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Vacancies in functional materials for clean energy storage and harvesting: the perfect imperfection

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Vacancies exist throughout nature and determine the physical properties of materials. By manipulating the density and distribution of vacancies, it is possible to influence their physical properties such as band-gap, conductivity, magnetism, etc. This can generate exciting applications in the fields of water treatment, energy storage, and physical devices such as resistance-change memories. In this review, we focus on recent progress in vacancy engineering for the design of materials for energy harvesting applications. A brief description of the concept of vacancies, the way to create and control them, as well as their fundamental properties, is first provided. Then, emphasis is placed on the strategies used to tailor vacancies for metal–insulator transitions, electronic structures, and introducing magnetism in non-magnetic materials. Finally, we present representative applications of different structures with vacancies as active electrode materials of lithium or sodium ion batteries, catalysts for water splitting, and hydrogen evolution.

Key learning points

- (1) A general introduction is given to various defects and why the study of vacancies is important for energy materials.
- (2) The classification of vacancies and the strategies to manipulate (create and remove) their distribution and concentration in various materials.
- (3) The way vacancies influence material properties. We focus on the control of band structures, magnetism and electrical transport by vacancy engineering.
- (4) We show how to design advanced clean energy harvesting materials, such as batteries electrode materials, solar cells, catalysts for water splitting, etc. based on various vacancy-induced properties.
- (5) The advantages/disadvantages of vacancy-engineering in the performance of energy materials.

1. Introduction

The saying ‘no one is perfect’ holds also as a universal principle in the field of materials science. There is no perfect crystal in nature despite the most elaborate efforts to achieve the minimum system energy. The imperfection of crystals offers the opportunity to tune properties in various applications, which otherwise would be determined only by the composition and crystal structure. Defects exist widely in metals, ceramics, organic semiconductors, and even polymers. Depending on the dimensionality of the crystal lattice, defects in solids can be classified into several different types, as illustrated in Fig. 1. Zero-dimensional defects (point defects) are places where an atom is missing or irregularly placed in the normal crystal array. This includes Schottky and Frenkel defects, and impurities. One-dimensional defects (line defects) designate extended dislocations, such as edge and screw dislocations or combinations thereof. Grain boundaries, twin boundaries, and stacking faults are typical 2-dimensional

Fig. 1 Schematic of various defects in crystals.

defects (planar defects), which are interfaces between homogeneous regions of the material. Three-dimensional defects (volume defects) are aggregates of atoms or vacancies such as precipitates, dispersants, and voids/cracks. Among them, vacancies are the most commonly observed type of defect. This is because most crystal synthesis strategies involve high temperature, resulting in frequent and random change of atomic positions, leaving behind empty lattice sites. In particular,

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if a crystal is composed of more than one element, it is difficult to control these elements in their proper chemical proportion, and vacancies occur due to deviation from stoichiometry. At any given temperature, the enthalpy of the system, as well as the entropy, will be changed as a result of broken bonds due to vacancies. Thus a certain equilibrium concentration of vacancies is required to make the total free energy minimal. The number of vacancies can be estimated by the Boltzmann distribution according to statistical thermodynamics:

$$N_V = N_S \exp(-Q_V/k_B T) \quad (1)$$

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where N_V is the number of vacancies, N_S is the number of regular lattice sites, k_B is the Boltzmann constant, Q_V is the energy required to form a vacant lattice site in a perfect crystal, and T is the absolute temperature. The above equation underestimates the number of vacancies and a larger number of non-equilibrium vacancies is expected to be generated during the crystal growth or post-treatment process. As an example, it can be estimated that there is one vacancy per 10^{15} lattice atoms in copper at room temperature. However, just below the melting point, there can be as many as one vacancy in every 10 000 atoms, which is a large concentration and will influence the properties of the material.

By controlling the vacancy concentration, distribution, and charge (cation, anion or neutral vacancy), one can manipulate effectively between structure, properties, and performance. For example, the presence of cation (anion) vacancies has a large influence on the local bond environment of migrating anions (cations), resulting in different energy barriers for individual diffusion hops. They act as dislocation pinning centers and enhance the mechanical strength of a solid significantly. The hardest oxide films to date have been successfully fabricated according to this vacancy hardening effect. A series of other transport-related phenomena are also influenced by vacancies. For instance, the diffuse dielectric anomaly, the giant dielectric response at low frequencies, and current-voltage characteristics can be strongly influenced by the migration and concentration of vacancies in a number of (organic-inorganic halide) perovskites. Vacancies, like other short-range disordered structural defects, can also act as scattering centers and create localized band tail states, which influence the mobility and conductivity. These unique vacancy-induced features play a very important role in

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the design of new functional materials, especially in the field of clean energy harvesting, such as lithium/sodium ion batteries, photocatalysts, hydrogen evolution, and thin film solid oxide fuel cells.

Our planet is on the brink of a serious environmental crisis, caused by air and water pollution, global warming, and acid rain. Obviously, our dependence on fossil fuels can be blamed for the deterioration of the environment. Finding alternatives to replace fossil fuels is essential to resolve the above mentioned problems. To achieve this goal, the design of various advanced energy materials is the first step. Fortunately, recent years have witnessed increased research efforts to develop various functional materials for clean energy usage, such as lithium/sodium ion batteries, water splitting, hydrogen storage, and solar cells. For a significant improvement of application performance, it is important to tailor/optimize their structures and properties.¹ Vacancy-engineering is one of the most studied and effective methods to this end. This strategy offers scientists a powerful tool to manipulate the various properties of materials, from surface stability, to electrical transport and band structures. One can even introduce new features, such as domains, magnetism, and superconductivity. Several reviews have been published during the last few years either focussing on a particular material, such as diamond and TiO_2 ,^{2,3} or on specific applications in the field, like charge transport and catalysis.^{4,5} In this tutorial review, we highlight the power of vacancy engineering to tailor various physical properties. We extend this principle to the design of advanced materials for clean energy harvesting and storage. Several fundamental features and properties of vacancies, that are rarely mentioned in previous reviews, are also described here. Finally, we formulate conclusions and perspectives for the study of various vacancy-related phenomena and applications. This review aims to provide useful guidelines for the control and manipulation of vacancy effects.

