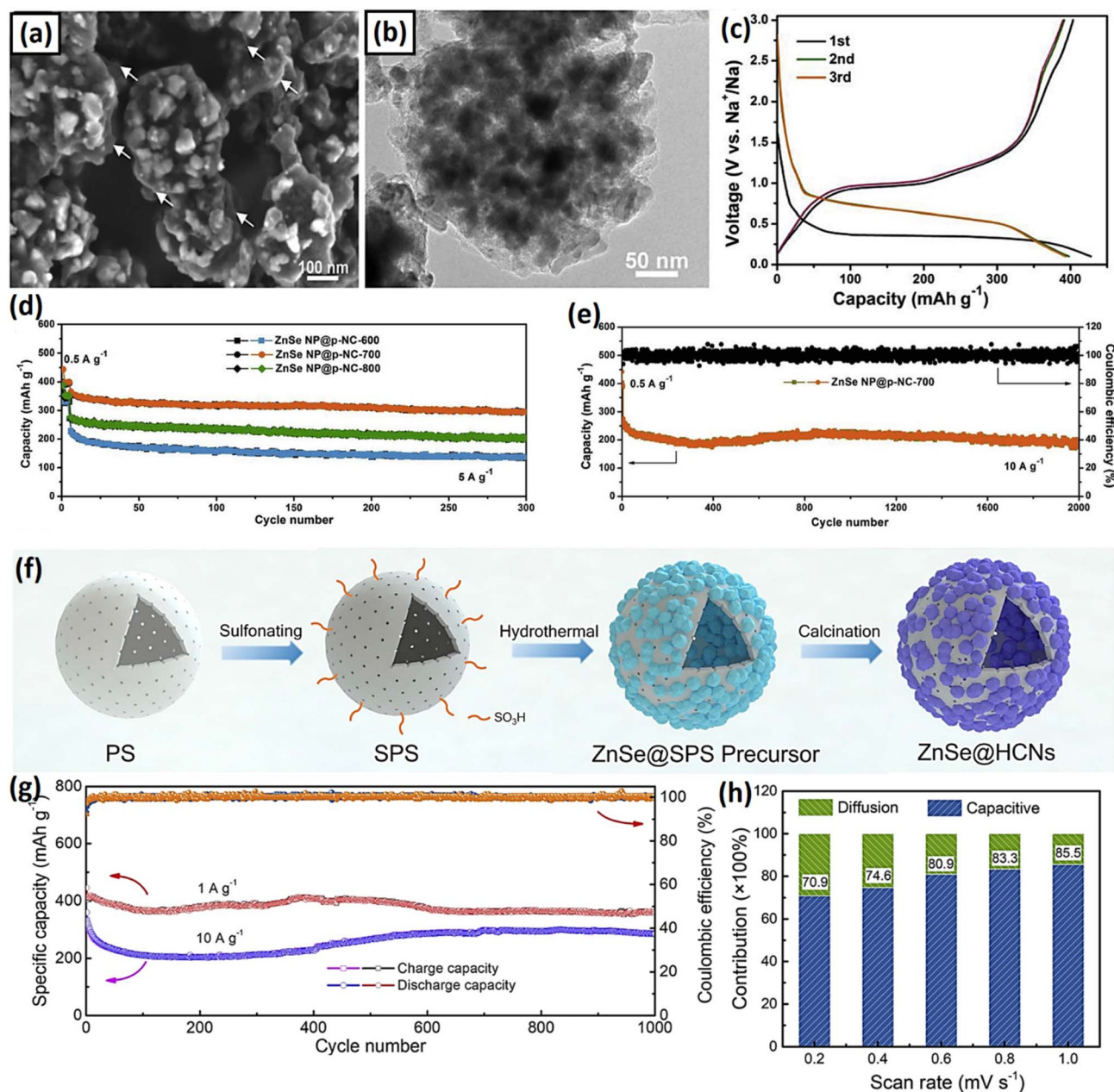


Fig. 31 (a) FESEM, and (b) TEM images of the synthesized ZnSe NP@p-NC-700, electrochemical performances: (c) GCD profiles of ZnSe NP@p-NC-700 at a current density of 0.5 A g⁻¹, (d and e) cycling performance of different ZnSe NP@p-NCs synthesized at varied temperatures at current densities of 5 and 10 A g⁻¹, respectively (reproduced from ref. 273); (f) schematic illustration of the formation of hybrid ZnSe@HCNs, electrochemical performance of ZnSe@HCNs: (g) cyclic stability at 1.0 and 10 A g⁻¹, and (h) percent of pseudocapacitive contribution at different scan rate (reproduced from ref. 274). "This figure has been reproduced from ref. 273 with permission from Elsevier, copyright 2019". "This figure has been reproduced from ref. 274 with permission from Elsevier, copyright 2019".

electrochemical activity as an anode material for SIBs, extending its potential beyond lithium-ion battery applications.²⁵³ For example, Li *et al.* synthesized a hierarchical hybrid material ZnSe nanoparticles intricately confined within a 3D porous nitrogen-doped graphitic carbon framework (ZnSe NP@pNC), using a self-templated *in situ* selenation reaction between Zn-based zeolitic imidazolate framework (ZIF-8) nanododecahedra and selenium powder (Fig. 31(a and b)).²⁷³

This "popcorn ball"-like architecture, with its tailored porosity and conductive carbon matrix, significantly enhances sodium-ion storage kinetics. The resulting ZnSe NP@pNC composite showcases remarkable electrochemical performance, including a high initial coulombic efficiency (94.3%), outstanding rate capability, and long-term cycling stability, delivering 294.2 mA h g⁻¹ after 300 cycles at 5 A g⁻¹ and retaining 181.7 mA h g⁻¹ even after 2000 cycles at 10 A g⁻¹ (Fig. 31(c-e)). The ZnSe NP@p-NC composites, featuring highly

Table 6 Summary of the Na-storage performance of previously reported ZnSe based materials

