Article type: Review

Atomically Thin Non-Layered Nanomaterials for Energy Storage and Conversion

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Abstract: After the discovery of graphene, two-dimensional nanomaterials with atomic thickness and large lateral size have attracted tremendous research interest due to their high specific surface areas, exotic electronic structures, and fascinating physical and chemical properties. Even though recent studies are mainly focused on atomically thin nanomaterials with layered structures due to their easy preparation and characterization, the investigation of non-layered nanomaterials is also proceeding as new types of ultrathin nanostructures are constantly being created, such as metals, metal oxides, metal chalcogenides, some transition metal dichalcogenides, and perovskites. Here in this review, we comprehensively summarize the preparation methods for atomically thin non-layered nanomaterials, study their exotic electronic structures, introduce electronic-structure manipulation strategies, and provide an overview of their applications in energy storage and conversion, with particular emphasis on lithium-ion batteries, sodium-ion batteries, catalysis of hydrogen evolution, oxygen evolution,

CO₂ reduction, CO oxidation reactions, *etc.* The central theme of this review is to provide correlation among the materials synthesis, structural and electronic properties, and their major applications. Finally, based on current research progress, we propose future directions yet to be explored for enhanced properties and novel functionalities in practical applications.

1. Introduction

In 2004, Novoselov and Geim successfully made graphene by repeatedly cleaving graphite with adhesive tape.¹ Following studies demonstrated the incredible properties of graphene, such as the quantum Hall effect, ultrahigh carrier mobility, large specific surface area (theoretical value: 2630 m² g⁻¹), and high Young's modulus (~1 TPa), as well as excellent mechanical flexibility, optical transparency (~97.7%) and thermal conductivity (3000-5000 W m⁻¹ K⁻¹).²⁻⁵ Since then, there has been a growing research interest in the development of two-dimensional (2D) graphene-like nanomaterials with atomic thickness (typically < 5 nm), which include black phosphorus,^{6,7} hexagonal boron nitride,^{8,9} graphitic carbon nitride,^{10,11} transition metal dichalcogenides,^{12,13} and layered double hydroxides,^{14,15} as well as some newly developed metal-organic frameworks,^{16,17} covalent-organic frameworks,^{18,19} MXenes,^{20,21} silicene,²²⁻²⁴ germanene,^{25,26} *etc.* The preparation and investigation of atomically thin nanomaterials are of great importance compared with other nanomaterials due to a number of unique advantages. First, the atomic thickness and strong in-plane chemical bonds endow them with excellent mechanical (high strength and flexibility), electronic (tunable band gap), and optical (high transparency) properties, which are essential for next-generation devices.^{27,28} Second, the high specific surface area facilitates surface-dominated and diffusion-controlled reactions in catalysis, supercapacitors, and rechargeable batteries.²⁹⁻³¹ Third, the large fraction of surface atoms allows easy surface engineering, by such means as defect creation and 2D heterostructure construction, for enhanced properties and novel

functionalities.³²⁻³⁴ Fourth, the ultrathin 2D geometry provides a simple and ideal model to study the electronic-state modulation and establish clear structure-property relationships.³⁵⁻³⁷ Based on these appealing advantages, atomically thin nanomaterials show great promise in a wide range of applications, including (opto)electronics, sensors, biomedicine, energy storage and conversion, *etc.*³⁸

Despite the great efforts that have been made in the development of graphene-like nanomaterials, previous works mainly focus on those with layered structures, which have strong in-plane chemical bonds but weak out-of-plane van der Waals bonds.⁵ These materials have been intensively studied because the nanosheets with single- or few-layer thickness can be easily produced by mechanical exfoliation, liquid exfoliation, chemical vapor deposition, *etc.*^{39,40} Actually, atomically thin non-layered nanomaterials with strong chemical bonds in the third dimension have also witnessed increasing research interest, especially over the past few years.³⁰ The study of atomically thin non-layered nanomaterials has not only provided great enrichment to the 2D nanomaterial family, but also offered some novel electronic properties due to their abundant surface dangling bonds and obvious structural distortion. A detailed comparison between atomically thin layered and non-layered nanomaterials in terms of their classifications and structural and electronic properties can be found in Scheme 1. As the top-down exfoliation method is ineffectual for the preparation of ultrathin non-layered nanomaterials, bottom-up wet-chemical synthesis and topochemical transformation have been widely exploited and gained substantial achievements.^{5,40} To date, more than 50 atomically thin non-layered nanomaterials have been successfully developed, which mainly include metals (*e.g.*, Co, Au, Ag, Pt and Rh), metal oxides (*e.g.*, Fe₂O₃, Co₃O₄, CeO₂ and In₂O₃), metal chalcogenides (M_aX_b, where M = Co, Ni, Zn, Cu, Pd, Cd, In, *etc.*, and X = S, Se, Te), transition metal dichalcogenides (TMDs, some of group VIII metal-based compounds, *e.g.*, CoS₂, CoSe₂ and FeS₂), perovskites (*e.g.*, CsPdBr₃ and CH₃NH₃PdI₃), *etc.* The unique and exotic structural and electronic properties of atomically thin non-layered nanomaterials endow

them with short ion-diffusion paths, numerous surface active sites, adjustable band gaps, as well as enhanced electrical conductivity and carrier mobility, which have greatly promoted their applications in advanced energy storage and conversion, such as supercapacitors, rechargeable batteries, catalysis, and photodetectors.^{41,42} A brief summary of the synthetic methods, dimensions, electronic structure manipulation strategies, physical and chemical properties, and energy-related performances of the reported atomically thin non-layered nanomaterials is provided in Table 1.

In the following sections, we will give a detailed and comprehensive overview of the research progress of atomically thin non-layered nanomaterials (Scheme 2). We start from the recently revealed advantages of synthetic approaches, including self-assembly, oriented attachment, lamellar intermediate-assisted exfoliation, 2D template synthesis, and topochemical transformation. Their structural and electronic properties are then briefly discussed. After that, we summarize the strategies for the manipulation of electronic states, such as thickness control, pit/pore creation, vacancy engineering, elemental doping, and 2D heterostructure construction. Furthermore, the advantages of atomically thin non-layered nanomaterials in energy storage and conversion applications, including supercapacitors, lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), catalysis of hydrogen evolution (HER), oxygen evolution (OER), CO₂ reduction, CO oxidation reactions, *etc.*, are introduced in detail. At the end of this article, we also provide some personal viewpoints on the challenges and opportunities of this promising field.

2. Synthetic Strategies for Atomically Thin Non-Layered Nanomaterials

Due to the intrinsic isotropic nature of metallic, ionic, and covalent bonds in non-layered bulk materials, it is very difficult to break these strong chemical bonds on a given plane, and we are thus unable to prepare atomically thin nanosheets through top-down exfoliation strategies.

In view of this, bottom-up wet-chemical synthesis has been successfully developed and continuously optimized to break the thermodynamic equilibrium state and control the aggregation kinetics, which consequently lead to the anisotropic growth of atomically thin non-layered nanocrystals.⁴⁰ In addition, in situ topotactic conversion from layer-structured precursor nanosheets has also emerged as an effective approach to produce various atomically thin non-layered nanomaterials.⁴¹ In this section, we introduce several well-developed synthetic strategies, including self-assembly, oriented attachment, lamellar intermediate-assisted exfoliation, 2D template synthesis, and topochemical transformation. The advantages and restrictions of each strategy are also discussed.

2.1. Self-Assembly

Self-assembly is the most widely used method for the synthesis of atomically thin non-layered nanomaterials.⁴³⁻⁴⁷ In a typical assembly process, nanocrystal building blocks are first generated in a hydrothermal or solvothermal reaction. Then, they spontaneously self-assemble by weak interactions, such as van der Waals forces, electrostatic interactions, and hydrogen bonds. The targeted ultrathin nanosheets are finally obtained after some post-treatments. For example, Kotov and co-workers prepared free-floating particulate CdTe nanosheets with an ultrathin thickness of ~ 3.4 nm by the self-assembly of small CdTe nanocrystals.⁴³ After performing experiments and computer simulations, they found that the dipole moment, small positive charge, and directional hydrophobic attraction are most likely the driving forces for the assembly process. Zuchermann *et al.* reported the synthesis of giant and free-floating organic 2D nanocrystals with atomic thickness of 2.7 nm by assembling two oppositely charged peptoid polymers. It was demonstrated that the self-assembly process was directed by periodic amphiphilicity, electrostatic recognition, and aromatic interactions.⁴⁴

In most cases, surfactants are incorporated to selectively adsorb on specific planes of nanocrystals, which prevent the assembly along these directions and achieve 2D lateral

growth. To date, many kinds of surfactants have been proved to be efficient in promoting the growth of atomically thin non-layered nanosheets, including 1-dodecanethiol,⁴⁸⁻⁵⁰ n-butylamine,⁴⁶ oleylamine,⁵¹ trioctylamine,⁵² aminoethanol,⁵³ poly(vinylpyrrolidone),⁴⁷ 1,5-pentanediol,⁵⁴ thiol-polyethylene glycol,⁵⁵ carbon monoxide (CO),^{56,57} salt species,⁵⁸⁻⁶⁰ *etc.*^{61,62} For instance, Xie's group prepared 4-atom-thick Co sheets (0.82 nm) with and without Co oxide using a ligand-confined growth approach.⁴⁶ In a typical synthesis, cobalt(III) acetylacetonate initially hydrolyzes to give $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ under heat treatment. At the same time, n-butylamine is adsorbed on the hydrated oligomers to reduce the surface energy and promote the condensation in two dimensions. Partially oxidized and pure Co atomic layers are finally achieved by controlled reduction of cobalt ions using dimethylformamide during the growth of the nanosheets (Fig. 1a and b). Li's group reported the synthesis of single-atom-thick rhodium nanosheets (< 0.4 nm) with poly(vinylpyrrolidone) as the capping agent (Fig. 1c and d).⁴⁷ Manna's group synthesized atomically-thin single-crystal CsPdBr_3 nanosheets (~3 nm) by using short ligands (octanoic acid and octylamine) mixed with long ones (oleic acid and oleylamine).⁶¹ The plane length of the nanosheets could be adjusted between 300 nm and 5 μm while the thickness remains almost constant by changing the ratio of short to long ligands. In addition to the capping effect, surfactants could also participate in the in-plane assembly of inorganic nanocrystals. For example, oleylamine molecules could adsorb at the side surfaces and corner sites of the Co_9S_8 nuclei, which then undergo in-plane connection and finally lead to the formation of atomically thin inorganic-organic hybrid nanosheets (Fig. 1e).⁵¹ The Co_9S_8 nanocrystals are half-unit-cell thick (~0.5 nm) and randomly distributed throughout the 2D hybrid nanosheets (Fig. 1f).

The self-assembly strategy is a simple, efficient, and cost-effective method for the synthesis of atomically thin non-layered nanomaterials with high yield. However, the synthesis is highly sensitive to the experimental conditions, especially the use of surfactants. Any changes in the type or amount of the surfactant would result in big differences in the

morphology of the final products. In addition, the thus-prepared nanosheets normally exhibit poor crystallinity as the nanocrystal building blocks are randomly distributed and connected with each other through the weak bonds of van der Waals forces, electrostatic interactions, or hydrogen bonds, which may lead to unsatisfactory electrical and optical properties, such as low electrical conductivity and poor luminescence performance.

2.2. Oriented Attachment

Different from the self-assembly approach with nanocrystal building blocks randomly distributed throughout the nanosheets, the oriented attachment strategy involves the rotation, alignment, attachment, and coalescence of nanocrystals by sharing a common crystallographic facet due to the entropy-driven elimination of high surface energy facets. The oriented attachment process could be well understood by the growth mechanism of ZnO nanosheets proposed by Wang's group. At the initial stage, tiny nanocrystals are generated and self-organized stochastically into a continuous amorphous film (Fig. 2a). Then, these nanocrystals attach to each other through the interatomic bonds between high energy facets at an aligned orientation (Fig. 2b). Finally, the amorphous film is fully crystallized and a single-crystal nanosheet is generated (Fig. 2c).⁶³

To date, many atomically thin non-layered nanomaterials have been successfully developed through the oriented attachment strategy, including CeO₂,⁶⁴ PdS,⁶⁵⁻⁶⁸ PdSe,^{69,70} ZnO,⁶³ Co₉Se₈,⁷¹ SnO₂,⁷² WO₃,⁷³ *etc.* For instance, ultrathin single-crystal CeO₂ nanosheets (~2 nm) were synthesized with their top and bottom surfaces enclosed by the {111} facets (Fig. 2d and e).⁶⁴ Single-crystal Co₉Se₈ nanosheets down to half-unit-cell thickness were prepared with {400} planes exposed on the surface (Fig. 2f).⁷¹ Sometimes, surfactants are applied to tune the surface energy of nanocrystals, which achieve 2D confined growth. As a typical example, considering that PdS nanocrystals have a cubic symmetry and easily aggregate into 3D structures, Weller's group used oleic acid as a surfactant, which adsorbs on

the {100} facets of the nanocrystal and facilitates 2D oriented attachment *via* the {110} facets.⁶⁵ Oleic acid was also selected as the capping agent to direct the formation of ultrathin single-crystal PdSe honeycomb superlattices with nanocrystals occupying two parallel planes (Fig. 2g and h).⁶⁹ Atomically thin CdSe can be obtained from the PdSe lattice through cation-exchange with the nanoscale honeycomb geometry intact, which indicates the robust structure of this honeycomb superlattice (Fig. 2i).

The oriented attachment strategy could prepare atomically thin non-layered nanosheets with a high degree of crystallinity and orientation. However, it is only efficient for a few nanomaterials and cannot be readily extended to others due to the rigorous synthetic conditions, such as on concentrations of reactants, surfactant selection, and reaction temperature and time. Therefore, more efforts are still needed to improve the applicability of this oriented attachment method.