2. Fundamental understanding

2.1. Types of vacancies

Vacancies can be categorized into different classes according to their characteristics as illustrated in Fig. 2. Based on their origin, vacancies can be divided into statistical and structural vacancies. The former is the result of thermodynamic equilibrium, and the latter is generally caused by non-stoichiometry, if the crystal includes more than one element. A representative example is the transition metal oxide FeO . There are always Fe-vacancies and the formula can be described as Fe_{1-x}O , where x can be as high as 0.1. This leads to a considerable concentration of iron vacancies and the appearance of Fe^{3+} to maintain electroneutrality. Based on the position of the vacancies, they can be random or ordered. A random distribution is not strange if we consider the synthesis conditions like high temperature and pressure. This presents a great challenge for the accurate control of vacancies in specific positions. In some cases, the “random vacancy distribution” is the dominant defect mechanism and sensitively influences the material's electronic

Fig. 2 The classification of vacancies based on different points of view.

and mechanical properties. In a few cases, the vacancies are ordered and become part of the crystal structure. To some extent they are no longer defects in the usual sense. Iron sulphide and selenide, such as Fe_3Se_4 , Fe_7S_8 , and Fe_7Se_8 , fall into this category. The Fe vacancies appear in a periodic way and lie in a particular plane. Finally, vacancies can be divided into equilibrium and non-equilibrium ones based on thermodynamics. The appearance of vacancies is generally accompanied by broken or missing bonds. Thus, it normally costs energy to form vacancies. However, the configurational entropy stabilizes this process. Therefore, the concentration of vacancies (N) will increase until the total Gibbs free energy (ΔG) is at a minimum at any given temperature as illustrated in the inset to Fig. 2. These are known as thermal, or equilibrium vacancies. According to formula (1), equilibrium vacancies will be present in all crystals. They are thermodynamically stable and cannot be removed by heat treatment. The concept of non-equilibrium vacancies is usually related to the generation of Frenkel pairs under *e.g.* high energy particle irradiation, quenching from high temperature, or cold working. It has an important effect in most diffusion-controlled processes, especially in nanosystems. Here, the characteristic size, such as the diffusion zone width or phase layer thickness, is of the same order as the free length of the vacancies. This results in a vacancy gradient at the surface/interface, where a sink and source of vacancies occurs. The rapid development of micro-machined technology such as silicon micromachining testifies to the increasing importance of non-equilibrium vacancies in the design process.

2.2. Vacancy creation

There are many ways to create vacancies. They may be built-in with the crystal growth, or activated by post treatment like annealing and redox reaction processes. Regulating the ratio of starting materials is one of the most straightforward methods to create vacancies in most binary or multiple compounds.⁶ For oxide thin films, cationic vacancies can be tailored by the oxygen pressure in the deposition process. This has obvious drawbacks. It is difficult to predict and control the precise vacancy distribution. Elemental doping is another effective way of generating vacancies. For example, doping with alkali elements such as Li, Na, or K in ZnO can decrease the formation energy of Zn vacancies by forming a defect complex. In addition,

Fig. 3 Schematic diagram of strategies to create vacancies. We consider the perovskite structure ABO_3 as an example, where red represents oxygen atoms, light blue represents B site atoms, and light green represents A site atoms. (1) Annealing, (2) irradiation, (3) hydrogen gas treatment, (4) bonding between O and Al, (5) doping with a small ion creates an O vacancy, (6) doping with a large ion creates an A-site vacancy. (7) Electric-field gating, and (8) intercalation/deintercalation of oxygen.

by choosing dopant elements with different ionic sizes, one can create vacancies in different sites in a compound. We take the research focus on perovskites (ABO_3) as an example (Fig. 3). Small ions are exclusively doped on the B-site and create oxygen vacancies for charge compensation if the dopant has lower valence. This doping can also result in the partial oxidation or reduction of ions on the B sites or result in the appearance of B-site vacancies if the dopant has higher valence. Intermediate size ions can be doped onto the A and B-sites simultaneously. Large ions substitute only on the A-site, thus creating either A-site, B-site or oxygen vacancies, depending on the charge balance. However, with the increase of doping concentration, a unit cell distortion will occur (expansion or compression depending on the size of the dopant ions). Then the system is not thermodynamically favored and degradation of metastable microstructures deteriorates the device or application performance.⁷ Heat treatment is also a simple and commonly used strategy. For most oxides, annealing in high vacuum leads to a loss of oxygen, and oxygen vacancies appear. The distribution and concentration can be manipulated by varying the sintering temperature, heating and cooling rate. Interestingly, if a sample with vacancies is reduced and re-oxygenated, some properties like conductivity and bandgap absorption can be recovered again. The annealing can also be carried out in a particular atmosphere. A reactive gas, like hydrogen, can combine with surface oxygen to form H_2O and evaporate. Thus, oxygen vacancies are formed on the material surface, while sintering in an inert gas, like argon, leads to the loss of anions in non-oxide-based perovskites containing elements such as sulfur and selenium.

New concepts have recently been developed for vacancy design. Some elements, such as aluminum, have a strong affinity for oxygen. When an Al-based film like $LaAlO_3$ is deposited on an oxide substrate without aluminum, the oxygen (O) atoms are pulled out and combine with the aluminum atoms. This way one can easily create oxygen vacancies in the substrate near the interface during the deposition process. As for structures like rutile, the formation energy of oxygen vacancies is relatively high. Electrolyte gating has been proven to be a good option. At the ionic liquid (IL)–oxide interface, sufficiently high electric fields create oxygen vacancies at the electric double layer, by the migration of oxygen into the IL.⁸ Experiments show that even modest gate voltages induce this phenomenon. It is considered to be universal because most IL gating experiments use much higher electric fields.

3. Properties tailored by vacancy engineering

The vacancy creation process is generally accompanied by a series of physical and chemical changes, such as bond breaking and re-forming, lattice distortion, electronic compensation, electron localization, and gap states at the Fermi level. The vacancy type, distribution, and concentration also contribute a lot to various changes. In particular, recent advances in scientific instrumentation have enabled scientists to create and manipulate vacancies locally with ultrahigh precision. Here, we present the theoretical and technological basis of how researchers can tailor and induce a broad range of physical properties.

3.1. Band structure tailoring

As discussed above, once atoms are removed from the bulk material, the atoms surrounding the vacancy will induce changes in the chemical environment such as electron redistribution. This will influence the band structure of the new structure even if the vacancy concentration is very low. We can take the extensively studied TiO_2 as an example. Both anatase and rutile are insulators with wide band gaps of 3.2 and 3.0 eV, respectively. The band edges lie in the UV region, which makes them inactive under visible light irradiation (Fig. 4a). By introducing oxygen vacancies, the electrons are localized at the vacancy site due to the Madelung potential of the highly ionic crystal. These localized electrons will form a donor level, which is generally 0.75–1.18 eV below the conduction band. However, if a neutral vacancy is created, the excess electrons associated with the oxygen vacancy will be transferred to the empty 3d orbitals of neighboring Ti atoms and form Ti^{3+} sites. This leads to an interstitial Ti species and the formation of shallow donor states below the conduction band. Still, there is controversy over which factor makes the dominant contribution to the vacancy density-of-states.¹³ The band structure can be further optimized by introducing surface disorder. A substantial shift (~ 2.1 eV) of the valence band position is reported and this induces a further bandgap narrowing to 1.85 eV (Fig. 4b).⁹ More importantly, the band gap can be tuned by manipulating the vacancy concentration.