Type	Current density (mA g ⁻¹)	Specific capacity (mA h g ⁻¹)	Cycle no.	Voltage region (V)	ICE %	Ref.
ZnSe@C@rGO	500/5000	293/224	140/1000	0.01–3.0	68.1	275
3D hierarchical ZnSe/C	500/5000	434/285	500/1000	0.1–3.0	86.3	276
CoSe ₂ /ZnSe@NC nanobox	10 000	232/212	3000/10 000	0–3.0	71.7	278
ZnSe/Sb ₂ Se ₃ @NC	500/5000	438/295	120/250	0.01–3.0	90.5	279
ZnSe-NC@CoSe ₂ -NC	100	309	150	0.005–3.0	56.9	270
ZnSe-FeSe ₂ /rGO	50	363	100	0.01–3.0	76.9	280
Willow-leaf-like ZnSe@NC	200	71(107)	1500 (550)	0.01–3.0	51.3	281
ZnSe@PCNF (N-doped mesoporous carbon nanofibers)	500	270	1000	0.01–3.0	66	282
SnSe ₂ /ZnSe@PDA nanobox	100/1000	744/616	200/1000	0.1–3.0	71.6	283
Open ZnSe/C nanocages	50/500	318/189	50/1000	0.01–2.5	47.8	284

crystalline ZnSe with minimal lattice defects and well-regulated particle dispersion, exhibit significantly reduced ion diffusion resistance and superior electrochemical performance, particularly enhanced rate capability. Furthermore, the elevated ZnSe content and increased graphitization degree of the carbon

matrix synergistically contribute to improved electronic conductivity within the composite.

Designing ZnSe at the nanoscale and integrating it with carbon-based matrices have emerged as effective strategies for enhancing electrochemical performance. Men *et al.* reported that the ZnSe@C electrode promoted the formation of

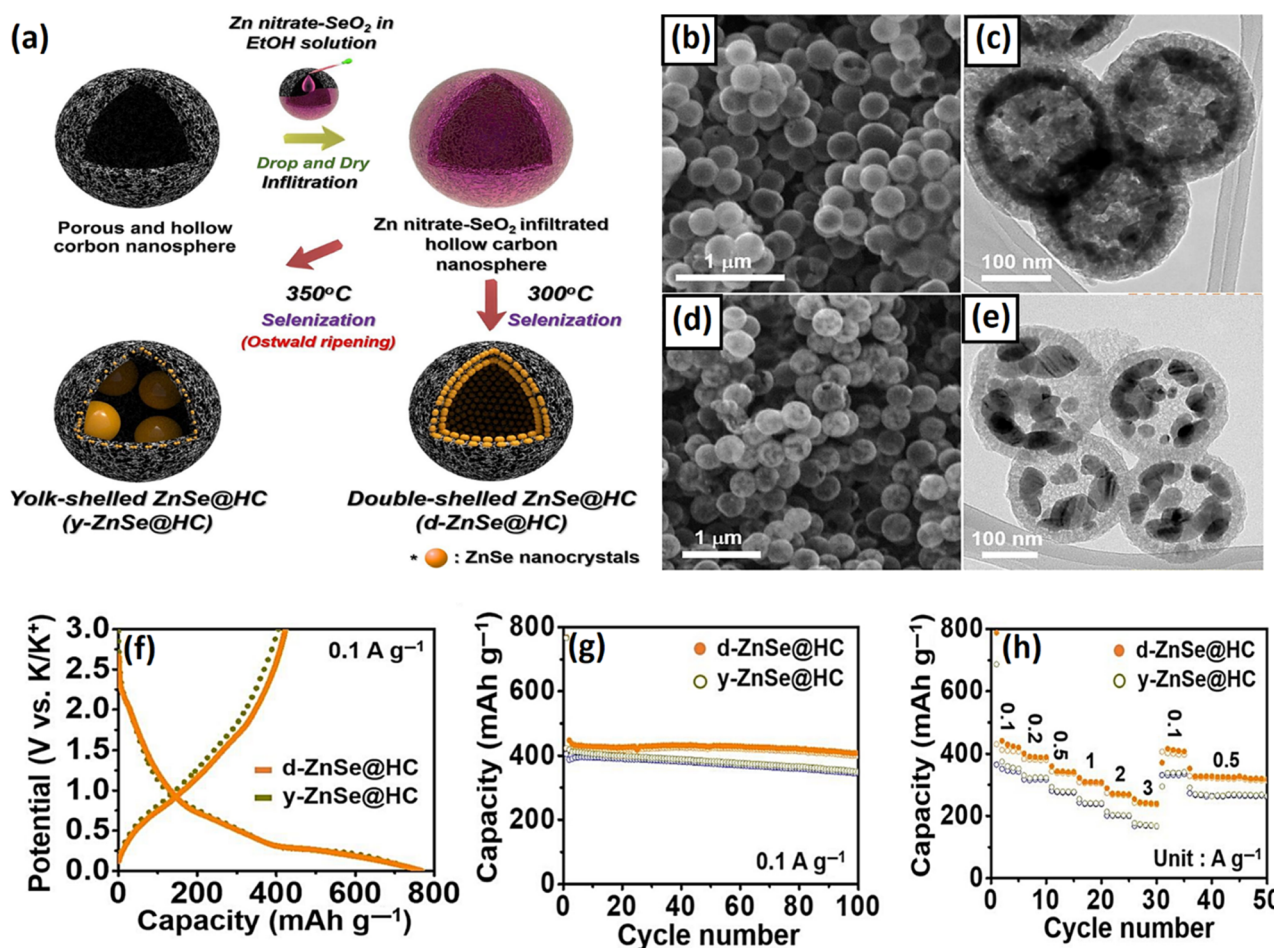


Fig. 32 (a) Schematic preparation diagram of y-ZnSe@HC and d-ZnSe@HC; TEM images of (b and c) d-ZnSe@HC, and (d and e) y-ZnSe@HC; (f) initial discharge/charge profile of d-ZnSe@HC and y-ZnSe@HC at 0.1 A g⁻¹, and (g) corresponding cycling performance, and (h) rate performance of d-ZnSe@HC and y-ZnSe@HC at various current densities from 0.1 to 3 A g⁻¹ (reproduced from ref. 289). "This figure has been reproduced from ref. 289 with permission from John Wiley and Sons, copyright 2021".