2.3. Lamellar Intermediate-Assisted Exfoliation

Considering the great challenge in breaking the robust metallic/covalent/ionic bonds in non-layered compounds through direct exfoliation, lamellar intermediate-assisted exfoliation has emerged as an effective strategy to prepare atomically thin non-layered nanomaterials. In this synthetic method, organic molecules, such as n-propylamine,⁷⁴ n-hexylamine,⁷⁵ n-octylamine,^{76,77} diethylenetriamine,⁷⁸ triethylenetetramine,⁷⁹ and mixtures of oleyamine and octylamine,^{80,81} are selected as soft templates, which combine with metal salts to form lamellar hybrids with inorganic slabs separated by organic amines. After that, the single-layer intermediates are obtained by ultrasonic-assisted exfoliation. Clean and freestanding atomically thin nanosheets are finally prepared after surfactant removal by heat treatment (Fig. 3a). Li and co-workers carried out some important preliminary works on synthesizing a group of inorganic-organic hybrid nanomaterials, namely [(MQ)(L)] and [(M₂Q₂)(L)] nanostructures (where M represents Mn, Zn, Cd; Q = S, Se, Te; and L stands for mono- or diamine molecules

or hydrazine).⁸² Based on these works, Xie's group successfully prepared a lamellar hybrid $(\text{Zn}_2\text{Se}_2)(\text{n-propylamine})$ intermediate. ZnSe single layers, 0.89 nm in thickness, were finally obtained after liquid exfoliation and surfactant removal (Fig. 3b).⁷⁴ Zhang's group employed octylamine and oleylamine as the surfactants and synthesized $(\text{CuCl}(\text{octylamine}, \text{oleylamine})_x)$ lamellar hybrid intermediate. The intermediate was finally converted to high-quality ultrathin CuS nanosheets (~ 3.2 nm) after the addition of sulfur powders and the subsequent removal of surfactants (Fig. 3c).⁸⁰ Similarly, ultrathin $\text{Zn}_{1-x}\text{Cd}_x\text{S}$,⁷⁵ CdSe (Fig. 3d),^{76,81} PdS,⁷⁷ CdS,⁷⁸ and Co_3S_4 (Fig. 3e)⁷⁹ nanosheets were also successfully prepared *via* the lamellar intermediate-assisted exfoliation strategy.

Our group proposed a generalized and fundamental approach for the synthesis of ultrathin transition metal oxide nanosheets, including TiO_2 , ZnO, Co_3O_4 , WO_3 , *etc.*⁸³ In our method, polyethylene-oxide–polypropylene-oxide–polyethylene-oxide was controlled to form inverse lamellar micelles based on the phase behavior of the surfactant-water-oil equilibrium system. The hydrated inorganic oligomers were then confined inside the inverse lamellar micelles, leading to the formation of layered inorganic oligomer agglomerates. Hydrothermal reaction was then performed to improve the organization and crystallization. Finally, atomically thin nanosheets were collected after removing the surfactant templates (Figure 3f). The thicknesses of different types of nanosheets vary between 1.6 and 5.2 nm, and the sizes between 0.2 and 10 μm (Fig. 3g).

The lamellar intermediate-assisted exfoliation strategy could be used to prepare high-quality (clean, flat, uniform, and free-standing) atomically thin non-layered nanosheets on a large scale and with high yield. Moreover, this method is also highly applicable and can be extended to the synthesis of other 2D non-layered nanomaterials. The poor crystallinity of the thus-prepared nanosheets, however, inevitably impedes their applications in energy-related electronic devices.

2.4. 2D Template Synthesis

Templates could direct the synthesis of various kinds of nanostructured materials, which has been widely investigated in the past two decades.⁸⁴ For the synthesis of atomically thin non-layered nanomaterials, the used templates can be classified into two types: 2D soft colloidal templates and 2D hard colloidal templates. Since the soft template method, which uses surfactant micelles as the structure directing agents, has already been included in self-assembly, oriented attachment, and lamellar intermediate-assisted exfoliation methods, we will focus on the hard template synthetic strategy in this section.

The selection of the template is of crucial importance, since the assembly of nanocrystals should be limited within a 2D confined space and the growth along the third dimension must be retarded.⁴¹ Graphene oxide (GO) has been recognized as the most popular template, as it possesses a large amount of oxygen-containing functional groups and shows strong affinity towards the inorganic materials.⁸⁵⁻⁸⁸ In addition, it is highly dispersible in solvent, which could direct the growth of ultrathin nanosheets with a high throughput. As a typical example, Li and Bai successfully synthesized ultrathin γ -Al₂O₃ nanosheets (~4 nm) by duplicating the shape of GO.⁸⁶ In detail, a continuous and uniform amorphous basic aluminum sulfate (BAS) layer was first coated on the GO surface through a homogeneous deposition method. After that, GO was removed from the composite and the BAS layer was converted into Al₂O₃ nanosheet by calcination at 800 °C (Fig. 4a and b). As another example, Zhang and co-workers reported the *in situ* preparation of colloidal form of Au square nanosheets on the surface of GO. The nanosheets have a thickness of ~2.4 nm and possess a hexagonal close-packed crystal structure (*hcp*) that has never been reported (Fig. 4c).⁸⁷ Besides GO, other inorganic 2D templates were also developed to assist in the synthesis of atomically thin non-layered nanosheets.⁸⁹⁻⁹² For example, the *hcp* Au nanosheets prepared on GO could further serve as templates to direct the growth of various noble metal heterostructures including

Au@Pt (Fig. 4d top), Au@Pd (Fig. 4d bottom), and Au@Ag (Fig. 4e).^{90,91} Half-unit-cell nanosheets of α -Fe₂O₃ (~0.59 nm) were also prepared *via* a CuO template-assisted oriented growth strategy (Fig. 4f).⁹²

The templates mentioned above can be regarded as physical templates that are not involved in obvious chemical transformations during the synthesis. There is also one kind of self-sacrificial templates which not only act as the directing agents, but also are chemically transformed into the resultant materials.^{93,94} For instance, a cation exchange reaction strategy was utilized to prepare ultrathin chalcopyrite-type CuInSe₂ nanoplatelets (~2 nm) by employing CuSe nanoplates as the sacrificial templates.⁹³ The well-matched crystal lattices and the similar Se atomic arrangements between (112) CuInSe₂ and (001) CuSe enable the epitaxial growth of CuInSe₂ nanoplatelets on CuSe nanoplates (Fig. 4g and h). It was also reported that hexagonal CuSe nanosheets can be successfully transformed into cubic Cu_{2-x}Se nanosheets with well-retained morphology in the presence of Cu^I cations under heat treatment (Fig. 4i).⁹⁴ This approach could also be applied in the synthesis of djurleite Cu_{1.97}S nanosheets from hexagonal CuS templates.

Generally, the 2D template synthesis is efficient in preparing some types of atomically thin non-layered nanomaterials. Nevertheless, some problems, such as the crystal growth along the third dimension and the selection of the 2D template, still need to be addressed in order to improve the quality of the nanosheets and extend this strategy to the preparation of a broad range of ultrathin non-layered nanomaterials.

2.5. Topochemical Transformation

The topochemical transformation strategy has been proved to be an easy and facile approach to fabricate atomically thin non-layered metals,^{89,95} metal oxides,⁹⁶⁻¹⁰² chalcogenides,^{95,103} nitrides,¹⁰⁴ and organic-inorganic perovskites,^{105,106} which is implemented by surface modification, heat treatment, sulfidization, nitrogenization, and molecules/ions intercalation

of/into the layered precursor nanosheets, respectively. For instance, Zhang and co-workers found that *hcp* Au square nanosheets could be converted to face-centered cubic (*fcc*) structure *via* surface ligand exchange or surface coating by ultrathin metal layers such as Ag, Pt, and Pd.⁸⁹⁻⁹¹ The phase transformation is mainly attributable to the surfactant-induced surface reconstruction or the interplay of surfactant-metal bonding energy. Our group reported the synthesis of graphene-like Co₃O₄ nanosheets by simply calcinating the amorphous Co(OH)₂ precursor.⁹⁶ The obtained nanosheets present an atomic thickness (1.6 nm) and mesoporous structure (Fig. 5a). Xie's group developed a fast-heating strategy to prepare a variety of ultrathin nanosheets including Co₃O₄ (1.5 nm, Fig. 5b; 1.72 nm, Fig. 5c),^{99,100} NiCo₂O₄ (1.6 nm, Fig. 5d),¹⁰² CeO₂ (0.6 nm, Fig. 5e),⁹⁸ and In₂O₃ (0.9 nm, Fig. 5f)⁹⁷ from their corresponding precursors α -Co(OH)₂/Co(CO₃)_{0.5}(OH)·0.11H₂O, NiCo hydroxides, CeCO₃OH, and In(OH)₃, respectively. These nanosheets possess numerous oxygen vacancies and low-coordinated surface atoms, which show exceptional properties for energy conversion and storage applications. They also reported the synthesis of ultrathin metallic Ni₃N nanosheets by nitrogenization of Ni-based precursor nanosheets (Fig. 5g),¹⁰⁴ which have a thickness of 3 nm and exhibit a mesoporous structure. Yang and co-workers prepared ultrathin iron-nickel sulfide nanosheets (~2 nm) by topotactic conversion from FeNi LDHs nanosheets (Fig. 5h).¹⁰³ The sulfidation transformation also leads to porous structure and rough surfaces. Bao and co-workers first reported the synthesis of atomically thin CH₃NH₃PdI₃ by taking the advantage of layered characteristic of PdI₂ and vapor-phase intercalation (Fig. 5i).¹⁰⁵ The resulted nanosheets are triangle and hexagonal in shapes and possess single or double unit cell thickness, respectively.¹⁰⁶

The topochemical transformation strategy shows its novelty and practicality in preparing atomically thin non-layered nanomaterials from their layered precursor nanosheets. This approach, however, similar to the self-sacrificial template strategy, also needs highly matched crystal lattices between the precursors and the final products. Otherwise, the

nanosheets could easily break into nanoparticles during the phase conversion process.

3. Structural and Electronic Properties of Atomically Thin Non-Layered Nanomaterials

As a class of graphene analogues, atomically thin non-layered nanomaterials possess atomic or molecular thickness and infinite planar dimensions, which endow them with ultrahigh specific surface areas and a large fraction of low-coordinated surface atoms.⁴⁷ More remarkably, the loss of neighboring layers causes an obvious lattice structure distortion, which contributes to reducing the surface energy and stabilizing the crystal structure. The lattice structure distortion of ultrathin nanosheets, normally accompanied by bond elongation, contraction, rotation, and even bond breaking and formation, results in different electronic states (*e.g.*, increased density of states (DOS) near the Fermi level) compared with their bulk counterparts.⁷⁴ The variation in electronic structures leads to predictable changes in their band gap, electrical conductivity, and carrier mobility, as well as the exceptional properties of ferromagnetism, half-metallicity, superconductivity, topological insulator, *etc.*³⁴

As a typical example, the electronic properties of 4-atom-thick ZnSe single layers were studied by synchrotron X-ray adsorption fine structure measurements (XAFS) and first-principles density functional theory (DFT) calculations.⁷⁴ The XAFS measurements at both Zn and Se K-edges show that there are big differences among clean ZnSe single layers, exfoliated ZnSe-*n*-propylamine (ZnSe-pa) single layers and bulk ZnSe in their Zn K-edge $k\chi(k)$ oscillation curves (Fig. 6a). In addition, there is also a decrease in peak density and a shift of the peak position for clean ZnSe single layers in the R-space curves (Fig. 6b). These results indicate the different local atomic arrangements of these three ZnSe samples. As clearly depicted from the structure model of clean ZnSe single layers, to maintain the structural stability, the surface Zn-Se bonds are stretched (2.48 Å), the nearest Zn-Zn bonds

are contracted (3.85 Å), and the Se-Se distances are elongated significantly (4.11 Å) (Fig. 6c). As a result of bond elongation and contraction, the surface Zn-Se-Zn bond angle of ZnSe single layers exhibits a considerable compression of 7.1°, while the Se-Zn-Se bond angle displays a slight stretching of 2.5°, compared with the bulk value of 109.5°, suggesting a noticeable structural distortion of clean ZnSe single layers. The lattice distortion has a substantial effect on the electronic properties. DFT calculations show that the ZnSe single layers display obviously increased DOS at the edge of the conduction band compared with bulk ZnSe, which ensures a high separation and migration rate of electrons (Fig. 6d).

As another example, half-unit-cell α -Fe₂O₃ nanosheets were prepared *via* a template-assisted oriented growth strategy.⁹² The X-ray photoelectron spectroscopy (XPS) spectrum of the Fe 2p_{3/2} peak for α -Fe₂O₃ nanosheets exhibits a negative shift and becomes asymmetric compared with bulk α -Fe₂O₃, suggesting splitting of the electronic structure for Fe ions. The X-ray absorption near-edge structure (XANES) results for the Fe K-edge reveal a difference in the Fe coordination environment between α -Fe₂O₃ nanosheets and their bulk counterpart. In contrast to the 6-coordinated Fe in bulk α -Fe₂O₃, the Fe ions in the ultrathin nanosheets are in the mixed states of 5- and 6-coordinations. As a consequence, contrary to the antiferromagnetism of bulk α -Fe₂O₃, the half-unit-cell α -Fe₂O₃ nanosheets exhibit robust intrinsic ferromagnetism of 0.6 μ_B /atom at 100 K and remain ferromagnetic at room temperature.