Fig. 4 (a) Schematic density of states for TiO₂ P25 Degussa (black dotted line) and black TiO₂ sample (red line). V_o represents the localized states created by oxygen vacancies in black TiO₂. (b) Illustration of the structure of black TiO₂, surrounded by a disordered shell layer. V_o represents the oxygen vacancy in the core. Reproduced with permission from ref. 9. Copyright 2012 American Chemical Society. (c) Band structure tailoring by introducing S-vacancies of different concentrations in 2H-MoS₂ (calculated using 4×4 unit cells). The bands nearest to the Fermi level are highlighted in black and the extra bands are due to the larger unit cell size needed to model the smaller S-vacancy concentrations. Reproduced with permission from ref. 10. Copyright 2016 Nature Publishing Group. (d) Illustration of energy band construction in two adjacent CdS nanoclusters, which are combined with electronic coupling of an interfacial cadmium cation–cation pair. Reproduced from ref. 11. with permission from the Royal Society of Chemistry. (e) HRTEM image showing a SnS₂/SnS superstructure, with S vacancies dispersed at the interface. Reproduced from ref. 12. with permission from the Royal Society of Chemistry.

The band structures of 2H-MoS₂ without sulfur (S) vacancies exhibit a band gap of 1.7 eV, as shown in Fig. 4c. When S vacancies are introduced, even in small concentrations (3.12%), new bands can be created in the gap near the Fermi level.¹⁰ With increasing S vacancy concentration, the generated bands are obviously closer to the Fermi level, and new gap states can be clearly observed. The corresponding Kohn–Sham orbitals for the band below the Fermi level confirm that the new gap states are localized around the vacancy areas. Thornton *et al.* created oxygen vacancies with different concentrations by bombarding the TiO₂ surface with low energy electrons. They found that the majority of band-gap states arise from oxygen vacancies and that there is a strong correlation between them. Other factors, such as interstitial Ti atoms and subsurface oxygen vacancies, contribute to a lesser degree.¹³ Our recent calculations on

marcasite FeSe₂ indicate that by introducing only 4% Fe vacancies, the band gap can decrease dramatically from 1.01 eV to 0.29 eV.⁶

Nanostructures such as nanoparticles and ultrathin nano-sheets are prone to have large densities of vacancies due to their high surface energy and surface-volume ratio. Once they are assembled into other complex hierarchical structures, rich interfaces can be created between or in the primary building blocks. This offers opportunities to influence band structures using interface vacancies. Studies on CdS nanotubes assembled from nanocrystals provide a good example. Compared with bulk CdS, it is found that the band gap of the nanocrystals is only slightly narrowed due to the formation of extra intra-band states arising from S surface vacancies. However, if S vacancies are created at the interface between neighbouring nanocrystals, the dangling bonds consisting of sp² hybrid orbitals of Cd atoms have a tendency to form Cd–Cd bonds to reach a stable state. In this case, the two electron-occupied Cd 5s(σ) bonding orbital splits from the Cd 5s orbital and will hybridize with the energy bands of the host nanocrystals. This results in a significant lifting of the reconstructed valence band in comparison with the original Cd 3p orbital as illustrated in Fig. 4d.¹¹ In addition, using manipulated vacancies, one can synthesize layered superstructures in misfit compounds that consist of two different phases (Fig. 4e). A band-gap reconstruction is also expected at the interface between the two phases.¹²

Other strategies to shape the band structure include the design of different types of vacancies. Depending on the vacancy type, they have different formation energies. This determines their structural stability and concentration in different materials. For example, at least four types of vacancies exist in chemical vapour deposition (CVD) grown MoS₂, as shown in Fig. 5, namely monosulphur vacancies (V_s), disulphur vacancies (V_{s2}), a vacancy

Fig. 5 Atomic resolution annular dark field (ADF) images of various intrinsic point defects present in monolayer CVD-grown MoS₂. Reproduced with permission from ref. 14. Copyright 2013 American Chemical Society.

Table 1 Lattice parameters, formation energies, magnetic moments, and electronic characteristics of monolayer TiS_3 calculated using a 3×3 supercell. Reproduced with permission from ref. 16. Copyright 2015 American Chemical Society

	a_1/a_2 (Å)	E_F (eV)	m (μ_B)	Conduction
Pristine TiS_3	14.98/10.18		0.0	Semiconductor
S Vac.	14.90/10.17	3.58	0.0	Semiconductor
Ti Vac.	15.05/10.14	12.00	0.5	Metal
Double S Vac.	14.96/10.18	8.48	0.8	Metal
Ti, S Vac.	14.90/10.13	16.15	0.3	Metal

complex comprising Mo and three surrounding S atoms (V_{MoS_3}), and a vacancy complex comprised of Mo near three disulphur pairs (V_{MoS_6}). V_S and V_{MoS_3} have the lowest formation energy and represent the majority. However, only V_S and V_{S_2} introduce unoccupied deep levels below the conduction band minimum and act as compensation centres in n-type MoS_2 .¹⁴ A similar case can be found in fully fluorinated graphene. Series vacancies, including carbon vacancies, fluorine vacancies, and fluorine vacancy clusters, are present in the system. All of them can introduce defect states within the band gap, but with different types and positions. The excitations between these intra-gap states and the states around the band gap result in a distinct optical spectrum.¹⁵ More powerfully, particular vacancies have the ability to redistribute the charges around them, and lead to the reconstruction of bonds between the neighboring atoms. The direct result of such a reconstruction is the creation of lattice distortions especially at the sample surface. New states can appear at the band gap maximum and shape the band structure. Theoretical study of a typical monolayer semiconductor, TiS_3 , without intrinsic magnetism, provides a good example. It is proven that single S vacancies can enhance the band gap without influencing the magnetization and conductivity. All other vacancies, including Ti vacancies, Ti-S vacancies, and double S vacancies, induce metallic behavior and a magnetic ground state, as shown in Table 1.¹⁶ Finally, the vacancy position is another factor that needs to be considered. The preferred location of anion vacancies is between cations with lower combined valence and larger covalency.¹⁷ If their atomic orbital contributions are in the vicinity of the conduction band minimum or valence band maximum, changes in the electronic structure can occur. This provides an efficient way for band gap engineering without changing the structural features significantly.