a relatively thick SEI layer.²⁷⁵ Notably, selenium actively participated in SEI formation and gets partially dissolved into the electrolyte as polyselenides during the reverse charging process, which in turn hindered ion diffusion kinetics and compromised structural stability of the electrode. In contrast, the incorporation of reduced graphene oxide (rGO) effectively mitigated electrolyte decomposition and facilitated the formation of a thin, stable SEI layer. Consequently, the ZnSe@C@rGO composite exhibited outstanding cycling stability, retaining 96.4% of its capacity after 1000 cycles at a high current density of 5 A g^{-1} . The formation of metal-oxygen-carbon (M-O-C) bonds has emerged as an effective strategy to enhance charge/ion transport, immobilize polyselenides, and improve structural integrity and electrochemical performance through deliberate structural design. In this context, Zn-O-C bonds were successfully engineered by anchoring ZnSe nanoparticles onto a 3D carbon matrix.²⁷⁶ These Zn-O-C linkages act as electron/ion conductive bridges, significantly boosting charge transfer kinetics and ion diffusion. As a result, the ZnSe/C anode demonstrated impressive electrochemical performance, delivering a high-rate capability of $281.1 \text{ mA h g}^{-1}$ at 5 A g^{-1} and maintaining a stable capacity of 434 mA h g^{-1} over 500 cycles at 0.5 A g^{-1} .

Interestingly, ZnSe and its composites generally follow a diffusion-controlled mechanism (battery-type behaviour) when used as anodes in SIBs, differing from the surface-controlled (capacitor-like) behaviour commonly seen in LIBs.^{37,273} However, an exception arises in the case of ultrafine ZnSe nanoparticles, which can exhibit significant pseudo-capacitive characteristics.²⁷⁷ Lu *et al.* developed a well-defined hollow hybrid structure, wherein ultrafine ZnSe nanoparticles were simultaneously deposited on the inner and outer surfaces of amorphous hollow carbon nanospheres (ZnSe@HCNs) (Fig. 31(f)).²⁷⁴ The unique hierarchical ZnSe@HCNs architecture facilitates a mixed sodium storage mechanism involving intercalation, conversion, and alloying reactions. During discharge to 0.1 V, ZnSe is transformed into Na_2Se and a cubic NaZn_{13} phase *via* multiple intermediates. This rational design effectively inhibits nanoparticle aggregation, preserves electrode architecture, and ensures structural robustness throughout cycling. As a result, the ZnSe@HCNs anode delivers excellent electrochemical performance, including a high reversible capacity, superior rate capability ($266.5 \text{ mA h g}^{-1}$ at 20 A g^{-1}), prolonged cycling stability ($361.9 \text{ mA h g}^{-1}$ at 1 A g^{-1} over 1000 cycles with 87% retention), and a high ICE of 92.2% (Fig. 31(g)).