Our group studied the surface chemical states of atomically thin TiO₂, ZnO, Co₃O₄, and WO₃ nanosheets by XPS and DFT calculations (Fig. 7).⁸³ The XPS spectra show that the core levels of Ti 2p, Zn 2p, Co 2p and W 4f in nanosheets exhibit a 0.5-2 eV negative shift as compared with those in bulk crystals. The lower binding energy originates from the electron transfer to metal atoms from the surrounding oxygen atoms. DFT calculations further suggest that the metal atoms in ultrathin nanosheets are surrounded by higher electron densities with reduced chemical states, which is accompanied by new bond formation, bond breaking or

bond distortion between the metal-oxygen atoms in the crystal structures. These findings demonstrate the unique chemical states of atomically thin non-layered nanomaterials, which may introduce some anticipated physical and chemical properties, such as enhanced electrical conductivity and widened bandgaps.

4. Electronic-Structure Manipulation Strategies for Atomically Thin Non-Layered Nanomaterials

The electronic structure establishes a direct correlation between the microscopic structure and the macroscopic physical and chemical properties. Therefore, it is of vital importance to manipulate the electronic structures of atomically thin non-layered nanomaterials to achieve enhanced properties and novel functionalities.^{34,37} To date, many strategies have been developed to modulate the electronic structures, including thickness control, pit/pore creation, vacancy engineering, elemental doping, 2D heterostructure construction, *etc.* In this section, we will discuss these modulation techniques in detail by providing some typical examples.

4.1. Thickness Control

To maintain the structural stability, surface lattice distortion inevitably occurs on ultrathin nanosheets with thickness down to the atomic scale, which leads to changes in the electronic states compared with their bulk counterparts. Therefore, one of the most reasonable ways to modulate the electronic structure is to control the thickness of the nanosheets. Xie and co-workers synthesized 0.66 nm SnO₂ nanosheets, 1.9 nm SnO₂ nanosheets, and bulk SnO₂ for catalytic oxidation of carbon monoxide (CO).¹⁰⁷ The 0.66 nm SnO₂ nanosheets possess a larger fraction of low-coordinated surface atoms (40%) and a higher DOS compared with 1.9 nm SnO₂ nanosheets (15%) and bulk SnO₂, which contributes to the elementary adsorption, dissociation, and diffusion steps during the catalytic oxidation of CO (Fig. 8a-c). They also

prepared 1.72 nm Co_3O_4 nanosheets, 3.51 nm Co_3O_4 nanosheets, and bulk Co_3O_4 for CO_2 catalytic reduction.¹⁰⁰ As revealed by DFT calculations, the DOS increases remarkably, and the charge density becomes more dispersive at the conduction band edge with decreasing nanosheet thickness (Fig. 8d-g). They believed that these changes are beneficial for CO_2 reduction reactions due to the enhanced electrical conductivity and fast carrier transport along the 2D conducting channels.

Our group studied the electronic structural features of Co_3O_4 nanosheets (1.6 nm in thickness), Co_3O_4 nanoflowers (1.8 nm in thickness), and Co_3O_4 nanocubes (100-150 nm in size).⁹⁶ The Raman spectra of Co_3O_4 nanosheets show significant peak broadening and shifts compared with those of nanoflowers and nanocubes, indicating the enhanced phonon confinement effect with the crystal evolving from bulk to atomic scale (Fig. 8h). In addition, they also present obvious differences in surface chemical states. As determined by XPS, the position of the Co 2p core level orbital in Co_3O_4 nanosheets experiences a more negative shift (1.0 eV) with respect to those of nanoflowers (0.6 eV) and nanocubes (0.0 eV), which originates from the improved electron density concentrated around the Co atoms due to the dramatic structural distortion (Fig. 8i). The unique surface chemical states of Co_3O_4 nanosheets reduce the energy barriers for facile mass conversion and transfer on the surface of the catalyst, which consequently enhance the OER catalytic activity.

4.2. Pit/Pore Creation

As is well known, the surface atoms are more disordered compared with interior ones due to their lower coordination number. To further decrease the coordination number, one can create pits or pores on the surface of the nanosheets, which consequently leads to obvious variations in the electronic states of the atoms surrounding the pits/pores. As a typical example, pits confined in 3-atom-thick CeO_2 nanosheets were reported to be highly active catalytic centers for CO oxidation.⁹⁸ More specifically, an ultrafast open space transformation strategy was

applied to convert precursor CeCO_3OH nanosheets to ultrathin CeO_2 nanosheets. At the same time, a great number of pits were formed on the surface of the nanosheets with an occupancy rate of $\sim 20\%$ (Fig. 9a). The Ce L_3 -edge $k^2\chi(k)$ curves from EXAFS measurements show obvious differences among bulk CeO_2 , CeO_2 nanosheets, and CeO_2 nanosheets with surface pits (Fig. 9b). The corresponding Fourier transformed $k^2\chi(k)$ functions display the shift of two main peaks towards lower R values along with remarkably decreased intensities for CeO_2 nanosheets with surface pits, indicating their distinct local atomic arrangement (Fig. 9c). The EXAFS data fitting results show that the Ce-O bond distance around the pits is contracted from 2.327 to 2.302 Å, and the coordination number decreases from 6.5 to 4.6. These results suggest that there is obvious lattice distortion surrounding the pits of ultrathin CeO_2 sheets. As revealed by the calculated DOS, the thus-created pits generate defect states near the Fermi level, which lead to obviously increased hole carrier concentration compared with the CeO_2 nanosheets and bulk CeO_2 (Fig. 9d). These changes in the electronic structure of CeO_2 nanosheets with surface pits facilitate O_2 activation and CO adsorption, and also accelerate the diffusion of CO along the 2D conducting channels, which consequently enhance the catalytic activity towards CO oxidation.

Atomically thin Co_3O_4 nanosheets with a porous structure were prepared *via* a fast-heating strategy for high-performance OER catalysis.¹⁰⁸ As is well known, the surface Co^{3+} atoms of Co_3O_4 have a coordination number of 5, lower than that of 6 for the interior ones. The creation of pores could further decrease the coordination number of surface Co^{3+} from 5 to 4 or even 3 (Fig. 9e). The low-coordinated surface atoms exhibit obvious structural distortion, which results in increased DOS at the edges of the valence and conduction bands (Fig. 9f and g). The low-coordinated surface atoms as well as the unique electronic structure enable efficient H_2O adsorption and fast electron transport, and therefore contribute to the high OER catalytic performance. In addition, other atomically thin non-layered nanomaterials, such as In_2O_3 and WO_3 ,^{97,109} were also prepared, which possess unique surface electronic

states and show enhanced performances in various energy-related applications.

4.3. Vacancy Engineering

Another way to decrease the coordination number and manipulate the electronic states of surface atoms is to incorporate vacancies, which are believed to be more efficient compared with pits and pores due to their atomic scale and high concentration.¹¹⁰ As a typical example, an atomic-level insight into CO₂ reduction catalysis by O-deficient cobalt oxide was provided by Xie's group.¹¹¹ In detail, oxygen-vacancy-rich (V_O-rich) and -poor (V_O-poor) single-unit-cell Co₃O₄ layers were prepared through the same lamellar intermediate-assisted exfoliation strategy, but followed by different heat treatments (Fig. 10a). The Co K-edge $k^3\chi(k)$ oscillation curve and corresponding Fourier transform $k^3\chi(k)$ function of V_O-rich Co₃O₄ layers are quite different from those of V_O-poor layers and the bulk counterpart, which is suggestive of different local atomic arrangements (Fig. 10b and c). The EXAFS curve fitting results for the V_O-rich Co₃O₄ layers show that the coordination numbers for the Co-Co₁, Co-Co₂, and especially the Co-O, Co-O₁, and Co-O₂ coordinations are reduced, whereas the degree of disorder increases, as compared with the V_O-poor layers and the bulk counterpart. They further performed DFT calculations, which reveal that the presence of abundant dangling bonds, as well as an obvious surface distortion, lowers the rate-limiting activation barrier *via* stabilizing the HCOO^{-*} intermediate, and hence, accelerates the speed of CO₂ reduction. The electronic states of iron-cobalt oxide,¹¹² NiCo₂O₄ (Fig. 10d),¹⁰² and In₂O₃ nanosheets⁹⁷ were also successfully optimized by creating oxygen vacancies, which exhibit great advantages in the catalysis of water splitting.

In addition to anion vacancies, cation vacancies were also incorporated to regulate the electronic structures. For example, ultrathin CoSe₂ nanosheets with abundant V_{Co} were prepared *via* a lamellar intermediate-assisted exfoliation strategy followed by ultrasonic treatment, which resulted in the detachment of Co atoms.¹¹³ The type and relative

concentration of the vacancies were determined from the positron annihilation spectrum (Fig. 10e). As revealed by XAFS measurements, the incorporation of V_{Co} results in low coordination numbers and a remarkably shortened Co-Se distance, thereby leading to significant lattice structure distortion and exotic electronic properties (Fig. 10f-h). The variation in electronic structure was proved to be beneficial for H_2O adsorption and the subsequent catalytic oxidation process. The effects of dual vacancies on electronic properties were also studied.¹¹⁴ It was reported that the coexistence of Sn and O vacancies in atomically thin SnO_2 nanosheets results in semiconductive behavior, while the isolated Sn vacancies display half-metallic characteristics (Fig. 10i-n). The type of vacancy can be tuned in a temperature independent manner under electric field, which enables a reversible transition between semiconductive and half-metallic properties.

4.4. Elemental Doping

Incorporating heterogeneous metal atoms with a similar atomic radius and electron configuration into the crystal lattice is also considered to be an effective approach to manipulating the electronic structures of atomically thin non-layered nanomaterials. The elemental doping results in micromechanically derived disturbance, and it consequently induces subtle distortion of the atomic arrangement and redistribution of the electron density. Dai's group reported the incorporation of Co dopants in FeS_2 nanosheets for HER catalysis.¹¹⁵ DFT calculations show that a much longer bond length of H-S is formed on Co-doped nanosheets compared with non-doped nanosheets, which dramatically lowers the kinetic energy barrier of H_2 evolution by promoting H-H bond formation. Xie's group successfully observed slight local-lattice-rotations in $CoSe_2$ after incorporating heterogeneous Mn spin states (Fig. 11a).¹¹⁶ They attributed the subtle distortion in the atomic arrangement to the following two reasons: (i) the localized Coulomb interaction around Mn atoms resulting from different electron spin states, and (ii) the mismatch in the degree of Jahn-Teller distortion

between the Mn-Se (for Mn^{2+} , $t_{2g}^5 e_g^0$ and t_{2g} orbitals are unevenly occupied, yielding a weak Jahn-Teller effect) and Co-Se (for Co^{2+} , $t_{2g}^6 e_g^1$ and e_g orbitals are unevenly occupied, yielding a strong Jahn-Teller effect) coordination octahedra (Fig. 11b). Similarly to Dai's results, they confirmed that the activation barrier of H-H bond formation is dramatically lowered due to the relatively weak H_{ads} -Se bonds, and hence promotes the evolution and release of H_2 gas. As another example, the effect of Co doping confined in 3-atom-thick In_2S_3 nanosheets on photocatalysis was investigated.¹¹⁷ DFT calculations demonstrate that the Co dopant endows In_2S_3 nanosheets with obviously increased DOS at the conduction band minimum as compared with non-doped nanosheets and their bulk counterpart (Fig. 11c,e,g). The spatial distribution of the charge density at conduction band minimum of doped In_2S_3 nanosheets illustrates that the vast majority of charge density originates from Co and S atoms, suggesting the high activity of Co doping sites (Fig. 11d,f,h). As a consequence, the Co-doped In_2S_3 nanosheets enable highly efficient visible-light water splitting owing to their easy electron excitation, high carrier density, and efficient carrier transport along the 2D conducting channels.

4.5. 2D Heterostructure Construction

2D heterostructures constructed from different types of ultrathin nanosheets through van der Waals interactions or chemical bonds usually exhibit enhanced electrochemical performances due to the variations in the work function, the density of states, and the positions of valence and conduction bands. Graphene and its derivatives are the most widely used materials to couple with atomically thin non-layered nanomaterials.¹¹⁸⁻¹²¹ The incorporation of graphene materials not only improves the electrical conductivity, but also enhances the intrinsic properties of the host materials. For instance, TiO_2 /graphene nanocomposites were synthesized through a direct hydrothermal growth method.¹¹⁸ Electron paramagnetic resonance (EPR) and XPS were applied to determine the electronic properties at the interface.

The TiO₂/graphene composites exhibit an apparent EPR response with a *g* value of 1.948, indicating the existence of the Ti³⁺ state on the TiO₂ surface (Fig. 12a). Moreover, the C 1s peak at 283.5 eV and the O 1s peak at 531.7 eV in XPS spectra reveal the formation of Ti-C and Ti³⁺-O bonds, respectively (Fig. 12b and c), further suggesting that the electronic structure of TiO₂ was modified after coupling with graphene. Our group prepared atomically thin Co₃O₄/graphene nanosheets using a two-step method and characterized their interfacial bonding states *via* Raman and XPS techniques.¹¹⁹ The Raman spectra of composite nanosheets show an obvious 10 cm⁻¹ shift in the G band to lower wavenumber, indicating that charge transfer occurs at the interface (Fig. 12d). Also, there is an extra peak located at 530.2 eV in the O 1s XPS spectrum, which is assigned to the formation of Co-O-C linkage through the oxygen-containing functional groups of graphene (Fig. 12e). Accordingly, the surface electronic properties were successfully optimized by incorporating graphene nanosheets.