3.2. Electrical transport

As we discussed above, all materials inherently possess vacancies to different degrees. They are thermodynamically stable and cannot be removed completely during the purification process. On the one hand, these anionic/cationic vacancies act as trapping centers for electrons or holes. On the other hand, they shape the band structure by introducing intra-band gap states as discussed above.^{20,21} Especially in polycrystalline nanostructure-like films, where a large proportion of the vacancies reside near grain boundary regions, the influence of vacancies cannot be neglected. Thus, understanding the effect of vacancies on charge transport is theoretically and

technologically important in order to design advanced materials for applications.

During the last few years, the rich and exciting properties of graphene have offered a new paradigm to develop other novel low-dimensional layered structures. MoS_2 is one of the best candidates that could compare with graphene. The presence of a bandgap and the significant spin-orbital coupling make it an ideal building block for next generation applications in nano-electronics and optoelectronics. However, as we mentioned above, all preparation methods ranging from mechanical exfoliation (ME) to physical and chemical vapour deposition (CVD and PVD) lead to the formation of various defects. While the theoretical mobility is $410 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the highest experimental mobility measured for back-gated MoS_2 FET devices thus far is $81 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for ME, and $45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for CVD samples.²² Thus, understanding the effect of vacancies on the electrical transport is the first step towards a successful design. Qiu *et al.* prepared few-layer MoS_2 films on degenerately doped Si substrates. Low concentrations of S vacancies of the order of 10^{13} cm^{-2} were observed on the surface.¹⁸ These act as electron donors and result in localized states in the bandgap. It is found that the transport is dominated by nearest-neighbour hopping at high temperatures (Fig. 6a). At low temperatures, the carriers hop over a longer distance but with a smaller energy difference. Mott variable ranging hopping (VRH) is displayed (Fig. 6b). DFT calculations confirm a high electron effective mass and strong localization near the five-fold Mo atoms surrounding the S vacancy, within a range of 0.3 nm. When the sample thickness exceeds a

Fig. 6 (a) Schematics of electron transport mechanism in perfect and vacancy-containing MoS_2 . The transport is band-like in perfect MoS_2 because of the periodic electron density. In MoS_2 with vacancies, however, electrons are localized near the defects and transport occurs through hopping. (b) Arrhenius plot of normalized conductivity (symbols) of MoS_2 with different vacancy concentrations at temperatures above T^* , and fit curves using a hopping model (lines, in the temperature regime below T^*). Reproduced with permission from ref. 18. Copyright 2013 Nature Publishing Group. (c) Schematic diagram of 2-DEG created by reducing STO substrate with TMA during growth of Al_2O_3 film. Reproduced with permission from ref. 19. Copyright 2013 American Chemical Society. (d) Sheet resistance versus temperature for various gate voltages varying from 0 to 1.8 V for $\text{VO}_2/\text{TiO}_2(001)$. The metal-insulator transition temperature is suppressed to below 5 K at $V_G \sim 1.8$ V. Reproduced with permission from ref. 8. Copyright 2013 American Association for the Advancement of Science.

threshold value, bulk metallic behavior becomes dominant. This is in accordance with the calculation that the electrons in the valence band of perfect MoS_2 are delocalized. Similarities can be observed in marcasite FeSe_2 with a small concentration of Se vacancies (4%). VRH across the one-dimensional FeSe_2 chains occurs over the whole temperature range.⁶

Vacancies are also reported to be responsible for the emergence of a two-dimensional electron gas (2-DEG) between the band insulators LaAlO_3 (LAO) and SrTiO_3 (STO), although there is still some controversy regarding the mechanism. Amorphous LAO/STO interfaces typically show metallic behavior and there is no critical overlayer thickness for the appearance of conductivity. However, after removing oxygen vacancies by post-annealing, the interface becomes insulating again. This proves that the oxygen vacancies provide the dominant mobile carriers.²⁰ Remarkably, a 2-DEG can even be generated in non-polar oxides such as YAlO_3 and Al_2O_3 layers (Fig. 6c). The oxygen vacancies introduced by reducing the STO substrate is the key factor.²³ More interestingly, electric field gating with ILs suppresses the metal-insulator transition significantly by creating vacancies. VO_2 films on a $\text{TiO}_2(001)$ substrate, exhibiting a metal-insulator transition at ~ 340 K, is a good example. With increasing gating voltage, the transition temperature can be suppressed down to 5 K (Fig. 6d). Here, a different mechanism for the MIT transition is proposed, based on the release and creation of vacancies in the substrate, rather than electrostatically induced carriers.⁸

The influence on electrical conductivity is not only limited to artificial vacancies, but also occurs for complex materials with a large concentration of intrinsic vacancies, as described in Section 2.1. Te-based phase-change materials (PCM) such as GeTe (8–10% Ge vacancies), $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (20% vacancies on Sb/Ge sites), and GeSb_2Te_4 (25% vacancies on Sb/Ge lattice) are good examples. The change between the crystalline and amorphous phase happens on a sub-nanosecond timescale, accompanied by a resistivity change that can exceed four orders of magnitude (Fig. 7a). This makes PCM promising candidates for rewritable data storage and non-volatile electronic memory. Both experimental and theoretical results confirm that the transition is the result of a strong localization and re-arrangement of vacancies.^{24,25} As illustrated in Fig. 7b, in the amorphous state,

Ge, Sb, and a large concentration of vacancies are randomly dispersed over the cation Te sublattice. The orbital overlap is very sensitive to distortions because of the strong directionality of the resonant p bonds. This results in disorder-induced localization effects around the vacancies and large electron scattering. Insulating behavior is obtained in this way. With increasing temperature, the crystalline disorder is reduced. The mobility edge increases in energy and passes the Fermi energy. Then, a transition from Anderson-like insulating to metallic behavior occurs.