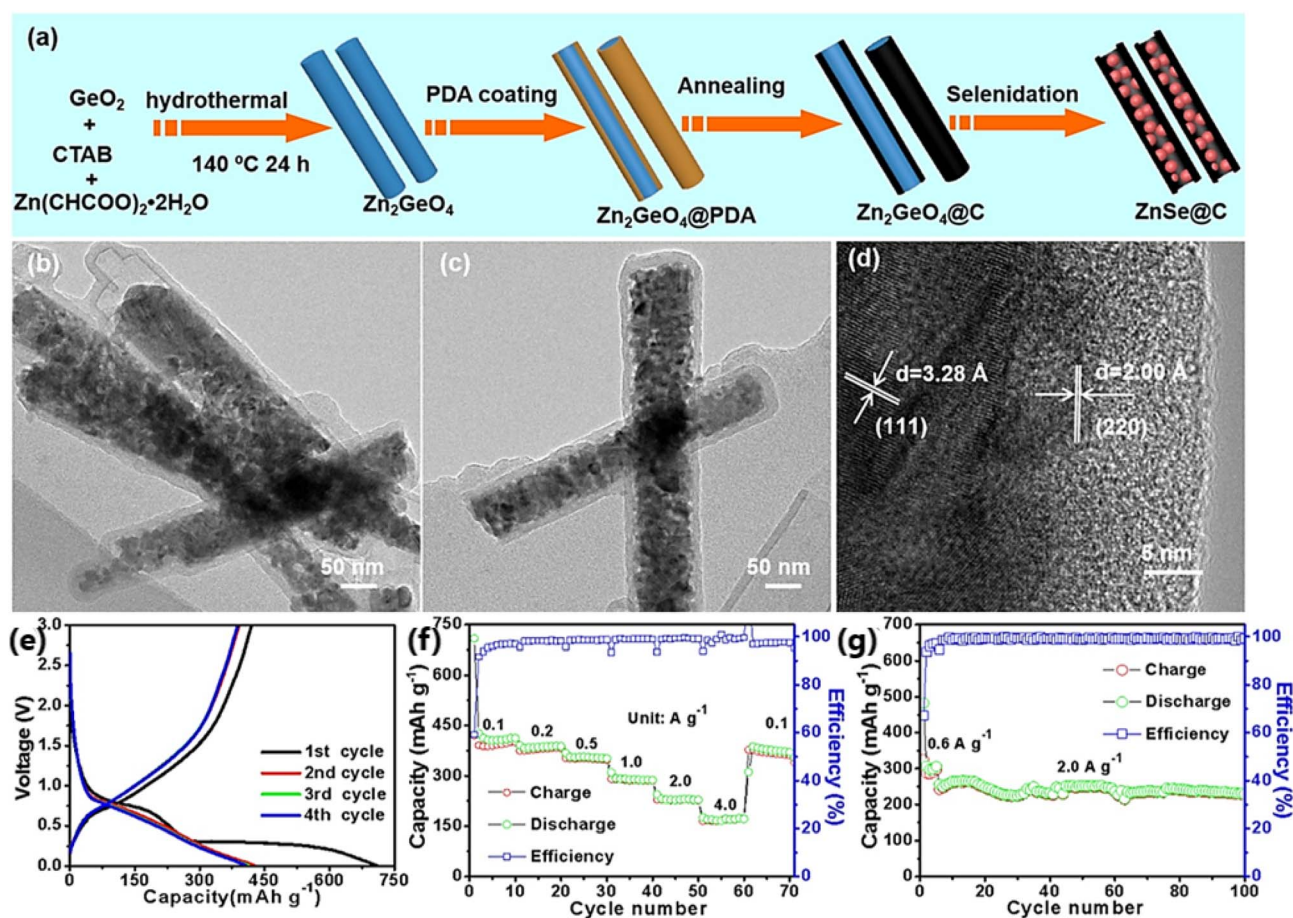


Fig. 33 (a) Schematic preparation diagram of porous ZnSe@C nanorods, (b and c) TEM, and (d) HRTEM image of ZnSe@C, (e) initial four discharge/charge profile at 0.1 A g^{-1} , (f) rate performance from 0.1 to 4.0 A g^{-1} , and (g) long-term cycling stability of ZnSe@C nanorods at 2.0 A g^{-1} (reproduced from ref. 285). "This figure has been reproduced from ref. 285 with permission from Elsevier, copyright 2020".

Table 7 Electrochemical performance comparisons of recently reported ZnSe-based materials for PIBs

Composite	Current density (mA g ⁻¹)	Specific capacity (mA h g ⁻¹)	Cycle no.	Voltage region (V)	ICE (%)	Ref.
ZnSe-C@NC	1000	326.6	1000	0.01–3.0	81.8	290
LN-ZnSe/C	200	383	100	0.01–3.0	59.5	291
	1000	179	1200	0.01–3.0		
MP-ZnSe@NC	500	247	500	0.01–3.0	61	38
ZnSe@NC NFs	200	337	300	0.01–3.0	62	292
ZnSe NP@NHC	100/200	133/111	1200/1600	0.3–2.9	47.7	293
ZnSe-FeSe ₂ /rGO	50	363	100	0.01–3.0	36.3	280
Open ZnSe/C nanocages	50/500	318/189	50/1000	0.01–2.5	47.8	284
Double-shell ZnSe-C nanospheres	100/200	400/230 (170)	100/200	0.01–3	55	289

and h)). Table 6 shows the summary of the Na-storage performance of the previously reported ZnSe based materials.

6.5.3. Anodes for potassium ion batteries. Potassium-ion batteries (PIBs) have emerged as a promising alternative to lithium-ion batteries (LIBs) due to the low redox potential and natural abundance of potassium, which is comparable to that of sodium but with a more favorable redox potential.^{285,286} Nevertheless, the relatively large ionic radius of K⁺ presents challenges such as sluggish reaction kinetics and potential structural degradation of electrode materials. To address these issues, extensive research has focused on the design of suitable active materials and advanced electrode architectures. Among these, TMCs, particularly ZnSe-based anodes, have garnered attention due to their advantageous potential plateau, high theoretical capacity, good electrical conductivity, and cost-effectiveness. ZnSe integrates the benefits of both conversion and alloying mechanisms, making it a promising anode

material for PIBs. It offers relatively high energy conversion efficiency, excellent electronic conductivity, and long cycling stability, and has thus garnered significant interest in recent years as a next-generation electrode material.^{277,287,288} Lee *et al.* synthesized carbon-coated ZnSe nanospheres with yolk-shell (y-ZnSe@HC) and double-shell (d-ZnSe@HC) architectures through an infiltration-assisted selenization strategy (Fig. 32(a)).²⁸⁹ SEM and TEM analyses confirmed the formation of uniformly shaped nanospheres with comparable diameters, although the y-ZnSe@HC displayed a slightly larger ZnSe core size (Fig. 32(b–e)). In terms of electrochemical performance, the y-ZnSe@HC exhibited a marginally higher reversible capacity than the d-ZnSe@HC, likely due to improved structural dynamics and ion transport pathways. When tested at a current density of 0.1 A g⁻¹, the double-shell structured ZnSe@C (d-ZnSe@HC) demonstrates a higher reversible capacity of 400 mA h g⁻¹ after 100 cycles, compared to 360 mA h g⁻¹ for the