In addition, other heterostructures constructed from semiconductors or metals were also reported.¹²²⁻¹²⁴ For example, MoS₂/CoSe₂ hybrids were synthesized *via* an *in situ* growth approach for HER catalysis.¹²² The S 2p XPS spectrum shows an extra peak centered at ~ 166 eV, which is ascribed to the formation of Co-S bonds (Fig. 12f). DFT calculations reveal that the coupling between Co and S-edges facilitates the HER kinetics by lowering the Gibbs free energy of adsorbed hydrogen. As another example, sub-monolayer Ru deposited on ultrathin Pd nanosheets was prepared through a wet-chemical approach.¹²³ The binding energy of Pd in Pd@Ru shows a 0.85 eV positive shift as compared with bare Pd nanosheets (Fig. 12g and h), which is mainly attributable to the change in the electronic structure of Pd due to the Ru coating. The binding energies of Ru 3d_{5/2} and Ru 3d_{3/2} located at 280.45 and 284.62 eV, respectively (Fig. 12i), also suggest the metallic state of Ru in the hybrid nanosheets. The synergistic effect between Pd and Ru is responsible for enhanced electrocatalytic performance in the reduction of 4-nitrophenol and the semihydrogenation of 1-octyne.

5. Energy Storage and Conversion Applications

As we have stated above, the atomic thickness of ultrathin non-layered nanomaterials endows them with ultrahigh specific surface areas and a large fraction of low-coordinated surface atoms. In addition, the exotic and easily manipulated electronic states usually result in an increased DOS near the Fermi level, which leads to some desirable properties, such as an optimized band gap, improved electrical conductivity, and enhanced carrier mobility.³⁴ Both the structural and electronic properties make atomically thin non-layered nanomaterials very promising for energy-related applications. In this section, we give an overview of their applications in energy storage and conversion, with particular emphasis on supercapacitors, LIBs, SIBs, and catalysis of hydrogen evolution, oxygen evolution, CO₂ reduction, and CO oxidation reactions.

5.1. Supercapacitors

The ever-growing popularity of and demand for portable electronics and electric vehicles have stimulated intensive research interest in exploring effective energy storage devices.¹²⁵ Electrochemical supercapacitors, including non-faradaic electrical double-layer capacitors that work by ion adsorption at the electrode/electrolyte interface and faradaic pseudocapacitors involving fast surface or near-surface redox reactions, typically exhibit high power density, long-term cycling stability and high safety, and thus are considered as a complement to rechargeable batteries.¹²⁶ Nevertheless, the relatively poor energy density of supercapacitors dramatically impedes their further development for energy storage applications. Atomically thin non-layered nanomaterials provide a promising approach to improving the energy density by substantially enhancing the double-layer capacitance and pseudocapacitance, both of which are highly dependent on the specific surface area of the electrode.¹²⁷ In addition, optimization of the structure of atomically thin nanomaterials can be

easily achieved by a number of techniques, such as pore creation and introducing heterostructures, which offers many possibilities to further enhance the capacitive charge storage.

To date, a variety of ultrathin transition metal oxides and chalcogenides have been investigated as supercapacitor materials due to their high theoretical capacitance, environmental benignity, and high abundance.¹²⁸⁻¹³³ For instance, ultrathin mesoporous NiO nanosheets grown on 3D Ni foam were fabricated for high-performance supercapacitors (Fig. 13a).¹²⁸ Their cyclic voltammetry (CV) curves with a clear rectangular shape and obvious redox peaks demonstrate the contribution of both double-layer capacitance and pseudocapacitance (Fig. 13b). The calculated specific capacitances are as high as 2578.1 and 1568.4 F g⁻¹ at 5 and 100 mV s⁻¹, respectively, and the capacitance shows a slight increase after 45000 continuous CV cycles at 100 mV s⁻¹, indicating its excellent cycling stability (Fig. 13c). The outstanding capacitive performance is mainly attributable to the *in situ* growth strategy for enhanced electrical conductivity, the high specific surface area of NiO nanosheets for a large number of active sites, and the mesoporous structure for efficient electrolyte diffusion and charge transfer. A very interesting study was carried out to enhance the pseudocapacitance of ultrathin Co₃O₄ nanosheets by phosphate ion functionalization (Fig. 13d).¹³² The CV curves of an asymmetric supercapacitor assembled from the functionalized Co₃O₄ nanosheets cathode and 3D porous graphene gel anode (PCO//3DPG) maintain similar shapes over a wide range of scan rates, indicating excellent pseudocapacitive behavior with fast and reversible charge storage capability (Fig. 13e). As a result, the asymmetric supercapacitor exhibits a high energy density of 71.58 Wh kg⁻¹ at an average power density of 1500 W kg⁻¹ and a high power density of 24000 W kg⁻¹ with energy density retaining 50 Wh kg⁻¹, which is substantially higher than previously reported asymmetric devices (Fig. 13f). In addition, it also exhibits excellent cycling stability with a capacitance retention of 95% after 2000 galvanostatic charge/discharge cycles (Fig. 13g). The surface chemical reactivity

stimulated by phosphate ion functionalization is likely to be the key factor that contributes to the fast and efficient faradaic pseudocapacitive reactions (Fig. 13h). It was calculated that Co-OPO(OH)₂ has a higher degree of covalency and smaller Co electronegativity compared with Co-O, and the resultant weaker attraction to electrons allows easy gain and loss of electrons during the redox reactions, leading to enhanced surface reactivity and fast reaction kinetics.

5.2. Lithium-Ion Batteries

Atomically thin nanomaterials could not only dramatically enhance the energy density of supercapacitors, but also provide a remarkable improvement in the power density and cycling stability of rechargeable batteries. They have demonstrated their obvious superiority in many aspects for pursuing high-performance LIBs.^{72,88,124} First, the atomic thickness provides a large fraction of surface atoms and highly accessible surface areas. Therefore, the electrode is in full contact with the electrolyte, dramatically shortening the Li⁺ diffusion paths into and out of the crystals. Second, the high elasticity and flexibility efficiently alleviate the volume expansion and structural degradation during the charge/discharge process. Third, the increased DOS near the Fermi level endow improved electrical conductivity and carrier mobility, thus relieving one of the most difficult challenges faced by non-carbonaceous electrodes. Fourth, it is easy to construct nanocomposites based on ultrathin 2D nanosheets, which dramatically enhances the synergistic coupling effect due to extremely large interfacial areas. Generally, these great advantages of atomically thin non-layered nanomaterials promise excellent lithium storage performance.

Ultrathin transition metal oxide nanosheets have been widely developed for LIBs due to their high theoretical capacities and safety characteristics. As a typical example, Xie's group reported the preparation of ultrathin Co₃O₄ nanosheets with a thickness of 1.5 nm for lithium storage (Fig. 14a).⁹⁹ The Co₃O₄ nanosheets exhibit a high reversible capacity of 1291.2 mAh g⁻¹ at 0.5 C (Fig. 14b) and excellent rate capability with high capacity retention

at large current densities (Fig. 14c), showing better performance than other Co_3O_4 nanostructures. In our group, atomically thin mesoporous Co_3O_4 /graphene nanocomposites were prepared and utilized as an anode material for LIBs (Fig. 14d).¹¹⁹ The nanocomposite delivers high specific capacities of 2014.7 and 1134.4 mAh g^{-1} at 0.11 and 2.25 C, respectively, presents excellent rate capability, and exhibits long-term cycling stability with a capacity retention of 92.1% after 2000 cycles at 2.25 C, which significantly outperforms bare Co_3O_4 nanosheets and any previously reported $\text{Co}_3\text{O}_4/\text{C}$ composites (Fig. 14e and f). The outstanding lithium storage performance is mainly attributable to the atomic thickness and mesoporosity of Co_3O_4 nanosheets, which afford sufficient electrode/electrolyte contact and a shortened Li^+ diffusion length; the high electrical conductivity and flexibility of graphene for efficient charge transportation and enhanced structural stability; and the highly exposed surface atoms and defects (including vacancies, edges, grain boundaries, *etc.*) of Co_3O_4 and graphene for extra lithium storage; as well as the large interfacial areas between Co_3O_4 and graphene for reversible pseudocapacitive storage. 2D Si nanosheets were also investigated as high performance anode materials for LIBs. For instance, ultrathin Si was synthesized from natural clays *via* a one-step simultaneous molten salt-induced exfoliation and chemical reduction method (Fig. 14g).¹³⁴ After being coated with a carbon layer, the Si nanosheets exhibit excellent lithium storage performance, including long cycle life (capacity retention of 93.1% at 0.2 C after 200 cycles; 92.3% at 0.5 C after 500 cycles; 91.7% at 1.0 C after 700 cycles) and high rate capability (with a capacity ratio of 60% at 20 C compared with that of 2.0 C) (Fig. 14h and i).

5.3. Sodium-Ion Batteries

As the radius of Na^+ (1.02 Å) is 34% larger than that of Li^+ (0.76 Å), electrode materials used for SIBs usually suffer from low specific capacity, poor rate capability and short cycle life due to slow Na^+ diffusion within the crystal and large volume expansion of the host

materials.¹³⁵⁻¹³⁷ In view of this, developing atomically thin nanomaterials with confined thickness and large specific surface areas is of particular importance for Na⁺ storage. On the one hand, the atomic thickness dramatically shortens the Na⁺ diffusion length and significantly improves the Na⁺ insertion/deinsertion kinetics. On the other hand, the large surface areas (or interfacial areas when coupled with other nanomaterials) enable highly efficient capacitive storage (double layer capacitance and pseudocapacitance) with Na⁺ stored at the surface (or interface) of the active materials rather than inserted into the crystal lattice, which consequently leads to high reversible capacity, excellent rate capability, and long-term cycling stability.

As a typical example, TiO₂/graphene nanocomposites were prepared and assessed as SIB anode by Huang's group (Fig. 15a).¹¹⁸ The composites achieve high rate capability with 90 mAh g⁻¹ capacity retention at 12000 mA g⁻¹ and long cycle life up to 4000 cycles with negligible capacity fading (Fig. 15b and c). CV measurements were performed to evaluate the electrochemical kinetics at various scan rates from 0.1 to 100 mV s⁻¹. By separating the capacitive storage from the total charge storage in CV curves, they found that the capacitive contribution increases with increasing scan rate, and reaches a maximum value of 90.2% at 10 mV s⁻¹ (Fig. 15d and e). First-principles DFT calculations reveal that the enhanced capacitive storage is mainly attributable to intercalation pseudocapacitive behavior at the interface of partially bonded graphene-TiO₂, which provides feasible channels for Na⁺ insertion/extraction with low energy barriers (Fig. 15f). As another example, we reported the growth of atomically thin Co₃O₄ nanosheets on steel mesh as an anode material for SIBs (Fig. 15g).¹³⁸ This anode delivers a high average capacity of 509.2 mAh g⁻¹ for the initial 20 cycles at 50 mA g⁻¹, presents excellent rate capability with an average capacity of 427 mAh g⁻¹ at 500 mA g⁻¹, and exhibits good cycling stability (Fig. 15h). The kinetic analysis also exhibits an improved capacitive contribution with increasing scan rate (Fig. 15i and j). We attribute the excellent electrochemical performance to the atomic thickness of Co₃O₄ nanosheets and the direct

growth method for electrode processing, which lead to remarkably enhanced surface redox pseudocapacitance and interfacial double layer capacitance (Fig. 15k).

5.4. Hydrogen Evolution Reaction Catalysis

As is well known, catalysis is a surface reaction process and is highly associated with the surface electronic structure of the catalyst. Atomically thin non-layered nanomaterials used for various electrocatalytic and photocatalytic reactions provide many distinct advantages.³⁷ Firstly, atomically thin non-layered nanomaterials possess numerous low-coordinated atoms at the surface, which are of great benefit for reactant adsorption, light harvesting, mass transport, *etc.* Secondly, the atomic thickness dramatically shortens the charge migration distance from the interior to the surface of the crystal, thus facilitating the charge separation. Thirdly, the exotic electronic properties exhibit increased DOS near the Fermi level, which significantly enhances the electrical conductivity and carrier mobility. Fourthly, and most importantly, atomically thin non-layered nanomaterials provide an ideal 2D platform to further manipulate the surface electronic states for enhanced performances in various catalytic applications.

As one of the most promising applications, HER catalysis has witnessed the extremely high catalytic activities of atomically thin non-layered nanomaterials, which are even comparable to those of the prevailing Pt-based catalysts.^{103,115,116,122,139} As a typical example, metallic Mn-doped CoSe₂ atomic layers were prepared and evaluated as a catalyst to promote hydrogen evolution (Fig. 16a).¹¹⁶ The doped nanosheets exhibit excellent HER catalytic performance with a low overpotential of 174 mV, a small Tafel slope of 36 mV dec⁻¹, a large exchange current density of 68.3 $\mu\text{A cm}^{-2}$, and high durability without significant decline in current density after 2000 CV cycles (Fig. 16b and c). The high catalytic activity is mainly ascribed to the variation of the electronic structure after incorporating foreign spin states in the crystal lattice, which efficiently lowers the energy barriers of H-H bond formation and

final H₂ release. 2D heterostructures were also prepared to promote the HER catalytic performance. Yu and co-workers reported that MoS₂/CoSe₂ catalyst exhibits remarkably enhanced H₂ evolution kinetics with a low onset potential of 11 mV, a small Tafel slope of 36 mV, and high catalytic stability with negligible decline in current density after 24 h, significantly outperforming the performances of the individual components (Fig. 16d-f).¹²² They believed that the superior HER catalytic performance is mainly attributable to the formation of Co-S bonds which decrease the Gibbs free energy of adsorbed hydrogen and afford fast proton adsorption kinetics. Apart from electrocatalysis, water splitting under solar irradiation has been regarded as another promising approach to produce H₂ as a clean energy source.^{30,78} O-vacancies confined in atomically thin In₂O₃ nanosheets were developed for visible-light water splitting (Fig. 16g).⁹⁷ The O-deficient photocatalyst delivers a current density of 1.73 mA cm⁻², over 2.5 and 15 times larger than O-vacancy-poor ultrathin In₂O₃ porous nanosheets and bulk In₂O₃, respectively (Fig. 16h), and an incident photon-to-current conversion efficiency (IPCE) of 32.3%, much higher than 12% and 3% for O-vacancy-poor ultrathin In₂O₃ porous nanosheets and bulk In₂O₃, respectively (Fig. 16i). Further evidence demonstrated that the presence of O-vacancies results in increased DOS at the valence band maximum and shifting of the onset light absorption from the ultraviolet (UV) to the visible region, which increases the carrier concentration and the light absorption, respectively, and consequently contributes to the excellent photocatalytic performance.