3.3. Room temperature magnetism

Room temperature ferromagnetic semiconductors, with their ability to couple both spin and charge with an external magnetic field, have attracted much attention because of their applications in various spintronics devices. However, semiconductors and insulators with ferromagnetism at room temperature are rare, and this has hampered applications in spintronics. We need to “create” or “induce” magnetic moments and endow them with robust room-temperature ferromagnetism. Doping with transition metals (Fe, Cu, Mn, *etc.*) is a convenient route and has been reported in many studies on materials such as doped ZnO and SnS_2 . However, clusters or secondary phases can form in the host semiconductors and this can be detrimental to their application performance. Doping with non-transition metal elements, for example C, K, B, and Mg, is a good solution since they do not form solid solutions that contribute to ferromagnetism. In finite size nanostructures, magnetism can be introduced by geometrical confinement. In short, lattice parameter changes influence the charge transfer between the majority- and minority-spin subbands. In the case of an increased lattice constant, weak hybridization is expected and charge transfer is inhibited. This results in an increase of the splitting of the two subbands and enhances the magnetic moment. The crystal distortion has a profound influence on the crystal-field splitting and the occupation of orbital states and also benefits the emergence of magnetism. This has been confirmed for many systems, such as various noble metal nanoparticles (Pd, Pt, Ru and Rh) and narrow t_{2g} -band perovskite oxides (YTiO_3 , LaTiO_3 , YVO_3 , and LaVO_3).²⁶

Vacancy engineering can influence the magnetic order easily by introducing broken symmetry, strain, and electronic or atom reconstructions, and is still the most attractive strategy. Here again we refer to $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures because of a series of startling phenomena observed, such as interface conductivity and superconductivity. Interface ferromagnetism can be observed clearly in the form of magnetization *versus* applied field hysteresis loops and extends up to room temperature (Fig. 8a).²⁷ This has triggered renewed interest to expand the applications of such interfaces. Orbital reconstruction of the Ti 3d states and reconstructed t_{2g} states, caused by the formation of oxygen vacancies at the interface, are believed to play an essential role. In contrast to pure SrTiO_3 with only Ti^{4+} , resonant soft-X-ray scattering (RSXS) clearly proved the existence of a low concentration of Ti^{3+} in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures.²⁸ This indicates the appearance of extra electrons at the interface

Fig. 7 (a) Temperature dependence of the sheet resistance of a 100 nm-thick GeSb_2Te_4 film measured in van der Pauw geometry on heating and subsequent cooling to room temperature. (b) Two-dimensional cut sketching the bonding situation in the rock-salt-like structure of GeSb_2Te_4 . Te atoms occupy the anion sublattice whereas the cation sublattice is randomly occupied by Ge atoms, Sb atoms, and vacancies respectively. All reproduced with permission from ref. 24. Copyright 2011 Nature Publishing Group.

Fig. 8 (a) Ferromagnetic magnetization versus applied field loops at different temperatures for ten unit cells of LaAlO_3 grown on SrTiO_3 . Reproduced with permission from ref. 27. Copyright 2011 Nature Publishing Group. (b) Schematic of the one-electron Ti 3d orbitals near the interface in SrTiO_3 films. Reproduced with permission from ref. 29. Copyright 2013 Materials Research Society. (c) Magnetic moment as a function of pressure for O-deficient SrTiO_3 . Negative pressure enhances the magnetic moment by formation of a high-spin state, while positive pressure stabilizes the low-spin state. Reproduced from ref. 31 with permission from the Royal Society of Chemistry.

due to oxygen vacancies. Tetragonally distorted TiO_6 octahedra are expected to form at the interface and this has been verified by Ti L-edge X-ray absorption linear dichroism (XLD). Such a distorted structure changes the degeneracy of the t_{2g} and e_g orbitals. Thus, a partially reduced orbital degeneracy of the 3d Ti states occurs. Specifically, both the in-plane d_{xy} orbital of the t_{2g} states and the $d_{x^2-y^2}$ orbital of the e_g states have lower energy than the out-of-plane orbitals d_{xz} , d_{yz} , and $d_{3z^2-r^2}$, respectively, as illustrated in Fig. 8b.²⁹ As a consequence, the additional electron ($3d^1$) in the Ti^{3+} state occupies the polarized d_{xy} orbital levels and is confined to the interface. A ferromagnetic moment of $\sim 0.1 \mu_B$ has been detected by surface-sensitive X-ray magnetic dichroism measurements.³⁰ More interestingly, the magnetic moment can be tailored by applying pressure, as shown in Fig. 8c. Theoretical work suggests that the formation enthalpy of oxygen vacancies can be reduced by chemical expansion and crystal-field effects. The resulting oxygen vacancies and charge imbalance at the interfaces can induce magnetism in nonmagnetic materials including LAO/STO heterostructures. With negative pressure, the three t_{2g} states in the 3d orbitals of Ti lead to the occupancy of majority spin states and an enhanced magnetic moment. A positive pressure results in an equal occupancy of both majority and minority t_{2g} and e_g states and the spins are switched from the high-spin to low-spin state.³¹

2D ultrathin nanosheets, represented by graphene and molybdenum disulfide, have been a central focus in attempts to induce ferromagnetism. The well-defined spin-splitting makes them ideal materials for spintronic devices. However, the creation of room temperature ferromagnetism in graphene is difficult because it is strongly diamagnetic and lacks d or f electrons. Bulk 2H-MoS_2 is nonmagnetic because the two 4d electrons of Mo^{4+} are low-spin. Generally, the existence of localized moments can be explained by Lieb's theorem considering a bipartite

Fig. 9 (a) Theoretical prediction of magnetic moments in graphene due to vacancies. Reproduced with permission from ref. 32. Copyright 2014 Nature Publishing Group. (b) Magnetization versus applied field loops for 2H-MoS_2 with an incorporated 1T phase at 5 K and 300 K. (c) Diagrammatic representation of the phase incorporation of 1T- MoS_2 in 2H-MoS_2 nanosheets, giving rise to ferromagnetism. (b) and (c) are reproduced with permission from ref. 34. Copyright 2015 American Chemical Society.