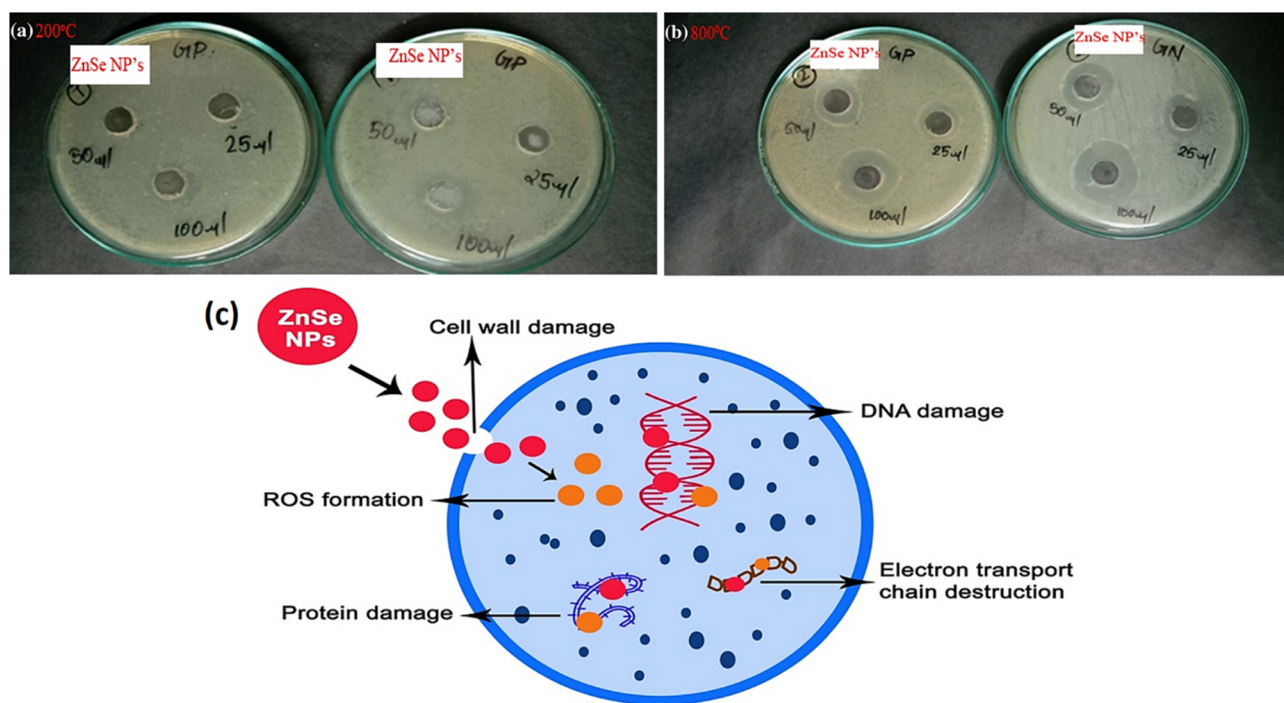


Fig. 34 Antibacterial activity of ZnSe nanoparticles calcined at (a) 200 °C, (b) 800 °C, and (c) mechanism of the action of ZnSe nanoparticles on bacterial cell (reproduced from ref. 72). "This figure has been reproduced from ref. 72 with permission from Springer Nature, copyright 2021".



yolk-shell counterpart (γ -ZnSe@HC) (Fig. 32(f and g)). Furthermore, under varying current densities of 0.1, 0.2, 0.5, 1, 2, and 3 A g⁻¹, d-ZnSe@HC delivers capacities of 400, 385, 340, 300, 270, and 240 mA h g⁻¹, respectively (Fig. 32(h)). These values consistently outperform those of γ -ZnSe@HC, which exhibits corresponding capacities of 380, 320, 275, 240, 200, and 170 mA h g⁻¹.

Porous and hollow nanostructures are advantageous and offer ample internal voids for mitigating volume expansion, due to their high surface area and open frameworks. Xu *et al.* strategically synthesized nitrogen-doped carbon-decorated porous ZnSe@C nanorods *via* a hydrothermal approach, which was coupled with *in situ* dopamine polymerization and a subsequent hydrothermal sulfidation process (Fig. 33(a)).²⁸⁵ The TEM images (Fig. 33(b–d)) confirm the presence of fine ZnSe nanoparticles encapsulated within a carbon shell, with a measured lattice spacing of 3.28 Å, corresponding to the (111) plane of ZnSe.

As shown in Fig. 33(e), the ZnSe@C anode delivered an initial discharge capacity of 709 mA h g⁻¹ with a reversible capacity of 420 mA h g⁻¹ and ICE of 59.2%. Upon increasing the current densities from 0.1 to 0.2, 0.5, 1.0, 2.0, and 4.0 A g⁻¹, the electrode retained capacities of 389, 380, 352, 286, 226, and 168 mA h g⁻¹, respectively (Fig. 33(f)). The unique ZnSe@C nanorod significantly buffered the volume fluctuations during cycling and improved electronic conductivity, resulting in a stable capacity of 204 mA h g⁻¹ after 100 cycles at 2.0 A g⁻¹ for potassium-ion battery applications (Fig. 33(g)).²⁸⁵ The outstanding rate capability of ZnSe@C can be attributed to its distinctive porous nanorod structure wrapped in a conductive carbon shell, which offers abundant active sites and sufficient

void space to accommodate K-ion insertion and mitigate volume changes. A comparative summary of the electrochemical performance of recently reported ZnSe-based anode materials for potassium-ion batteries is presented in Table 7.

6.6. Antimicrobial activities

Bacterial infections pose a serious global health risk, impacting economic and social progress. Developing stable antibiotic molecules could provide new strategies for controlling the rising spread of pathogenic and antibiotic-resistant bacteria.^{294,295} The increase in bacterial mutations and the spread of hospital-acquired infections make treating resistant pathogens even more complex, especially in developing nations. This urgent situation calls for the discovery of innovative anti-bacterial agents to tackle antibiotic-resistant strains like *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Escherichia coli*. Zinc chalcogenides offer promising results, showing effective antimicrobial properties against these harmful pathogens.^{295,296} Conventional antibiotics disrupt bacterial cell wall construction, interfere with protein synthesis, or inhibit DNA replication. Nanoparticles, on the other hand, employ different strategies to destroy bacterial cells: (i) binding to the target cell surface and rupturing the cell wall, (ii) penetrating the cell wall to disrupt essential biochemical pathways, and (iii) producing reactive oxygen species that degrade the cell wall, causing cell death.²⁹⁷ For instance, the antimicrobial activities of the ZnSe NPs calcined at 200 °C and 800 °C were analyzed by Beena *et al.*, tested against *B. subtilis* and *E. coli*, as shown in Fig. 34(a) and (b).⁷² ZnSe nanoparticles at 800 °C show better anti-bacterial activity than