5.5. Oxygen Evolution Reaction Catalysis

The efficiency of water splitting is highly limited by the oxidative half reaction (OER) due to its sluggish reaction kinetics associated with a complex four-electron redox process.³⁰ Although some noble metal (*e.g.*, Ru and Ir) based compounds exhibit high catalytic activity, their commercial applications are severely impeded by their scarcity and high cost. In the light of this, developing highly efficient OER catalysts that have low overpotential as well as being

earth-abundant and inexpensive should be of great benefit for practical applications.

Atomically thin non-layered nanomaterials have been proven to be promising alternatives to noble metal compounds due to their high specific surface areas and tunable electronic structures. To date, a variety of atomically thin non-layered nanomaterials with exotic electronic properties have been successfully developed for efficient OER catalysis with high catalytic activities, including Co_3O_4 ,^{96,108} NiCo_2O_4 ,¹⁰² WO_3 ,¹⁰⁹ iron-cobalt oxide,¹¹² ZnSe ,⁷⁴ Co_3S_4 ,⁷⁹ CoSe_2 ,^{113,140} In_2S_3 ,¹¹⁷ Ni_3N ,¹⁰⁴ Co-Bi/graphene ,¹²¹ *etc.*¹⁴¹ For instance, 4-atom-thick ZnSe nanosheets with unique structural and electronic properties were fabricated for efficient solar water splitting (Fig. 17a).⁷⁴ The ZnSe nanosheets deliver a high photocurrent density of 2.14 mA cm^{-2} at $0.72 \text{ V vs. Ag/AgCl}$, about 195 times higher than that of the bulk counterpart (Fig. 17b). Moreover, the highest IPCE of the ZnSe nanosheets at 300 nm reached 42.5%, far beyond the values obtained from the other ZnSe samples (Fig. 17c). The outstanding photocatalytic performance should be ascribed to the large specific surface area and large fraction of distorted surface atoms, which greatly enhance the UV light absorption efficiency. In addition, the lattice structure distortion modifies the electronic states at the surface, enabling highly efficient carrier transport and charge separation, which consequently contribute to the high photocatalytic activity. Xie's group studied the effect of the surface coordination number on OER catalysis based on atomically thin Co_3O_4 nanosheets (Fig. 17d).¹⁰⁸ They found that the presence of nanopores on the surface could decrease the coordination number of the surrounding Co^{3+} atoms to 4 or 3, which is lower than 6 for interior Co^{3+} atoms. DFT calculations demonstrate that the H_2O adsorption energy increases with decreasing coordination number, which leads to increased catalytic activity (inset in Fig. 17e). As expected, the porous Co_3O_4 nanosheets exhibit a high current density of 341.7 mA cm^{-2} at $1.0 \text{ V vs. Ag/AgCl}$ and a Tafel slope as low as 25 mV (Fig. 17e and f), which are superior to those of previously reported Co-based OER catalysts. Zhu's group created O-vacancies on ultrathin Fe-Co oxide nanosheets for enhanced OER catalytic performance (Fig.

17g).¹¹² The ultrathin Fe-Co nanosheets exhibit a mass activity as high as 54.9 A g⁻¹ at an overpotential of 350 mV and a Tafel slope as low as 36.8 mV dec⁻¹ (Fig. 17h and i). The excellent OER catalytic performance results from the improved electrical conductivity and enhanced H₂O adsorption of the catalyst due to the vacancy-optimized electronic structure. In addition, other electronic manipulation strategies, such as elemental doping (*e.g.*, Co-doped In₂S₃) and 2D heterostructure construction (*e.g.*, Co-Bi/graphene composite),^{117,121} were also successfully employed to enhanced the OER catalytic performances of atomically thin non-layered nanomaterials.

5.6. Carbon Dioxide Reduction Catalysis

Increasing concerns about the depletion of fossil fuels and CO₂-induced global warming have stimulated the investigation of electrochemical reduction of CO₂ to hydrocarbon fuels.¹⁴² The electroreduction of CO₂ involves the adsorption of CO₂, activation of CO₂ to form CO₂^{•-}, HCO₂⁻, or HCOO⁻ intermediates, dissociation of the C-O bond *via* stepwise proton and electron transfer, and release of the reduced products from the catalyst surface. Among them, the most critical bottleneck lies in the activation of CO₂ to generate different intermediates, due to its high overpotential and the simultaneously formed competitive reduction products such as H₂.^{100,111} In view of this, developing effective electrocatalysts that could facilitate CO₂ activation holds the key for enhanced is highly attractive and desirable.

Atomically thin non-layered nanomaterials have been demonstrated to be an excellent choice due to their unique structural and electronic properties. The atomic thickness provides a large fraction of low-coordinated surface active sites for efficient CO₂ adsorption, which satisfies the prerequisite requirements for the following reduction reactions. In addition, the increased DOS and electron charge density near the conduction band edge increase remarkably, which promote carrier transport along the 2D conducting channels and enable fast reduction kinetics. More importantly, the easy tailoring of the surface electronic structure

could dramatically facilitate CO₂ activation by stabilizing the intermediates.^{73,143} Taking Co₃O₄ as an example, Co₃O₄ nanosheets with different thicknesses were investigated for CO₂ electrocatalytic reduction.¹⁰⁰ The 1.72 nm thick Co₃O₄ layers with a large amount of surface active sites and obvious surface structure distortion exhibit enhanced CO₂ adsorption, 2D electronic conductivity and CO₂^{•-} stabilization compared to 3.51 nm Co₃O₄ layers and the bulk counterpart. Insight at the atomic-level into the role of oxygen vacancies in CO₂ electrocatalytic reduction was provided by Xie's group.¹¹¹ Oxygen vacancies could further decrease the coordination number of surface atoms and consequently promote the adsorption of CO₂. Moreover, DFT calculations reveal that the O-vacancies confined in Co₃O₄ single-unit-cell layers accelerate the rate-limiting proton transfer step *via* stabilizing the HCOO⁻ intermediate, thereby lowering the CO₂ activation energy barrier for facile electrochemical reduction. Their group also demonstrated that the surface Co atoms of atomically thin cobalt layers exhibit higher intrinsic activity and selectivity towards formate production compared with those on bulk counterparts.⁴⁶ Partial oxidation of the cobalt layers drastically enhances the catalytic performance, achieving a large current density of 10.59 mA cm⁻² at -0.85 V *vs.* saturated calomel electrode (SCE) (Fig. 18b), a high Faradaic efficiency of 90.1% at -0.85 V for the production of formate (Fig. 18c), and high catalytic stability without any obvious decay in current density after 40 h (Fig. 18d). Therefore, rational design of the structure and electronic states can transform an inert material into a highly active catalyst. Metallic tin quantum sheets confined in graphene were also prepared and evaluated as a catalyst for CO₂ electroreduction (Fig. 18e).¹²⁰ The nanocomposites display a current density of 21.1 mA cm⁻² at -1.8 V *vs.* SCE (Fig. 18f), a maximum faradaic efficiency of 89% for the formate (Fig. 18g), and high catalytic stability with negligible decline in current density after 50 h (Fig. 18h). The outstanding electrocatalytic activity is mainly attributable to the atomic thickness of the tin nanosheets for high-capacity CO₂ adsorption, the high electrical conductivity of graphene for fast rate-determining electron transfer from CO₂ to CO₂^{•-} intermediate, and the low

coordination number of surface tin atoms for highly stabilized $\text{CO}^*_2^-$ intermediate.

5.7. Carbon Monoxide Oxidation Catalysis

Considering the increased CO emissions from transportation sources, developing low cost, efficient, and durable catalysts for the conversion of CO to CO_2 is highly desirable and beneficial to address the air pollution issue.¹⁴⁴ Metal oxides have recently gained tremendous interest in catalyzing CO oxidation due to their earth-abundance and remarkable activity, and thus are considered promising alternatives to noble metal catalysts. According to the widely accepted Mars-van Krevelen mechanism, the adsorbed CO molecule can be oxidized by the labile and low-coordinated oxygen atom on the surface of metal oxides with an oxygen vacancy simultaneously created. The oxygen vacancy subsequently facilitates the dissociation of O_2 molecules into highly reactive O atoms, with one of them replenishing the oxygen vacancy. The other dissociated O atom attracts a second CO molecule to form CO_2 and leads to the end of the catalytic cycle.¹⁰⁷

Atomically thin non-layered metal oxides provide a large fraction of low-coordinated surface atoms with abundant dangling bonds, which could serve as highly active sites for efficient CO and O_2 adsorption. Moreover, the surface structural distortion with increased DOS at the edge of the valence band facilitates the CO diffusion along the 2D conducting channels to react with the dissociated O atom.¹⁰⁷ Furthermore, the surface electronic states could be rationally designed to tune the adsorption states of CO and O_2 , and facilitate their dissociation, diffusion and conversion, which further optimize the catalytic process and achieve enhanced catalytic performance. For instance, SnO_2 nanosheets with different thicknesses were synthesized for catalytic CO oxidation. Owing to their large surface area with numerous catalytic active sites and increased DOS at the valence band edge with efficient electron transport, the 0.66 nm thick SnO_2 nanosheets exhibit faster catalytic reaction with lower apparent energy than 1.9 nm SnO_2 nanosheets, SnO_2 nanoparticles, and bulk SnO_2 .

The roles of different active sites in catalytic CO oxidation were investigated based on 3-atom-thick CeO₂ nanosheets with 20% pit occupancy and an average coordination number of 4.6 (Fig. 19a).⁹⁸ DFT calculations reveal that CO and O₂ molecules tend to adsorb at 4-coordinated Ce sites (P₂) and 5-coordinated Ce sites (P₁) surrounding the pits, respectively, due to their having the highest adsorption energies (Fig. 19b and c). The difference in adsorption position effectively avoids catalyst poisoning. Further calculations demonstrate that O₂ molecules adsorbed at two adjacent 5-coordinated Ce sites (2P₁) exhibit the lowest activation energy for rate-limiting dissociation (Fig. 19d and e). In addition, CO diffuses much more easily on the Ce sites surrounding the pits than the Ce sites on the surface owing to the increased DOS near the Fermi level around the pit sites. As a consequence, the CeO₂ layers occupied by pits can enable the catalytic oxidation of CO at relatively low reaction temperatures compared with intact layers and their bulk counterpart (Fig. 19f). The superior CO catalytic oxidation was also confirmed by Arrhenius plot, which shows much lower apparent activation energy for CeO₂ layers occupied by pits compared with the other two samples (Fig. 19g).

5.8. Other Energy Storage and Conversion Applications

Atomically thin non-layered nanomaterials also show promising applications in some other energy-related fields, such as solar cells,¹⁴⁵ catalysis of formic acid oxidation and oxygen reduction (ORR),^{56,146,147} and photodetectors,^{62,83,93,106} to name but a few.^{85,123} For instance, freestanding hexagonal palladium nanosheets with less than 10 atomic layer thick were reported by Zheng and co-workers (Fig. 20a).⁵⁶ The ultrathin nanosheets exhibit strong electrocatalytic activity toward the oxidation of formic acid, which is 2.5 times greater than commercial palladium black catalyst (Fig. 20b). Core-shell structured Pd@Pt monolayer nanosheets were prepared and evaluated for ORR catalysis (Fig. 20c), which exhibit about seven-fold enhancement in mass-activity and much superior durability compared with

commercial Pt/C catalyst (Fig. 20d).¹⁴⁶ Our group designed transparent and flexible ultraviolet photodetectors by depositing atomically thin transition metal oxides (TiO_2 , ZnO , Co_3O_4 , WO_3) on a single-layer graphene backed electrode (Fig. 20e).⁸³ The I-V characteristics demonstrate ideal linear responses and good ohmic behaviors (except for WO_3) (Fig. 20f), and the photoresponses show excellent stability and quick-response of the ultraviolet photodetectors (Fig. 20g), indicative of great potential for photoelectric or photochemical devices.

6. Conclusions and Outlook

In the past few years, scientists have witnessed the emergence, development, and superiority of atomically thin non-layered nanomaterials. These nanomaterials, with inherent non-layered structures while atomic thickness, undoubtedly exhibit some fascinating structural and electronic properties. In this review, we have given a comprehensive summary of the progress on these nanomaterials including the synthetic strategies, electronic-structure manipulations, and energy storage and conversion applications. This graphene-like 2D nanostructure not only provides an ideal platform to disclose the structure-property relationships, but also leads to dramatically enhanced performances in supercapacitors, rechargeable batteries, and catalysis.