Hubbard model. Then, the total spin of the ground state can be determined by $S_{\text{tot}} = |H_A - H_B|/2$, where H_A and H_B are the moments of the sublattices. Thus, it is expected that the vacancy-induced inequality between the two sublattices can produce a net moment. Removing one carbon atom in graphene (Fig. 9a) results in the formation of three $\text{sp}^2\sigma$ dangling bonds at the three surrounding carbon atoms, and a local spin-polarized electronic density is created, as shown in Fig. 9b. The three dangling bond states will split due to the crystal field and Jahn-Teller distortion. One state is doubly occupied and resides deep in the Fermi sea. Another state is close to the Fermi level, singly occupied and localized at the σ bands. This produces a moment of $1 \mu_B$. The third state is quasi-localized and forms a narrow resonant state. A net magnetic moment ranging between 1 and $1.7 \mu_B$ is obtained this way.³² The high sensitivity to the smearing width, even for a large number of k points of thousands per unit cell, can explain the range of values for the magnetic moment.³³ More interestingly, the magnetic moments of 2D systems can be enhanced significantly by incorporating nanoregions of a second nonmagnetic phase, as illustrated in Fig. 9c. By introducing the 1T- MoS_2 phase in the 2H-MoS_2 lattice, a magnetic moment of $0.25 \mu_B/\text{Mo}$ is obtained at room temperature. The transformation from the 2H to the 1T phase is driven by the extra electrons from sulphur vacancies. The spins associated with a localized S vacancy align those of the surrounding Mo ions in the 1T phase and a net magnetic moment emerges. The ferromagnetic interaction occurs because the distance between neighbouring Mo ions in the 1T phase is smaller than the radius of a polaron.³⁴

4. Applications in energy conversion and storage

The 2015 United Nations Climate Change Conference held in Paris resulted in a landmark deal aimed to reduce greenhouse gas emissions to limit the global temperature increase. The G20 made an agreement to double their investment in clean energy research over the next five years. Solar cells, lithium ion batteries, supercapacitors and hydrogen are among the most promising and effective technologies to replace fossil fuels as the principal source of world energy. The performance of associated energy devices is strongly influenced by the functional materials used such as electrode materials and photocatalysts. Up to now, many materials have been developed and some of them have begun commercial production. The economic interests and energy efficiency of clean energy technology still poses a huge challenge. Fortunately, multifunctional vacancy engineering provides a powerful tool to continuously improve and optimize functional materials. This section summarizes some recent research progress in vacancy engineering for clean energy harvesting and storage.

4.1. Lithium ion batteries

Since the appearance of devices with lithium ion batteries (LIBs) as power sources in 1991, they have become considered as one of the most important energy storage systems. Extensive research has been performed and various portable electronic devices and vehicles driven by LIBs have been launched in the market. LIBs have high potential to store renewable energy, which will change the global energy equation fundamentally. LIBs generally consist of three parts: anode and cathode electrodes separated by an electrolyte that transfers the Li ions. In the charging process the lithium ions are moved from the cathode to the anode through the electrolyte. In the following discharge process, the lithium ions move back to the cathode across the electrolyte and produce energy. Many figures of merit are used to evaluate the performance of LIBs, including the specific capacity, specific power, cost, safety, and cycling ability. Clearly, reversible capacity and safety are prerequisite.

Among the numerous electrode materials, transition metal oxides and sulfides such as Fe_2O_3 , TiO_2 , FeS_2 , and MoS_2 have been researched extensively due to their low toxicity and high redox potential of the $\text{M}^{a+}/\text{M}^{b+}$ couples (here M represents transition metals with different valences). Vacancies, spontaneous or induced, influence the performance in many respects. For example, the diffusivity of Li in the electrode material depends on two transport processes: the electronic conductivity and the Li^+ diffusivity.³⁵ The diffusion coefficient can be improved by nanosizing, while the electronic conductivity can be tailored by the vacancy concentration. TiO_2 nanocrystals annealed either in vacuum or in hydrogen show a significant capacity enhancement and improved storage kinetics (Fig. 10a). The potential difference between the charge and discharge cycles for heat-treated samples was found to be 42.1% smaller than for the pristine sample. This result is associated with the formation of oxygen vacancies,³⁶ as shown in Fig. 10b. With increasing thermal treatment time,

Fig. 10 (a) Variation of discharge capacity with cycle number for pristine and vacuum-treated TiO_2 nanocrystals. Reproduced with permission from ref. 41. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Relaxation plot of electrical conductivity at 723 K under 5% H_2 /95% Ar atmosphere for TiO_2 nanocrystals. Reproduced with permission from ref. 36. Copyright 2012 American Chemical Society. (c) Schematic illustration of N-doped graphene during cycling: defect sites or vacancies gradually extend, facilitating more intercalation of Li^+ ions. The green circle represents vacancy areas in the first cycles. The red circle represents vacancy areas after many cycles. Dark atoms represent Li ions. Reproduced with permission from ref. 42. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Change in ionic conductivity of $\text{LiCB}_{11}\text{H}_{12}$ (blue) and $\text{NaCB}_{11}\text{H}_{12}$ (red) structures as a function of inverse temperature. Reproduced with permission from ref. 40. Copyright 2015 The Royal Society of Chemistry.

the conductivity is increased by one order of magnitude after 1 h, and by more than two orders of magnitude after 7 h of treatment. One should keep in mind that a higher conductivity does not always lead to better performance. Excess electrons suppress the concentration of free Li^+ and are detrimental for the reversible capacity. Vacancies can also act as Li^+ active sites in the cycling process. As illustrated in Fig. 10c, a number of ions are trapped in the vacancy areas during the initial cycles. With increased cycling, the vacancy areas are gradually extended and this benefits Li^+ intercalation. This is one explanation for the widely reported increasing capacity after cycling in many systems. In addition, high-valent substituents, such as Mo^{6+} or V^{5+} , can increase the vacancy content by a factor of 2–3 with respect to pure samples. This can significantly raise the electrode potential and is helpful for Li^+ insertion.^{37,38}

In recent years increasing efforts have been made to develop new electrolytes for LIBs based on the principle of vacancy effects. Most commercial LIBs contain flammable organic compounds, and these are blamed for the recent battery fire accidents caused by ignition of the electrolyte. Replacing them with inorganic solid-state Li-ion conductors has many advantages such as the absence of electrolyte leakage, superior electrochemical and thermal stability, and robustness to vibration and physical impact. An ideal solid state conductor requires high Li-ion conductivity and interfacial stability, especially at the interface with the anode and cathode material. A low activation

energy is preferred in order to achieve a broad range of operating temperatures. The most promising superionic conductor is $\text{La}_{2/3-x}\text{Li}_x\text{TiO}_3$ (LLTO), which is a perovskite with alternating Li-rich and La-rich A-site layers. It was found that the local structure of LLTO strongly depends on the distribution and concentration of A-site vacancies. In Li-poor areas the Li-ion conduction is confined within the La-poor layers. Migration along the *c*-axis is blocked and results in two-dimensional diffusion. In Li-rich areas migration between alternate La layers suggests three-dimensional conductivity. Simulations indicate that there is an optimal vacancy concentration with $x = 0.067$. This provides LLTO with the highest diffusion coefficient and lowest diffusion energy barrier among oxide Li ion conductors. A local lattice expansion of 8–10% was found when Li^+ diffuses through bottleneck structures formed by oxygen ions. It was proposed that the enlarged bottleneck size induced by the existence of A-site vacancies is the reason for the increased Li ion conductivity at this vacancy concentration.³⁹ The creation of more available cation vacancies per unit cell in $\text{LiCB}_{11}\text{H}_{12}$ and $\text{NaCB}_{11}\text{H}_{12}$ yields the largest high-temperature ionic conductivities among all polycrystalline electrolytes studied thus far (Fig. 10d).⁴⁰