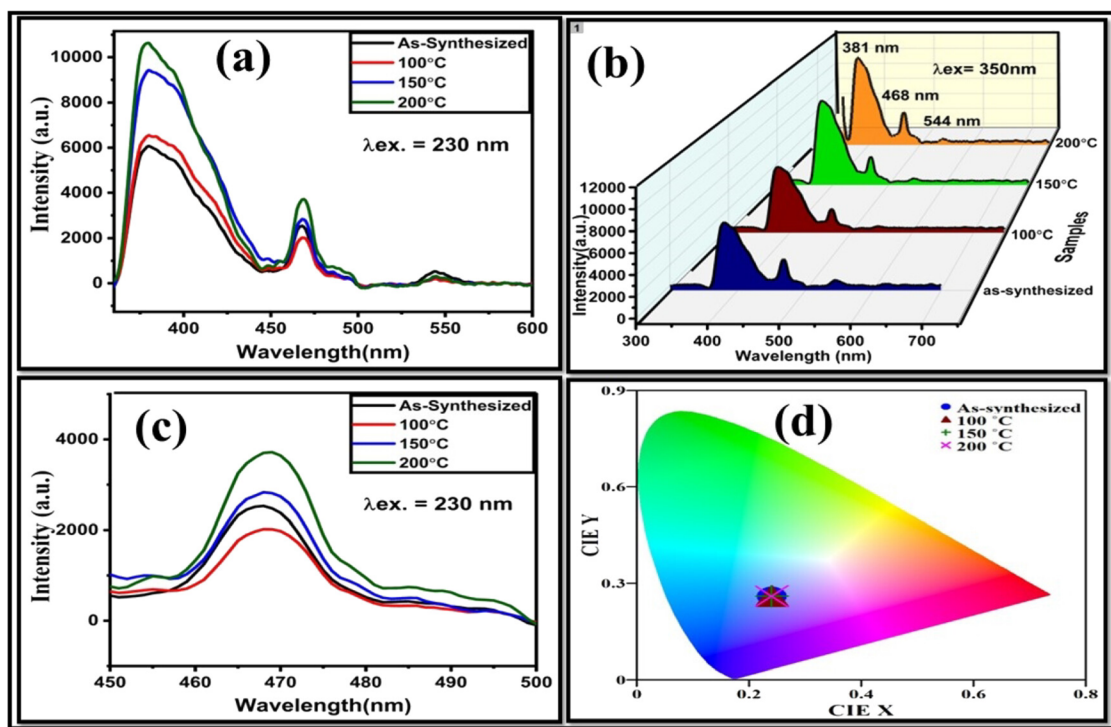


Fig. 35 (a) Photoluminescence spectra, (b) 3D image of photoluminescence spectra, (c) enlarged portion of photoluminescence spectra from 450 to 500 nm, (d) CIE plot of ZnSe NSs (reproduced from ref. 106).

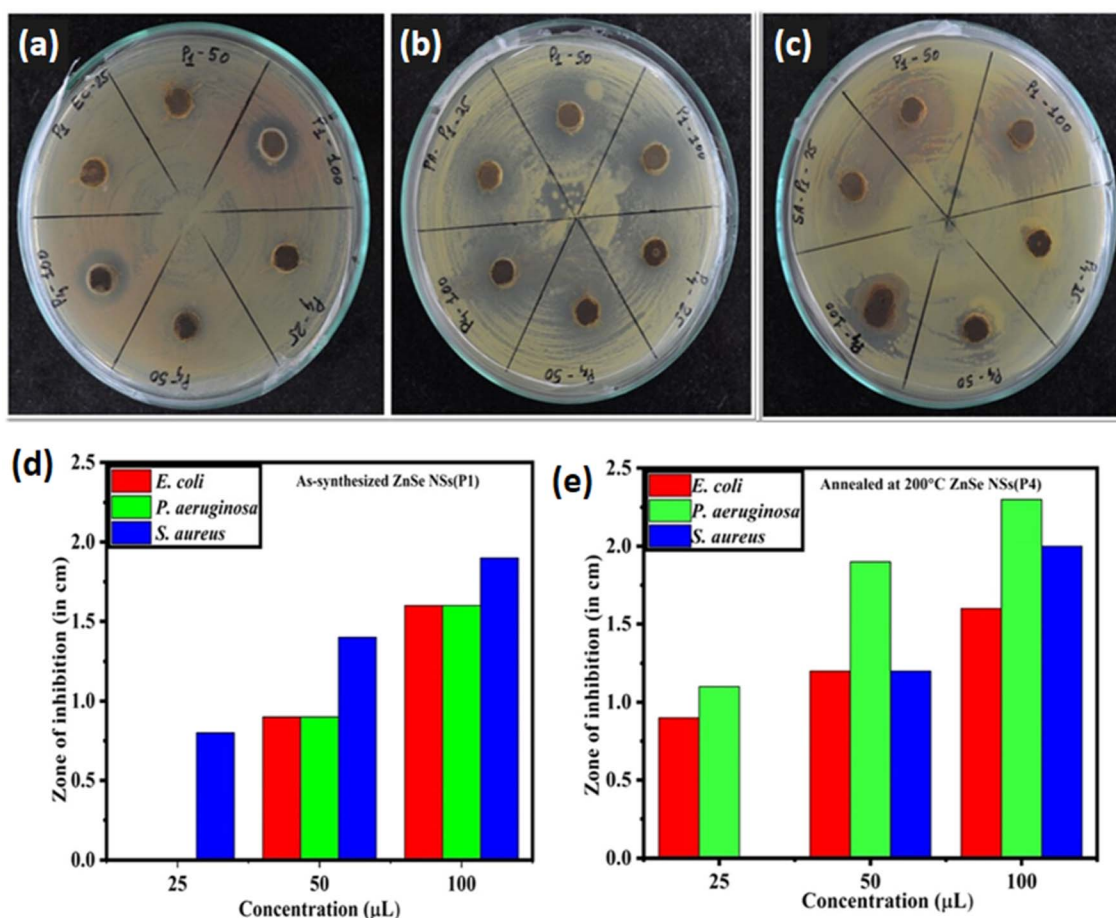


Fig. 36 Antibacterial activity of ZnSe NSs (P1 and P4) against: (a) *Escherichia coli*, (b) *Pseudomonas aeruginosa*, (c) *Staphylococcus aureus*, (d and e) bar graph displaying the antibacterial activities, highlighting the zones of inhibition (ZOI) against *Escherichia coli* (red), *Pseudomonas aeruginosa* (green), and *Staphylococcus aureus* (blue) (reproduced from ref. 106).

those at 200 °C, with lattice imperfections in the latter leading to reduced activity. The Zn and Se ions disrupt the cell wall and DNA, impairing DNA replication and destabilizing proteins. ROS formation from ZnSe NPs also affects the electron transport chain. The antibacterial mechanism is illustrated in Fig. 34(c).