In spite of considerable past efforts, the current research on atomically thin non-layered nanomaterials is still far from mature, and enormous work remains to be done to promote the development of this brand-new research field. First, new types of atomically thin non-layered nanomaterials should be developed. Theoretically speaking, any kind of ultrathin non-layered nanomaterials could be successfully prepared as long as its growth is confined within a 2D space down to the atomic scale. Nevertheless, the variety of the reported materials is still limited at present, just the tip of the iceberg for non-layered materials, including naturally existing and artificially synthesized ones. Therefore, one of the major tasks in the future is to synthesize more kinds of ultrathin non-layered nanomaterials by

already existing or newly developed synthetic methods. Second, more effective approaches should be developed for rational design and fine modulation of the electronic structure. As the physical and chemical properties are highly dependent on the electronic structure, it is very essential to optimize the electronic states through a facile and efficient approach, which may involve the variations in nanosheets thickness, crystallinity, phase composition, and defect types and concentrations. Third, effectual characterization techniques are needed to better understand the structure-property relationships. Since some structural features, such as crystal phase evolution and element doping position, can not be clearly identified at present, developing more effective techniques is highly desirable to give us exact information on crystal and electronic structures. We believe that some advanced characterization techniques, *e.g.* scanning transmission electron microscopy (STEM) and scanning tunneling microscopy (STM), as well as newly developed *in-situ* methods, *e.g. in situ* TEM, *in situ* XPS and *in situ* Raman spectroscopy, could provide atomic-level insights into the electronic structure-property relationships. Fourth, preparing 2D heterostructures has become a compelling and irresistible trend. The construction of 2D heterostructures not only overcomes the drawbacks of each individual component, but also yields some novel appealing properties. This is particularly important for improving the performance and exploring new functionalities of atomically thin non-layered nanomaterials in practical applications. Fifth, from a commercial point of view, it is essential to prepare non-layered nanosheets with high quality (*e.g.*, large lateral size and controllable layer number), on a large-scale, and at low cost. Therefore, efficient and economical technologies for massive production of high-quality atomically thin nanomaterials are urgently demanded. Sixth, the ability of atomically thin non-layered nanomaterials to add new capability to energy conversion and storage is also expected to enhance the efficiency of energy harvesting technologies which capture clean and useful energy from existing sources that would otherwise be wasted. In particular, the large active surface area, adjustable band gap, and improved electrical conductivity and carrier mobility of

ultrathin non-layered nanomaterials are of great importance for high-performance thermoelectric, piezoelectric, photovoltaic, electromagnetic, and triboelectric devices.

Generally, the study of atomically-thin non-layered nanomaterials is still in its infancy, and there is great room to make further improvements. We believe that the novelty and distinctiveness of these nanomaterials will provide a major boost for the commercialization of energy-related devices and introduce some new opportunities into the fields of condensed matter physics, materials science, and chemistry in the near future.

Acknowledgements

This work is financially supported by a Australian Research Council (ARC) Discovery Project (DP160102627) and the UOW-BUAA Joint Research Centre. We also thank Dr. Tania Silver for her help in revising the manuscript.

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Table 1. Research progress on atomically thin non-layered nanomaterials.

Atomically thin non-layered nanomaterial	Synthetic methods	Dimensions (thickness, lateral size)	Electronic structure manipulation	Energy-related application	Properties and performances	Ref.
Partially oxidized Co	Sel-assembly	0.84 nm, 500 nm	2D heterostructure construction	Electrocatalytic reduction of CO ₂	A stable current density of ~ 10 mA cm ⁻² over 40 h, with about 90% formate selectivity at a η of 0.24 V	46
Cu	Self-assembly	2.1 nm, 0.20-2.0 μ m	—	Luminescence	Excellent performance with enhanced luminescence intensity	49
Sn quantum sheets confined in graphene	Topochemical transformation	<1.4 nm, 5.0 nm for Sn quantum sheets	2D heterostructure construction	Electrocatalytic reduction of CO ₂	An onset potential of -0.85 V vs. SCE and a current density of 21.1 mA cm ⁻² at -1.8 V vs. SCE	120
Rh	Sel-assembly	0.40 nm, 500-600 nm	—	—	—	47
Ru	Self-assembly	3.0 nm, 23.8 nm (triangle); 1.5 nm, 15.1 nm (irregular)	—	Electrocatalytic CO-selective methanation	Comparable activity but higher CO selectivity than nanosphere structures	59
Au ₁₅	Self-assembly	1.5 nm, 600 nm	—	—	—	50
<i>hcp</i> Au	2D template synthesis	2.4 nm, 200-500 nm	—	—	Electron beam-induced phase transformation from <i>hcp</i> to <i>fcc</i>	87
<i>hcp/fcc</i> Au	2D template synthesis	5.0 nm, 200-400 nm	2D heterostructure construction	—	—	89
Metals						
Au@Pt, Au@Pd	2D template synthesis	3.5 nm, 100-400 nm; 3.4 nm, 100-400 nm	2D heterostructure construction	—	Pt- or Pd-layer growth-induced <i>hcp</i> -to- <i>fcc</i> phase transformation	90
Au@Ag	2D template synthesis	3.0-4.6 nm, 100-500 nm	2D heterostructure construction	—	Surface ligand exchange or Ag-layer coating-induced <i>hcp</i> -to- <i>fcc</i> phase transformation	91
Ag	Self-assembly	5.0 nm, 50 nm	—	—	Widely tunable surface plasmon bands	60
Pd	Self-assembly	1.8 nm, 100 nm	—	Electrocatalytic formic acid oxidation	The catalytic activity is 2.5 times higher than commercial palladium black catalyst	56
Pd@Au	Self-assembly	4.0 nm, 30 nm	2D heterostructure construction	Photothermal therapy	Photothermal ablation of tumors was achieved under the irradiation of 808 nm laser at a power density of only 0.5 W cm ⁻²	55
Pd@Pt _{monolayer}	2D template synthesis	4.7 nm, 200 nm	2D heterostructure construction	Electrocatalytic ORR	Seven-fold enhancement in mass-activity and superior durability compared with commercial Pt/C catalyst	146
Pd@Ru	2D template synthesis	1.5 nm, 7.2 nm	2D heterostructure construction	Electrocatalytic reduction of 4-nitrophenol and semihydrogenation of 1-octyne	Superior catalytic activity compared with pure ultrathin Pd and Ru nanosheets	123
Al ₂ O ₃	2D template synthesis	4.1 nm, > 10 μ m	—	—	—	86
TiO ₂	Lamellar intermediate-assisted exfoliation	3.3 nm, 200 nm	—	Photodetectors	Enhanced photosensitive properties with fast response speed and excellent stability	83
	Lamellar intermediate-assisted exfoliation	1.66 nm, 200 nm	—	Photocatalytic reduction of CO ₂	A formate formation rate of 1.9 μ mol g ⁻¹ h ⁻¹ , 450 times higher than bulk counterpart	143
	Lamellar intermediate-assisted exfoliation	3.0 nm, 200-500 nm	—	Solar cells	A solar conversion efficiency of 8.28%, outperforming that of commercial P25 TiO ₂ nanoparticles (5.12%)	145
TiO ₂ /graphene	2D template	< 5.0 nm, > 50 nm for TiO ₂ nanosheets	2D heterostructure construction	SIBs	Enhanced Na ⁺ intercalation pseudocapacitance with a specific capacity of 90 mAh g ⁻¹ at 36 C	118
Mn ₃ O ₄	Self-assembly	1.1 nm, 500 nm	—	—	Lower Curie-Weiss temperature and greater coercivity than bulk material	53
α -Fe ₂ O ₃	2D template synthesis	0.55-0.59 nm, 1.0 μ m	—	—	Robust intrinsic ferromagnetism of 0.6 μ B/atom at 100 K and remain ferromagnetic at RT	92
Fe _x Co _y O	Lamellar intermediate-assisted exfoliation	1.2 nm, 200-500 nm	O vacancies	Electrocatalytic OER	The mass activity reaches 54.9 A g ⁻¹ at a η of 350 mV, and the Tafel slope is 36.8 mV dec ⁻¹	112
Co ₃ O ₄	Lamellar intermediate-assisted exfoliation	1.6 nm, 2.0 μ m	—	Photodetector	Enhanced photosensitive properties with fast response speed and excellent stability	83
Metal oxides	Topochemical transformation	1.5 nm, 2.0 μ m	Thickness control and pore creation	Electrocatalytic OER; SIBs	Superior catalytic performance compared with nanoflowers and nanocubes; remarkably enhanced capacitive Na ⁺ storage with excellent rate capability and long cycling stability	96, 138
	Topochemical transformation	1.5 nm, 400 nm	Pore creation	LIBs	A high reversible capacity of 1291.2 mAh g ⁻¹ with 0.23% loss per cycle at 0.5 C	99
	Topochemical transformation	1.72 nm, 300 nm	Thickness control	Electrocatalytic reduction of CO ₂	1.5 and 20 times higher catalytic activity compared with 3.51 nm-thick Co ₃ O ₄ nanosheets and bulk Co ₃ O ₄	100
	Topochemical transformation	0.43 nm, > 500 nm	Pore creation	Electrocatalytic OER	An extremely high current density of 341.7 mA cm ⁻² and a small Tafel slope of 25 mV	108
	Topochemical transformation	0.84 nm, > 200 nm	O vacancies	Electrocatalytic reduction of CO ₂	A large current density of 2.7 mA cm ⁻² with ~ 85% formate selectivity during 40 h tests	111
	Self-assembly	2.9 nm, > 10 μ m	—	Supercapacitors	A specific capacitance of 1400 F g ⁻¹ with only a slight decay of 3% after 1500 cycles	130
Co ₃ O ₄ -H ₂ PO ₄ ⁻ /PO ₃ ³⁻	Heat treatment	2.0-3.0 nm, > 2.0 μ m	Surface functionalization	Supercapacitors	The asymmetric supercapacitor coupled with 3D porous graphene gel delivers a high energy density (71.58 Wh kg ⁻¹ at 1500 W kg ⁻¹) and a high power density (24000 W kg ⁻¹ at 50 W kg ⁻¹)	132
Co ₃ O ₄ /	Lamellar intermediate-	2.0 nm, 2.5 μ m	2D	LIBs	High discharge capacities of 1014.7 and	119

Metal chalcogenides	graphene	assisted exfoliation	for Co ₃ O ₄ nanosheets	heterostructure construction and pore creation		1134.4 mAh g ⁻¹ at 0.11 and 2.25 C, respectively, excellent rate capability, and ultralong cycle life	
		Topochemical transformation	2.0-3.0 nm, 10 nm	2D heterostructure construction	Supercapacitors	A ultrahigh specific capacitance of 3344.1 F g ⁻¹ at 1.25 A g ⁻¹ , excellent rate capability, and 87.9% capacity retention after 6000 cycles	131
	NiO	Topochemical transformation	1.16 nm, > 1.0 μm	Pore creation	Supercapacitors	A high specific capacitance of 1576 F g ⁻¹ at 4 A g ⁻¹ with 99.1% retention after 2000 cycles	101
		Topochemical transformation	5.3 nm, 1.0 μm	Pore creation	Supercapacitors	A ultrahigh specific capacitance of 2504.3 and 1568.4 F g ⁻¹ at 5 and 100 mV s ⁻¹ , respectively, with no capacitance degradation after 45000 cycles	128
	NiCo ₂ O ₄	Topochemical transformation	1.6 nm, 150 nm	O vacancies	Electrocatalytic OER	A high current density of 285 mA cm ⁻² at 0.8 V and a small η of 0.32 V	102
	NiCo ₂ O ₄ /NiO	Topochemical transformation	< 5.0 nm, > 2.0 μm for NiCo ₂ O ₄ nanosheets	2D heterostructure construction	Supercapacitors	A high specific capacitance of 2210 F g ⁻¹ at 0.5 A g ⁻¹ , good rate capability, and excellent cycling stability	129
	ZnO	Oriented attachment	2.0 nm, 20 μm	—	—	—	63
		Lamellar intermediate-assisted exfoliation	3.4 nm, 2.0 μm	—	Photodetectors	Enhanced photosensitive properties with fast response speed and excellent stability	83
	SnO ₂	Oriented attachment	2.1 nm, 200 nm	—	LIBs	A high specific capacity of 534 mAh g ⁻¹ after 50 cycles at 156 mA g ⁻¹	72
		Self-assembly	0.66 nm, 500 nm	Thickness control	Electrocatalytic oxidation of CO	Low activation energy (59.2 kJ mol ⁻¹) compared with 1.9 nm-thick nanosheets (83.4 kJ mol ⁻¹) and nanoparticles (101.6 kJ mol ⁻¹)	107
		Self-assembly	1.3-2.0 nm, > 500 nm	Sn and O dual vacancies	—	Reversible transition between semiconductor and half-metal	114
	SnO ₂ /Fe ₂ O ₃	2D template synthesis	5.0 nm, 2.0-10 μm	—	Supercapacitors	High specific capacitances of 471 and 138 F g ⁻¹ at 5 and 100 mV s ⁻¹ , respectively, outperforming SnO ₂ and Fe ₂ O ₃ nanosheets	85
	WO ₃	Oriented attachment	4.0-5.0 nm, 1.0 μm	—	Photocatalytic reduction of CO ₂	Efficient photocatalytic performance in the presence of water into hydrocarbon fuels that does not exist in bulk form	73
		Lamellar intermediate-assisted exfoliation	2.1-5.2 nm, 2.0 μm	—	Photodetectors	Poor photosensitive properties but increasing photocurrent with prolonged irradiation due to the photochromic effect	83
	In ₂ O ₃	Topochemical transformation	0.90 nm, 500 nm	O vacancies	Photocatalytic HER	A photocurrent density of 1.73 mA cm ⁻² at 1.6 V vs. RHE and an IPCE of 32.3% at 450 nm	97
	CeO ₂	Topochemical transformation	0.60 nm, > 100 nm	Pit creation	Electrocatalytic oxidation of CO	Reduced conversion temperature and enhanced CO catalytic ability due to low apparent activation energy (61.7 kJ mol ⁻¹) compared to their bulk counterparts (122.9 kJ mol ⁻¹)	98
	Eu ₂ O ₃	Self-assembly	3.8 nm, 200-600 nm	—	—	Strong quantum size effect	54
	Fe-doped NiS	Topochemical transformation	2.0 nm, > 1.0 μm	Elemental doping	Electrocatalytic HER	A η as low as 105 mV at 10 mA cm ⁻² and a small Tafel slope of 40 mV dec ⁻¹	103
	Co ₃ S ₄	Lamellar intermediate-assisted exfoliation	1.0 nm, 500 nm	—	Electrocatalytic OER	A low onset potential of 0.31 V in neutral solutions	79
	Co ₉ S ₈	Self-assembly	0.50 nm, 500 nm	—	—	—	51
	Co ₉ Se ₈	Oriented attachment	0.52 nm, 200 nm	—	—	Half-metallic ferromagnetism	71
	CuS	Lamellar intermediate-assisted exfoliation	3.2 nm, 453 nm	—	LIBs	A high reversible capacity of 600 mAh g ⁻¹ after 600 cycles and excellent rate capability	80
	CuInSe ₂	2D template synthesis/Topochemical transformation	2.0 nm, > 30 nm	—	Photodetectors	High flexibility and fast photoresponse	93
	Cu _{2-x} Se	2D template synthesis/Topochemical transformation	< 6.0 nm, 0.60-1.6 μm	—	—	—	94
	ZnSe	Lamellar intermediate-assisted exfoliation	0.91 nm, > 500 nm	—	Photocatalytic OER	A photocurrent density of 2.14 mA cm ⁻² at 0.72 V vs. Ag/AgCl under 300 W Xe lamp irradiation, 195 times higher than bulk counterpart	74
	Zn _{1-x} Cd _x S	Lamellar intermediate-assisted exfoliation	1.6 nm, 300 nm	—	Luminescence	White light emission with high brightness and superior photostability	75
	PdS	Self-assembly	1.8 nm, 0.20-20 μm	—	—	Enhanced in-plane carrier conductivity	52
		Oriented attachment	2.5 nm, 15-30 nm	—	—	—	65
		Oriented attachment	2.0-5.0 nm, > 1 μm	—	—	—	66
		Oriented attachment	2.4 nm, > 500 nm	Thickness control	—	The energy gap increases with decreasing thickness of the nanosheets	67
		Oriented attachment	2.2 nm, 500 nm	—	Photodetectors	The nanosheets can be readily integrated into the device without further treatment	68
		Lamellar intermediate-assisted exfoliation	1.0 nm, > 50 nm	—	—	—	77
	PdSe	Oriented attachment	5.3 nm, > 2 μm	—	—	—	69, 70
	CdS	Self-assembly	< 5.0 nm, 40 nm	—	Fluorescent emitters	An extremely narrow emission spectrum with full-width at half-maximum less than 40 meV at RT	45
		Lamellar intermediate-assisted exfoliation	4.0 nm, 100-300 nm	—	Photocatalytic HER	High photocatalytic activity and excellent stability	78
	CdSe	Self-assembly	< 5.0 nm, 20-100 nm	—	Fluorescent emitters	The radiative fluorescent life time reaches 1 ns at 6 K, two orders of magnitude less than spherical nanoparticles	45
		Self-assembly	2.2 nm, 6-40 nm	—	—	—	58
		Topochemical transformation	5.3 nm, > 2.0 μm	—	—	—	69
		Lamellar intermediate-assisted exfoliation	1.5-3.0 nm, 0.50-1.5 μm	—	—	—	76