4.2. Solar cells

The sun provides energy through photosynthesis. Every year 4×10^{24} J solar energy is absorbed on the earth. It is estimated that this number is twice as much as the energy available from all of the earth's non-renewable resources including coal, natural gas, crude oil, and mined uranium combined. Thus, solar energy provides renewable energy along with other sources such as wind, tidal and waves. Solar cells convert sunlight into electricity using the photovoltaic effect. The light absorbed in a semi-conducting material excites electrons to the conduction band. The activated electron moves from the cell into an external circuit, dissipates its energy and then returns to the solar cell. The challenge for solar cells is to manufacture a semiconductor that is economically viable, environmentally friendly, and resistant to oxidation and humidity. Obviously, a high conversion efficiency is required.

$\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) and related chalcopyrite materials have attracted strong interest because of their low cost and high efficiency, with values higher than 20% achieved. Commercial modules with stable efficiencies of about 13% have entered industrial mass production. Their performance is influenced significantly by the chemical composition and defect density. Raman scattering revealed the existence of Cu-poor Cu–In–Se ordered vacancy compound (OVC) phases in the surface region of the absorber. By preparing CIGS samples with different OVC concentrations, both the efficiency and open circuit voltage could be optimized as shown in Fig. 11a.⁴³ The inhibition of the formation of electronic defects with increasing OVC content may be the underlying reason for the improved performance. However, instability of solar cells with respect to long-term exposure to air and ultraviolet radiation remain a concern. Recent studies indicate that using a non-stoichiometric inorganic layer as the transparent hole contact is a good solution. As illustrated in

Fig. 11 (a) Open circuit voltage and cell efficiency versus relative intensity of the OVC Raman peak. Reproduced with permission from ref. 43. Copyright 2014 AIP Publishing LLC. (b) *J*–*V* curve for a $\text{MoO}_x/\text{n-Si}$ heterojunction solar cell measured under standard test conditions. The inset shows a false-coloured cross-sectional SEM image of the solar cell. Reproduced with permission from ref. 44. Copyright 2014 American Chemical Society. (c) Schematic illustration of PLD-deposited thin, nanostructured, and disordered NiO films fabricated as an electron blocking layer/hole extraction layer in $\text{MAPbI}_3\text{-PCBM}$ heterojunction solar cells. Reproduced with permission from ref. 45. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

the inset to Fig. 11b,⁴⁴ a film of MoO_x with a thickness of 15 nm was deposited on an etched silicon substrate. This was covered with a sputtered indium tin oxide (ITO) film and an evaporated, 100 nm thick Ag grid. A *J*–*V* curve for this solar cell is shown in Fig. 11b. The device shows an open-circuit voltage of 580 mV, a short-circuit current (J_{sc}) of 37.8 mA cm^{-2} and a fill factor (FF) of 65%, which corresponds to a power conversion efficiency of 14.3%. The existence of oxygen vacancies in the thin film was proven by XPS measurements. The concentration can be manipulated by changing the sintering temperature. The defect band inside the band gap caused by the oxygen vacancies is responsible for the high work function metal MoO_x with a low density of states at the Fermi level. This value can be further enhanced by nanostructuring (Fig. 11c), which allows more efficient electron blocking (recombination is suppressed) and hole extraction.⁴⁵ Importantly, many other transition metal oxides such as WO_x , VO_x and NiO_x show a similar effect.

Recently, organic–inorganic hybrid (OIH) solar cells, which combine the advantages associated with inorganic and organic (polymeric) materials, have become highly promising. In particular, perovskite ABX_3 ($X = \text{halide}$) solar cells have shown enormous progress. The conversion efficiency has improved from 3.8% to more than 20% in just 5 years. However, despite many investigations, several fundamental issues still remain unresolved. The anomalous hysteretic behavior in the current–voltage behaviour, even in cells exhibiting 20% efficiency (Fig. 12a), is one example.⁴⁶ Many explanations have been proposed, including charge carrier trapping, the ferroelectric effect, or ionic displacement. Recent studies indicate that ion diffusion processes involving vacancy

Fig. 12 (a) Forward and reverse current–voltage curves for a planar solar cell, showing hysteresis. Reproduced with permission from ref. 46. Copyright 2014 Nature Publishing Group. (b) Ion transport routes in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite structure. There are three ionic transport mechanisms involving conventional vacancy hopping between neighbouring positions: (left) I^- migration along an octahedron edge; Pb^{2+} migration along the diagonal direction $\langle 110 \rangle$; (right) CH_3NH_3^+ migration into a neighbouring vacant A-site cage involving motion normal to the unit cell face composed of four iodide ions. (c) Schematic diagrams indicating the influence of vacancy drift on the band energies of a p–i–n device at short circuit. E_c is the conduction band energy, E_v is the valence band energy and V_{bi} is the built-in potential. Iodide ion vacancies are represented by the squares with ‘plus’ signs. Implicit in the diagram is that the vacancies with effective positive charges are balanced by immobile cation vacancies (not shown) with effective negative charges. (b) and (c) are reproduced with permission from ref. 47. Copyright 2015 Macmillan Publishers Limited.

migration are the origin of the photocurrent hysteresis. It is reported that in perovskite structures like MAPbI_3 (MA = methylammonium), various vacancies such as iodine (V_i), MA (V_{MA}) and Pb (V_{Pb}) are present in the system with concentrations of up to 0.4% at room temperature. This makes ion diffusion across the vacancy sites possible in these close-packed structures. Generally, vacancy-assisted diffusion involves hopping between neighbouring positions and there exist three possible paths, as illustrated in Fig. 12b. Calculations suggest that the hopping of iodine ions possesses the lowest activation energy of about 0.58 eV. This value is almost the same as the measured activation energy for hysteresis, which lies between 0.60–0.68 eV. A built-in electric field is formed in the perovskite structure due to the difference in contact work function in the short circuit state (Fig. 12c). This built-in field is changed under forward bias and further influences the ability of ionic or vacancy charges to diffuse. This results in a different collection efficiency of

photo-generated charges and leads to hysteresis.⁴⁷ Studies by another group claimed an activation energy of 0.1 eV for V_i . The migration time is predicted to be less than 1 μs and is too fast to explain the slow response in the hysteresis. For V_{MA} and V_{Pb} , the estimated migration times are of the order of tens of ms to minutes, and the likely reason for the hysteresis.⁴⁸ Replacing MA^+ with larger cationic organic molecules like $(\text{NH}_2)_2\text{CH}^+$ (FA^+) can increase the activation energy. In any case, organohalide perovskites are prone to possess defects due to their low thermal stability. The migration of various ions will result in increasing lattice distortions, which are detrimental to cell performance. Introducing optimized vacancy concentrations or replacing MA with larger molecules are beneficial for the structural stability and suppression of hysteresis.