Similar studies were performed by Gupta *et al.* by employing synthesized ZnSe nanostructures (NSs) through an eco-friendly co-precipitation method, followed by annealing at 100, 150, and 200 °C.¹⁰⁶ They assessed the antimicrobial activities of both the as-synthesized (P1) sample and the 200 °C annealed sample (P4) against *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*. The PL spectra of the as-fabricated and annealed samples in Fig. 35(a) demonstrates a progressive enhancement in the intensity of the emission peaks with increasing annealing temperatures. Fig. 35(b) and (c) present the 3D surface plots of the PL spectra and an enlarged portion of Fig. 35(a), respectively, both demonstrating the enhanced emission peak intensity. The CIE plot of ZnSe NSs, in Fig. 35(d), shows all samples emit blue light. The sample annealed at 200 °C displays the strongest blue emission, highlighting that annealing improves this property. The antibacterial activity of P1 and P4 ZnSe samples is shown in Fig. 36(a–c). Fig. 36(d) and (e) presents a bar chart displaying the antimicrobial effectiveness of P1 and

P4 against *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*. P1 (as-synthesized ZnSe NSs) was most effective against *Staphylococcus aureus*, with ZOI increasing with concentration. P4 exhibited activity against all three bacteria, with ZOI also increasing with concentration. The ZOI against *Pseudomonas aeruginosa* was higher than that against *Escherichia coli* and *Staphylococcus aureus*. These results indicate that annealed ZnSe nanostructures possess enhanced blue emission and improved antibacterial activity, suggesting their potential for applications in bioimaging and antibacterial treatments.

7. Conclusion

Zinc selenide (ZnSe), an intrinsic semiconductor characterized by a direct bandgap of 2.7 eV, has emerged as a highly renowned material for photocatalytic applications owing to its optimally aligned conduction band (CB) and valence band (VB) positions. Its versatility spans a wide array of domains, including wastewater treatment, environmental remediation, gas sensors, and energy conversion. Nevertheless, the practical employment of ZnSe is often hampered by intrinsic limitations such as rapid charge carrier recombination and structural instability. To address these challenges, various modification strategies, such as doping and



heterojunction engineering, have been employed to augment its photocatalytic efficacy. The review particularly elaborates the Z-scheme heterojunctions, which have demonstrated superior capabilities in facilitating efficient charge separation and enhancing photocatalytic performance compared to conventional heterojunction systems. Integrating ZnSe with complementary semiconductor materials exhibiting suitable band edge alignments has proven highly effective in amplifying its photocatalytic efficacy. Additionally, core-shell heterostructures based on ZnSe have garnered attention for their ability to remarkably improve optoelectronic properties.

Beyond photocatalysis, ZnSe has showcased considerable promise in gas sensing applications, particularly for NO₂, NH₃, and acetone detection, although its potential for sensing other gases such as VOCs and SO₂ remains underexplored. Its intrinsic semiconducting nature, coupled with favourable surface chemistry and photo responsiveness, positions ZnSe as a compelling candidate for next-generation sensing technologies. ZnSe-based electrodes have also been extensively investigated for energy storage applications. Their well-developed porosity, nanoscale dimensions, and high electrical conductivity render them attractive materials for devices such as Li⁺, Na⁺, and K⁺ ion batteries. Transition metal selenides, by virtue of their unique electronic structures and the high conductivity imparted by selenium atoms, exhibit remarkable electrochemical properties. Consequently, ZnSe has demonstrated significant potential as an anode material, offering high theoretical capacities and robust redox activity. However, despite outperforming analogous metal oxides in several respects, research on metal selenides, particularly for energy storage, remains relatively limited. Moreover, challenges such as volume expansion and cycling instability highlight the necessity for further structural optimization and hybridization with conductive matrices. Additionally, due to their exceptional fluorescence properties and inherent biocompatibility, ZnSe nanocrystals hold considerable promise for biomedical applications.^{298,299}

In this context, the present review provides a comprehensive examination of the intrinsic attributes of ZnSe nanostructures, encompassing their structural, optical, and electronic properties. It further summarizes the various fabrication methodologies which have been instrumental in fine-tuning parameters like particle size, morphology, and crystallinity to optimize performance across diverse applications. Special emphasis is placed on the surface modification strategies, including elemental doping and the construction of heterostructures. This review not only highlights the pioneering advancements in ZnSe-based photocatalysts, with a particular focus on Z-scheme heterojunction systems, but also highlights the multifaceted applications of ZnSe nanomaterials. These include the photodegradation of dyes, antibiotics, phenolic contaminants, CO₂ reduction, Cr(vi) remediation, gas sensing, energy storage, and antimicrobial activity.

8. Limitations and future outlook

ZnSe nanostructures have garnered substantial research pursuit, primarily owing to their rich physicochemical properties and expansive scope of potential applications. Among

inorganic semiconductors, ZnSe stands out for its diverse and intricate nanoscale morphologies. Over the past decade, considerable strides have been made in elucidating the fundamental properties of ZnSe-based nanostructures and identifying their key challenges, thereby enriching the scientific knowledge pool. However, these advances remain relatively modest compared to the extensive progress witnessed for more prevalent electronic and optoelectronic materials, such as ZnO nanostructures. Nevertheless, the distinctive properties, noteworthy recent progress, and broad functional prospects collectively affirm ZnSe nanostructures as compelling candidates for advanced technological applications. It is anticipated that a systematic exploration of the “synthesis–property–application” nexus will catalyze intensified research endeavours, not only to address the existing challenges but also to promote intense investigations into inorganic semiconductor nanostructures. Despite substantial advancements, several critical challenges must be addressed to facilitate the practical deployment of ZnSe-based systems:

(i) A paramount priority for future research is to enhance the long-term structural and operational stability of ZnSe materials under optimized conditions. While they exhibit exceptional photocatalytic performance, issues such as surface corrosion, structural degradation, and rapid charge carrier recombination can significantly deteriorate their efficacy over time. Strategies including the design of protective coatings, the introduction of novel dopants, or the development of composite matrices are imperative to augment environmental resilience without compromising multifunctionality. Such improvements are essential for realizing real-world applications.

(ii) Another critical aspect lies in scaling up of ZnSe production to meet industrial demands. Industrial process mainly relies on methods such as Bridgman–Stockbarger process, Molecular Beam Epitaxy (MBE), solution based methods (spin coating and dip coating), Chemical Vapour Deposition (CVD), and Physical Vapour Deposition (PVD).^{300–302} However, each of these methods often faces challenges such as solution-based routes often produce lower crystalline quality. Similarly, ZnSe grown in CVD is prone to exhibits some defects such as tiny pores and impurities, due to raw material quality and limited growth control, and the advanced technology required for CVD significantly increase production cost.³⁰³ Likewise, PVD also faces limitations such as requirement of high vacuum conditions, material volatilization at high temperature, defect formation. Therefore, future research should focus on cost-effective, scalable, and environmentally friendly synthesis strategies, such as green chemistry or continuous-flow production to enable large scale fabrication of high quality ZnSe materials suitable for commercial applications.