Transition metal dichalcogenides	CdTe	Lamellar intermediate-assisted exfoliation	1.4 nm, 50-200 nm	—	—	A narrow emission band with full-width at half-maximum of 700 meV at RT	81
		Self-assembly	3.4 nm, > 1.0 μm	—	—	—	43
		Self-assembly	< 5.0 nm, 100 nm	—	Fluorescent emitters	An extremely narrow emission spectrum with full-width at half-maximum less than 40 meV at RT	45
	Co-doped In_2S_3	Lamellar intermediate-assisted exfoliation	0.59 nm, > 200 nm	Elemental doping	Photocatalytic OER	A photocurrent density of 1.17 mA cm^{-2} at 1.5 V vs. RHE, about 10 and 17 times higher than intact nanosheets and bulk counterpart, respectively	117
	Co-doped FeS_2/CNT	Self-assembly	< 5.0 nm, 100 nm for FeS_2 nanosheets	Elemental doping/Heterostructure construction	Electrocatalytic HER	A low η of 120 mV at 20 mA cm^{-2} , a small Tafel slope of 46 mV dec^{-1} , and long stability for 40 h	115
	CoS_2	Self-assembly	5.0 nm, 50 nm	—	Supercapacitors	A high specific capacitance of 1301 F g^{-1}	133
	CoSe_2	Lamellar intermediate-assisted exfoliation	1.4 nm, 200 nm	Co vacancies	Electrocatalytic OER	A η as low as 320 mV at 10 mA cm^{-2} in pH 13 medium	113
		Lamellar intermediate-assisted exfoliation	0.66 nm, 300 nm	—	Electrocatalytic OER	Metallic character, a low η of 270 mV, a small Tafel slope of 64 mV dec^{-1} , and a high turnover frequency of 745 h^{-1}	140
	Mn-doped FeS_2	Lamellar intermediate-assisted exfoliation	1.2 nm, 500 nm	Elemental doping	Electrocatalytic HER	A large exchange current density of 68.3 $\mu\text{A cm}^{-2}$, a low η of 174 mV, and a small Tafel slope 36 mV dec^{-1}	116
	$\text{CoSe}_2/\text{MoS}_2$	Lamellar intermediate-assisted exfoliation	5.0 nm, 1.0 μm for CoSe_2 nanosheets	2D heterostructure construction	Electrocatalytic HER	A low onset potential of 11 mV and a small Tafel slope of 36 mV dec^{-1}	122
	CsPdBr_3	Self-assembly	3.0 nm, 0.30-5.2 μm	—	—	—	61
Perovskites		Self-assembly	3.3 nm, 1.0 μm	—	Photodetectors	High photosensitivity, stability and flexibility	62
	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Topochemical transformation	1.3 nm, 6.0 μm	—	Photodetectors	With a voltage bias of 1 V, photoresponsivities of 22 and 12 AW^{-1} were detected by shining 405 and 532 nm lasers, respectively	106
	Organic 2D nanocrystals	Self-assembly	2.7 nm, > 1.0 μm	—	—	—	44
Others	Si	2D template synthesis	1.4 nm, 4.0 μm	—	LIBs	A discharge capacity of 600 mAh g^{-1} with a Coulombic efficiency of 96.2% after 100 cycles	88
	Si/C	Topochemical transformation	5.0 nm, 2.0 μm for Si nanosheets	2D heterostructure construction	LIBs	A high reversible capacity of 865 mAh g^{-1} at 1.0 A g^{-1} with a capacity retention of 92.3% after 500 cycles, excellent rate capability, and small volume expansion	134
	Ni_3N	Topochemical transformation	2.0-3.0 nm, > 2.0 μm	—	Electrocatalytic OER	Metallic character, a small Tafel slope of 45 mV dec^{-1} , and a mass activity of 572 A g^{-1} at a η of 500 mV	104
	Co-B _i /graphene	2D template synthesis	< 5.0 nm, 50 nm for Co-B _i nanosheets	2D heterostructure construction	Electrocatalytic OER	A low η of 290 mV at 10 mA cm^{-2} and a small Tafel slope of 53 mV dec^{-1}	121

2D, two-dimensional; LIBs, lithium-ion batteries; SIBs, sodium-ion batteries; HER, hydrogen evolution reaction; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; RHE, reversible hydrogen electrode; SCE, saturated calomel electrode; η , overpotential; RT, room temperature; Co-B_i, cobalt-based borate.

Scheme 1. Comparisons between atomically thin layered and non-layered nanomaterials.

a) Atomically thin layered nanomaterials. b) Atomically thin non-layered nanomaterials.

Scheme 2. Central theme of this review work. Summary of the research progress of atomically thin non-layered nanomaterials, including the synthetic strategies, structural and electronic properties, electronic structure manipulation strategies, and energy storage and conversion applications.

Figure 1. Self-assembly synthesis of atomically thin non-layered nanomaterials. a) Schematic illustration showing the synthesis of partially oxidized and pure 4-atom-thick Co nanosheets through a surfactant-assisted self-assembly approach.⁴⁶ b) Transmission electron microscope (TEM) image of the partially oxidized Co 4-atom-thick layers and the corresponding elemental mapping (inset shows the thickness as observed by atomic force microscopy (AFM)).⁴⁶ c) TEM image of PVP-capped rhodium nanosheet.⁴⁷ d) AFM image and the corresponding profiles of a bare Rh nanosheet.⁴⁷ e) Schematic illustration showing the in-plane coassembly synthesis of ultrathin inorganic-organic hybrid nanosheets.⁵¹ f) High resolution TEM (HRTEM) image of Co₉S₈-oleylamine hybrid nanosheets with the inset showing a typical Co₉S₈ nanoplate.⁵¹ All the figures are reproduced with permission. a,b) Copyright 2016 Nature Publishing Group. c,d) Copyright 2013 Nature Publishing Group. e,f) Copyright 2013 American Chemical Society.

Figure 2. Oriented-attachment growth of atomically thin non-layered nanomaterials. a-c) Schematic drawings showing the oriented-attachment growth of ZnO nanosheets and the corresponding TEM images and selected area electron diffraction (SAED) patterns (insets).⁶³ d) TEM image of CeO₂ nanosheet.⁶⁴ e) AFM image and corresponding height profile of CeO₂ nanosheet.⁶⁴ f) TEM image of Co₉Se₈ nanosheets with the inset showing the fold edge of a nanosheet.⁷¹ g) High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of single-crystal PbSe honeycomb structure.⁶⁹ h) High-resolution HAADF-STEM image of PdSe.⁶⁹ i) HAADF-STEM image of CdSe converted from PdSe through cation exchange, indicating the high robustness of the honeycomb superlattice.⁶⁹ All the figures are reproduced with permission. a-c) Copyright 2015 Nature Publishing Group. d,e) Copyright 2010 John Wiley and Sons. f) Copyright 2012 American Chemical Society. g-i) Copyright 2014 The American Association for the Advancement of Science.

Figure 3. Lamellar intermediate-assisted exfoliation for the synthesis of atomically thin non-layered nanomaterials. a) Schematic drawing of the lamellar intermediate-assisted exfoliation strategy.⁷⁴ b) TEM image of ZnSe single layers with insets displaying the Tyndall effect (left) and the nanosheet thickness (right).⁷⁴ c) Ultrathin CuS nanosheets.⁸⁰ d) Single-layered CdSe nanosheets, with the SARD pattern in the inset.⁸¹ e) Ultrathin Co₃S₄ nanosheets.⁷⁹ f) Schematic illustration showing the synthesis of ultrathin transition metal oxide nanosheets.⁸³ g) Scanning electron microscope (SEM) images of the prepared TiO₂, ZnO, Co₃O₄ and WO₃ nanosheets.⁸³ All the figures are reproduced with permission. a,b) Copyright 2012 Nature Publishing Group. c) Copyright 2012 Nature Publishing Group. d) Copyright 2009 John Wiley and Sons. e) Copyright 2015 John Wiley and Sons. f,g) Copyright 2014 Nature Publishing Group.

Figure 4. 2D template synthesis of atomically thin non-layered nanomaterials. a) schematic drawing illustrating the synthesis of atomically thin $\gamma\text{-Al}_2\text{O}_3$ nanosheets with GO as the templates.⁸⁶ b) SEM image of the thus-prepared $\gamma\text{-Al}_2\text{O}_3$ nanosheets.⁸⁶ c) TEM image of Au square nanosheets on GO surface with the inset displaying the crystallographic models.⁸⁷ d) fcc Au@Pt (top) and Au@Pd (bottom) rhombic nanoplates with presynthesized hcp Au as the templates.⁹⁰ e) fcc Au@Ag square nanosheets.⁹¹ f) $\alpha\text{-Fe}_2\text{O}_3$ nanosheets synthesized on CuO template surface with Tyndall effect and lattice spacing in insets.⁹² g) Schematic illustration showing the formation of CuInSe_2 nanosheets by using CuSe sacrificial templates.⁹³ h) TEM image of the thus-prepared CuInSe_2 nanosheets.⁹³ i) SEM image of Cu_{2-x}Se nanosheets transformed from CuSe templates.⁹⁴ All the figures are reproduced with permission. a,b) Copyright 2016 John Wiley and Sons. c) Copyright 2011 Nature Publishing Group. d) Copyright 2015 John Wiley and Sons. e) Copyright 2016 Nature Publishing Group. f) Copyright 2014 American Chemical Society. g,h) Copyright 2012 Royal Society of Chemistry. i) Copyright 2014 John Wiley and Sons.

Figure 5. Topochemical transformation for the synthesis of atomically thin non-layered nanomaterials. a-c) Ultrathin Co_3O_4 nanosheets converted from $\text{Co}(\text{OH})_2$ (inset),⁹⁶ $\alpha\text{-Co}(\text{OH})_2$,⁹⁹ and $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$,¹⁰⁰ respectively. d) NiCo_2O_4 ,¹⁰² e) CeO_2 ,⁹⁸ f) In_2O_3 ,⁹⁷ g) Ni_3N ,¹⁰⁴ h) iron-nickel sulfide,¹⁰³ and i,j) $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanosheets^{105,106} converted from their corresponding layered precursor nanosheets. The insets of (c-h) show the nanosheet thickness, and the second insets in (d and e) show the Tydall effect. All the figures are reproduced with permission. a) Copyright 2016 Elsevier. b) Copyright 2013 Royal Society of Chemistry. c) Copyright 2015 John Wiley and Sons. d) Copyright 2015 John Wiley and Sons. e) Copyright 2013 Nature Publishing Group. f) Copyright 2014 American Chemical Society. g) Copyright 2015 American Chemical Society. h) Copyright 2015 American Chemical Society. i) Copyright 2016 American Chemical Society. j) Copyright 2016 American Chemical Society.