4.3. Hydrogen evolution

The concept of the hydrogen economy was proposed in 1970 and describes a system that delivers energy using hydrogen. The application spectrum of hydrogen is vast, from household use to the industrial production of methanol and methane, and includes hydrocarbon manufacture using CO_2 as the carbon feedstock. Hydrogen is also an excellent fuel to power our mobility and transportation needs. Hydrogen powered cars that can drive 500 km have been produced and their range is expected to reach 800 km in 2020. The main challenge is the production of hydrogen in an efficient and economical way. At present, there are several methods to produce hydrogen. The simplest strategy is to split water through the following electro-catalytic reaction:

Abundant solar energy and water combined with vacancy engineering make water splitting an ideal method of hydrogen production.

There are two ways to improve the photocatalytic efficiency. First, we need a broad absorption band, especially for visible light. Second, an improvement in the charge-carrier separation efficiency is required. As discussed in Section 3.1, vacancy engineering is a powerful tool to tailor band structures. For example, the band gap of CdS nanocrystals is narrowed by 0.17 eV by introducing S vacancies. This results in a significant red-shifted absorption edge and the onset of hydrogen production at about $\lambda = 600 \text{ nm}$.¹¹ By thermal treatment of bulk 2D graphitic carbon nitride, large concentrations of carbon vacancies are created. This can increase the electrical conductivity and the mobility of photo-generated charge carriers.⁴⁹ The light absorption can be extended into the near-infrared, yielding a lower, flat potential band. The larger donor density (Fig. 13a), reduces the probability of recombination. The hydrogen production rate is 20 times larger than for samples without vacancies (Fig. 13b). In addition, the localized surface plasmon resonance (LSPR) can be applied in semiconductors due to the presence of outer d-valence electrons. In combination with an appropriate concentration of vacancies, this enhances the local electric field and accordingly promotes charge-carrier separation. It should be noted that the location of vacancies is important. In some cases,

Fig. 13 (a) Diffuse reflectance spectrum and Tauc plots (inset), and (b) photocatalytic H_2 evolution performance of 2D graphitic carbon nitride with and without carbon vacancies. Reproduced with permission from ref. 49. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Free energy for different S-vacancy concentrations in the range 0–25%. (d) Schematic top (upper panel) and side (lower panel) views of MoS_2 with strained S-vacancies on the basal plane, where the S-vacancies serve as the active sites for hydrogen evolution and applied strain further tunes the hydrogen evolution activity. Reproduced with permission from ref. 10. Copyright 2015 Nature Publishing Group. (e) Minimum-energy structure of the distorted bulk truncation model for Fe_3O_4 and (f) side views of the subsurface cation vacancy structure. A pair of Fe_{oct} cations from the third layer is replaced by an interstitial Fe_{tet} (labeled Fe_{int}) in the second layer. Reproduced with permission from ref. 50. Copyright 2014 American Association for the Advancement of Science.

the existence of vacancies can change the d-electron states of the adjacent atoms by trapping the electrons from the vacancy. The created levels can act as recombination centres for the photo-induced electrons and holes, leading to a decrease in photocatalytic activity.

Interestingly, vacancies can create new catalytic sites in inert planes of a photocatalyst. For example, the basal plane of pristine 2H- MoS_2 is inert with a high hydrogen adsorption free energy (ΔG_{H}) of 2 eV. ΔG_{H} is known to scale with the activation energy for dissociation and can act as a figure of merit for catalytic efficiency. $\Delta G_{\text{H}} = 0$ indicates the highest intrinsic reaction activity. The introduction of S-vacancies can significantly decrease ΔG_{H} . A small value of 0.08 eV can be obtained for S-vacancy concentrations of 9–19% (Fig. 13c). Applying uniaxial elastic strain further decreases ΔG_{H} and activates the inert plane, as shown in Fig. 13d. The active site density and the structural stability are optimized for a vacancy concentration of 11%. In addition, vacancies can induce atom redistribution on the surface. Ordered arrays of Fe vacancies and interstitials on the (001) facets of Fe_3O_4 act as an important catalyst for

heterogeneous reactions and hydrogen production, as shown in Fig. 13e and f.⁵⁰ In this case, noble metals like Au, Ag and Pt have a tendency to bond with the surface oxygen atoms without the second layer Fe_{tet} atoms. They are extremely stable and can resist agglomeration into clusters up to 700 K. This provides an ideal system to uncover single-atom catalytic mechanisms.

5. Summary and outlook

Defects, especially elemental vacancies, exist universally and are inevitable in materials. Due to the difficulty in precisely mapping vacancy distributions and concentrations, their influence on properties is often underestimated. In fact, by careful manipulation, one can control the electrical, magnetic, thermal and mechanical properties. Moreover, in comparison with other strategies, vacancy engineering does not need to introduce impurities. Thus, the problem of lattice distortions and secondary phase formation, which is often detrimental to material performance, can be avoided. Recent years have witnessed fruitful studies on tailoring properties and application performance, especially in the field of clean energy storage and harvesting materials. Obviously, the design of superior functional materials is key for energy devices. It is important not only in terms of fundamental scientific research, but also to limit global warming.

Our understanding of how vacancies influence various properties is limited by the lack of an absolute method to determine their positions and concentrations. Although some techniques, for example tracking electron energy-loss spectroscopy (EELS) fine structure, or intensity refinement of high-resolution transmission electron microscopy images allow us to map elemental vacancies with high resolution, a general quantitative tool that is suitable for most energy materials is desired. In addition, we note that vacancies are not always beneficial for semiconductor applications. For example, they can form scattering centres and decrease the electron mobility, limiting the performance of electronic devices. In addition, vacancies on the surface can give rise to serious lattice distortions or even the formation of second phases. This can mask the inherent properties of the material and lead to poor performance. Therefore, the removal of vacancies is also an important objective in vacancy engineering. In summary, the rich physical properties induced by vacancies, coupled with the recent success in the design of superior functional materials for energy device applications, inspire growing research interest in vacancy engineering.

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