(iii) More rigorous investigations are necessary to correlate the photocatalytic performance with light absorption, surface architecture, particle size, morphology, and synthetic methodology of ZnSe-based nanocomposites.

(iv) Integration of ZnSe with advanced materials, such as graphene, carbon nanotubes, or conductive polymers, can dramatically elevate photocatalytic and electrochemical functionalities by improving the charge separation dynamics, increasing surface area, and extending light absorption spectra.



This would further broaden their utility in solar-driven environmental remediation, gas detection, and next-generation battery technologies.

(v) While ZnSe-based sensors have demonstrated promising sensitivity toward NO₂, investigations into their efficacy for detecting other analytes, such as VOCs (*e.g.*, formaldehyde, benzene) and SO₂, remain limited. Future efforts should explore innovative sensor architectures and surface functionalization to achieve improved selectivity, sensitivity, and rapid response across a diverse array of target gases.

(vi) Comprehensive mechanistic studies including elucidation of degradation pathways and photocatalytic kinetics under complex water matrices are crucial for translating laboratory success into field applications. Density functional theory (DFT) simulations can provide atomic-level insights into the reaction mechanisms and evaluate the stability of the catalyst, thereby guiding the rational design of ZnSe-based systems. Also, advanced characterization techniques such as *in situ* XRD, soft X-ray absorption spectroscopy, *in situ* TEM, *in situ* Raman spectroscopy, and neutron diffraction can unravel dynamic processes and structural evolutions during catalysis.

(vii) Finally, environmental and toxicological assessment profiles of ZnSe-based hybrid materials are indispensable to ensure their safe and sustainable integration into practical technologies.

(viii) In energy storage, improving the structural integrity of ZnSe-based electrodes is crucial to mitigate issues such as volume changes and interfacial instability. Optimizing metal selenide electrodes through careful control of precursors, processing conditions, calcination parameters, porosity, and morphological and electrochemical attributes is essential. Nanostructuring, composite formation, and innovative electrode architectures hold promise for enhancing cycling stability and rate capability. Notably, ternary and multinary ZnSe systems represent largely untapped avenues that could unlock superior electrochemical performance, akin to their well-studied metal oxide counterparts.

(ix) A deeper understanding of the interfacial behaviour, achieved through synergistic *in situ* experimental studies and theoretical modelling, will be vital for optimizing material design.

(x) A pivotal future direction for ZnSe-based gas sensors lies in engineering systems capable of high-performance operation at room temperature. Presently, many sensors necessitate elevated temperatures (>200 °C) to attain optimal sensitivity and rapid response, imposing significant energy demands that constrain their applicability, particularly in portable and wearable devices. Advancing this field will require the design of novel nanostructures and composite materials leveraging techniques such as strategic doping, heterojunction integration, and activation *via* external stimuli like UV irradiation to enable efficient low-temperature sensing. Such innovations will facilitate the development of energy-efficient, practical devices tailored for environmental monitoring and healthcare diagnostics.

(xi) Beyond achieving room-temperature operation, future research must prioritize enhancing the sensitivity and

selectivity of ZnSe-based gas sensors, particularly for detecting low concentrations of hazardous gases such as NO₂, NH₃, and CO. Sensor sensitivity is intrinsically linked to tailored surface properties and material composition. Advanced doping approaches including the incorporation of metals like Cu, Ni, and Pd have demonstrated improvements in gas-sensing performance, though often with a trade-off between sensitivity and operating temperature dictated by dopant choice. Strategic introduction of novel dopants can modulate electronic structures, promoting faster charge carrier dynamics and more efficient gas adsorption. Additionally, exploring innovative dopant combinations and engineering heterojunction nanocomposites will be crucial for achieving superior sensitivity and selectivity. Such advancements will enable precise detection of trace gases, broadening applicability from industrial safety systems to urban environment monitoring.

(xii) Addressing the influence of environmental factors, particularly humidity, on the performance of gas sensor remains a critical challenge. Humidity can disrupt gas adsorption dynamics, compromising sensitivity and accuracy, especially in variable environments like outdoor air quality monitoring and industrial settings. Future research should prioritize the development of novel materials and hydrophobic coatings, as well as sensor architectures that limit water molecule interactions with active sensor surfaces, to enhance reliability under humid conditions. Additionally, deeper mechanistic insights into the influence of humidity on the sensing processes are essential for devising effective mitigation strategies.

(xiii) Advancing flexible, transparent, and portable gas sensors represents a compelling research frontier, propelled by the rise of wearable technologies and real-time environmental monitoring needs. Integrating ZnSe nanostructures into flexible substrates promises lightweight, robust, and highly sensitive devices. However, critical challenges persist in preserving sensor performance under mechanical stress, ensuring long-term durability, and maintaining stability amid fluctuations in humidity and temperature.

(xiv) Additionally, integrating gas sensors into wearable health monitoring devices holds immense promise for delivering personalized assessments of pollutant exposure, thereby advancing individualized health tracking. These emerging applications highlight the imperative for sustained innovation in sensor design, with a focus on miniaturization, energy efficiency, and seamless wireless integration.

Collectively, these advancements highlight the extraordinary multifaceted potential of ZnSe in tackling pressing environmental and technological imperatives, thereby charting a course for pioneering innovations in sustainable remediation, advanced sensing platforms, and next-generation energy storage systems.

Abbreviation

QDs	Quantum dots
EDTA	Ethlenediamine tetraacetic acid
MO	Methyl orange
SC	Semiconductor



CB	Conduction band
VB	Valence band
ASS	All-solid-state
MB	Methylene blue
AY 17	Acid yellow 17
RhB	Rhodamine B
CR	Congo red
MV	Methyl violet
SY	Sunset yellow
TC	Tetracycline
OTC	Oxytetracycline
RGO	Reduced graphene oxide
ZOI	Zones of inhibition

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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