Figure 6. Synchrotron radiation XAFS measurements, calculated DOS, and structural model of ZnSe single layers with 4-atom layer thickness.⁷⁴ a) Zn and Se K-edge extended XAFS oscillation function $k\chi(k)$, in which the red, blue, and black lines correspond to ZnSe single layers, ZnSe-pa single layers, and bulk ZnSe, respectively. b) Fourier transforms of a). c) Structural model of ZnSe single layer viewed along the (110) plane. d) Calculated DOS with the black, blue, and olive lines denoting the total, Se sp and Zn sp state density, respectively. All the figures are reproduced with permission, copyright 2012 Nature Publishing Group.

Figure 7. Surface chemical states of atomically thin transition metal oxides.⁸³ XPS spectra of a) TiO₂, c) ZnO, e) Co₃O₄, and g) WO₃ nanosheets, showing 0.5-2 eV negative shifts in core-level bonding-energy; and atomic structures and slices of the total charge density distributions for b) TiO₂ (010), d) ZnO (001), f) Co₃O₄ (010), and h) WO₃ (100) planes of bulk (top) and nanosheet (bottom) crystals, illustrating the redistribution of electron densities accompanied by extra bond formation, breaking, and distortion. All the figures are reproduced with permission, copyright 2014 Nature Publishing Group.

Figure 8. Manipulation of electronic structures through thickness control. a) Crystal structure of SnO₂ nanosheets showing different coordination numbers for surface and interior atoms.¹⁰⁷ b,c) DOS for bulk SnO₂ and 0.66 nm thick SnO₂ nanosheets, respectively, displaying the increased DOS at the valence band edge of SnO₂ nanosheets.¹⁰⁷ d,e) DOS and f,g) charge-density distributions of bulk Co₃O₄ and atomic Co₃O₄ layers, respectively. The yellow shaded area in e) and partial charge density in g) suggest an increased DOS at the conduction band edges of Co₃O₄ atomic layers.¹⁰⁰ h) Raman and i) XPS spectra of Co₃O₄ nanosheets (1.6 nm in thickness), nanoflowers (1.8 nm), and bulk nanocubes, with the insets showing higher resolution in the indicated regions. The broadening and shifts in the spectral peaks of Co₃O₄ nanosheets originate from the enhanced phonon confinement effect and the obvious lattice structural distortion.⁹⁶ All the figures are reproduced with permission. a-c) Copyright 2013 John Wiley and Sons. d-g) Copyright 2015 John Wiley and Sons. h,i) Copyright 2016 Elsevier.

Figure 9. Manipulation of electronic structures through pit/pore creation. a) Schematic illustration of pits in CeO₂ bulk and atomically thin nanosheet, and intact CeO₂ nanosheet.⁹⁸ b) Ce L₃-edge extended XAFS oscillation function $k^2\chi(k)$.⁹⁸ c) Fourier transforms $FT(k^2\chi(k))$.⁹⁸ d) Calculated DOS.⁹⁸ e) Crystal structure showing the difference in coordination numbers of surface or pore-surrounding Co³⁺ atoms.¹⁰⁸ f) Calculated DOS for bulk Co₃O₄ and g) porous Co₃O₄ atomically thin nanosheets.¹⁰⁸ All the figures are reproduced with permission. a-d) Copyright 2013 Nature Publishing Group. e-g) Copyright 2014 Royal Society of Chemistry.

Figure 10. Manipulation of electronic structures through vacancy engineering. a) XPS spectra of V_O -rich and -poor Co_3O_4 single-unit-cell layers.¹¹¹ b,c) Synchrotron radiation XAFS measurements of V_O -rich and -poor Co_3O_4 single-unit-cell layers.¹¹¹ d) Schematic drawing of the adsorption of H_2O molecules onto the spinel structure and the spatial charge density of $NiCo_2O_4$ around the oxygen vacancy.¹⁰² e-h) Positron lifetime spectra and XAFS measurements of bulk $CoSe_2$ and V_{Co} -rich $CoSe_2$ nanosheets.¹¹³ i-k) DOS diagrams, schematic representation of trapped positrons, and slab ($2 \times 2 \times 2$) containing coexisting Sn and O vacancies in ultrathin SnO_2 nanosheets.¹¹⁴ l-n) DOS diagrams, schematic representation of trapped positrons, and slab ($2 \times 2 \times 2$) containing an isolated Sn vacancy.¹¹⁴ All the figures are reproduced with permission. a-c) Copyright 2017 Nature Publishing Group. d) Copyright 2015 John Wiley and Sons. e-h) Copyright 2014 American Chemical Society. i-n) Copyright 2015 American Chemical Society.

Figure 11. Manipulation of electronic structures through elemental doping. a) Metallic Mn-doping of CoSe₂ results in subtle distortion of the atomic arrangement.¹¹⁶ b) Schematic representations of the mechanisms behind distortion of the atomic arrangement.¹¹⁶ c,e,g) Calculated DOS of bulk In₂S₃, perfect In₂S₃ atomic layers, and Co-doped In₂S₃ atomic layers, respectively.¹¹⁷ d,f,h) Distribution of charge density of bulk In₂S₃, perfect In₂S₃ atomic layers, and Co-doped In₂S₃ atomic layers, respectively.¹¹⁷ All the figures are reproduced with permission. a,b) Copyright 2016 American Chemical Society. c-h) Copyright 2015 John Wiley and Sons.

Figure 12. Manipulation of electronic structures through 2D heterostructure construction. a-c) EPR and high-resolution XPS spectra of TiO₂/graphene hybrid, showing the chemical state of Ti at the interface.¹¹⁸ d,e) Raman and O 1s XPS spectra of Co₃O₄/graphene nanosheet composite. The peak shift in the Raman spectrum and the extra peak existing in the XPS spectrum indicate that a charge transfer has occurred and a Co-O-C linkage has been formed at the interface.¹¹⁹ f) S 2p XPS spectra of MoS₂/CoSe₂ hybrids with an extra peak located at around 166 eV, indicating the formation of Co-S bonds between them.¹²² g) Pd 3d XPS spectra of Pd nanosheets. h,i) Pd 3d and Ru 3p XPS spectra of Pd/Ru nanosheets.¹²³ All the figures are reproduced with permission. a-c) Copyright 2015 Nature Publishing Group. d,e) Copyright 2016 John Wiley and Sons. f) Copyright 2015 Nature Publishing Group. g-i) Copyright 2016 John Wiley and Sons.

Figure 13. Electrochemical performances of atomically thin non-layered nanomaterials in supercapacitors. a-c) TEM image, CV curves, and cycling performance (100 mV s^{-1}) of ultrathin mesoporous NiO nanosheets.¹²⁸ d) SEM image of phosphate ion functionalized ultrathin Co_3O_4 nanosheets.¹³² e-h) CV curves, Ragone plots, cycling performance, and mechanism for enhanced pseudocapacitance of the PCO//3DPG asymmetric supercapacitor.¹³² All the figures are reproduced with permission. a-c) Copyright 2015 Royal Society of Chemistry. d-h) Copyright 2016 John Wiley and Sons.

Figure 14. Electrochemical performances of atomically thin non-layered nanomaterials in LIBs. a-c) TEM image, cycling performance (0.5 C), and rate capabilities of atomically thin Co_3O_4 nanosheets.⁹⁹ d,e) TEM image and cycling performance (2.25 C) of atomically thin mesoporous Co_3O_4 /graphene nanocomposites.¹¹⁹ f) Comparison of specific capacity and cycling performance between Co_3O_4 /graphene nanosheets and previously reported Co_3O_4 /C composites.¹¹⁹ g) TEM image of ultrathin Si nanosheets.¹³⁴ h,i) Long-term cycling stability and rate capability of carbon-coated Si nanosheets.¹³⁴ All the figures are reproduced with permission. a-c) Copyright 2013 Royal Society of Chemistry. d-f) Copyright 2016 John Wiley and Sons. g-i) Copyright 2016 American Chemical Society.

Figure 15. Capacitive storage behavior of atomically thin non-layered nanomaterials in SIBs. a) HRTEM image of TiO_2 nanosheets grown on graphene nanosheets.¹¹⁸ b) Rate capability at different current densities.¹¹⁸ c) Cycling performance and Coulombic efficiency at 500 mA g⁻¹.¹¹⁸ d) Separation of capacitive storage from total charge storage.¹¹⁸ e) Contribution ratio of capacitive storage vs. scan rate.¹¹⁸ f) Illustration of Na⁺ intercalation pseudocapacitance at the partially bonded TiO_2 -graphene interface.¹¹⁸ g-k) Na⁺ capacitive storage behavior of Co_3O_4 nanosheets grown on stainless steel mesh.¹³⁸ All the figures are reproduced with permission. a-f) Copyright 2016 Nature Publishing Group. g-k) Copyright 2016 IOP Publishing.

Figure 16. HER catalytic performances of atomically thin non-layered nanomaterials. a-c) TEM image, polarization curve, and corresponding Tafel slopes of $\text{Mn}_{0.05}\text{Co}_{0.95}\text{Se}_2$ ultrathin nanosheets.¹¹⁶ d-f) TEM image, polarization curve, and corresponding Tafel slopes of $\text{MoS}_2/\text{CoSe}_2$ hybrids.¹²² g-i) TEM image, photocurrent density under 300 W Xe lamp irradiation, and IPCE at 1.6 V vs. RHE of V_O -rich ultrathin In_2O_3 porous nanosheets.⁹⁷ All the figures are reproduced with permission. a-c) Copyright 2016 American Chemical Society. d-f) Copyright 2015 Nature Publishing Group. g-i) Copyright 2014 American Chemical Society.

Figure 17. OER catalytic performances of atomically thin non-layered nanomaterials. a) TEM image of free-standing ZnSe single layers.⁷⁴ b,c) Photocurrent density under 300 W Xe lamp irradiation, and IPCE at 0.6 V vs. Ag/AgCl. The magenta, blue, olive, cyan, purple and red plots correspond to ZnSe single layers, ZnSe-pa double layers and quadruple layers, ZnSe-pa octuple layers, (Zn₂Se₂)(pa) and bulk ZnSe, respectively.⁷⁴ d-f) TEM image, polarization curve, and corresponding Tafel slopes of atomically thin porous Co₃O₄ nanosheets, with the inset showing the H₂O adsorption energy vs. coordination number.¹⁰⁸ g-i) TEM image (with inset SAED pattern), polarization curve, and corresponding Tafel slopes of ultrathin Fe-Co oxide nanosheets.¹¹² All the figures are reproduced with permission. a-c) Copyright 2012 Nature Publishing Group. d-f) Copyright 2014 Royal Society of Chemistry. g-i) Copyright 2017 John Wiley and Sons.

Figure 18. Catalytic performances of atomically thin non-layered nanomaterials for CO₂ reduction. a) HRTEM image of partially oxidized 4-atom-thick Co layers.⁴⁶ b-d) Catalytic performances for CO₂ reduction including linear sweep voltammetric curves in CO₂-saturated (solid line) and N₂-saturated (dashed line) 0.1 M Na₂SO₄ aqueous solution, Faradaic efficiencies of formate at each given potential for 4 h, and chrono-amperometry results at potentials with the highest Faradaic efficiencies. The lines in b-d) stand for partially oxidized 4-atom-thick Co layers (red), 4-atom-thick Co layers (blue), partially oxidized bulk Co (violet) and bulk Co (black).⁴⁶ e-h) HRTEM image and catalytic performances in CO₂ reduction of Sn quantum sheets confined in graphene.¹²⁰ All the figures are reproduced with permission. a-d) Copyright 2016 Nature Publishing Group. e-h) Copyright 2016 Nature Publishing Group.

Figure 19. Catalytic performance of atomically thin CeO_2 nanosheets for CO oxidation.⁹⁸ a) HRTEM image of 3-atom-thick CeO_2 nanosheets with numerous pits on the surface. b) Schematic drawing showing the Ce sites ($P_1 \sim P_3$) surrounding a pit and Ce sites on the surface ($S_1 \sim S_3$) with coordination numbers 5, 4, 6, 6, 6, and 6, respectively. c) Calculated adsorption energies of CO and O_2 on different Ce sites. d) Calculated activation energies for O_2 dissociation on different adjacent Ce sites. e) Schematic drawing showing that CO prefers to adsorb at P_2 sites, while O_2 tends to adsorb and dissociate at adjacent P_1 sites. f) Catalytic activity towards CO oxidation as a function of reaction temperature. g) Arrhenius plots showing the apparent activation energies. All the figures are reproduced with permission, copyright 2013 Nature Publishing Group.

Figure 20. Other energy-related applications of atomically thin non-layered nanomaterials. a) TEM image of the palladium nanosheets with inset showing an ethanol dispersion.⁵⁶ b) Electrochemical properties of palladium nanosheets and palladium black for catalytic oxidation of formic acid.⁵⁶ c) TEM image of Pd@Pt_{monolayer}.¹⁴⁶ d) ORR polarization curves of Pd@Pt_{monolayer} at 10 mV s⁻¹ under 1600 rpm.¹⁴⁶ e) Schematic illustration showing the fabrication of the transparent and flexible photodetector device.⁸³ f) I-V characteristics of the photodetectors constructed from TiO₂, ZnO, Co₃O₄, and WO₃ nanosheets, respectively.⁸³ g) Photoresponse behaviors of the photodetectors under alternating on and off 325 nm ultraviolet light.⁸³ All the figures are reproduced with permission. a,b) Copyright 2010 Nature Publishing Group. c,d) Copyright 2015 Royal Society of Chemistry. e-g) Copyright 2014 Nature Publishing Group.

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