

Ultrathin Two-Dimensional Inorganic Materials: New Opportunities for Solid State Nanochemistry

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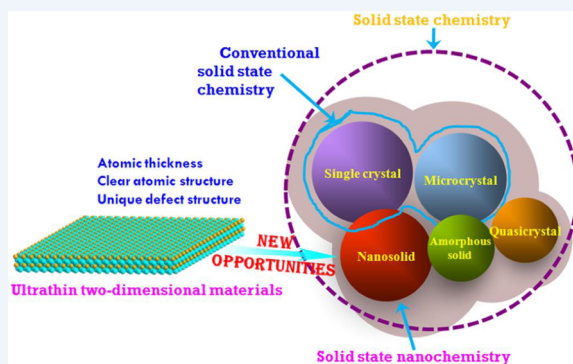
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CONSPECTUS: The ultimate goal of solid state chemistry is to gain a clear correlation between atomic, defect, and electronic structure and intrinsic properties of solid state materials. Solid materials can generally be classified as amorphous, quasicrystalline, and crystalline based on their atomic arrangement, in which crystalline materials can be further divided into single crystals, microcrystals, and nanocrystals. Conventional solid state chemistry mainly focuses on studying single crystals and microcrystals, while recently nanocrystals have become a hot research topic in the field of solid state chemistry. As more and more nanocrystalline materials have been artificially fabricated, the solid state chemistry for studying those nanosolids has become a new subdiscipline: solid state nanochemistry. However, solid state nanochemistry, usually called “nanochemistry” for short, primarily studies the microstructures and macroscopic properties of a nanomaterial’s aggregation states. Due to abundant microstructures in the aggregation states, it is only possible to build a simple but imprecise correlation between the microscopic morphology and the macroscopic properties of the nanostructures.

Notably, atomically thin two-dimensional inorganic materials provide an ideal platform to establish clear structure–property relationships in the field of solid state nanochemistry, thanks to their homogeneous dispersion without the assistance of a capping ligand. In addition, their atomic structures including coordination number, bond length, and disorder degree of the examined atoms can be clearly disclosed by X-ray absorption fine structure spectroscopy. Also, their more exposed interior atoms would inevitably induce the formation of various defects, which would have a non-negligible effect on their physicochemical properties. Based on the obtained atomic and defect structural characteristics, density-functional calculations are performed to study their electronic structures. Then, after the properties of the individual ultrathin two-dimensional materials or their assembled highly oriented thin film-based nanodevices are measured, the explicit relationship between atomic, defect, and electronic structure and intrinsic properties could be established.

In this Account, we focus on our recent advances in the field of solid state nanochemistry, including atomic structure characterization of ultrathin two-dimensional inorganic materials by X-ray absorption fine structure spectroscopy, characterization of their different types of structural defects by positron annihilation spectra and electron spin resonance, and investigation of their electronic structure by density-functional calculations. In addition, we summarize the close correlation between atomic, defect, and electronic structure variations and the optoelectronic, electrical, magnetic, and thermal properties of ultrathin two-dimensional materials. Finally, we also propose the major challenges and opportunities that face solid state nanochemistry. We believe that all the past achievements in ultrathin two-dimensional materials could bring new opportunities for solid state nanochemistry.



1. INTRODUCTION

Solid state chemistry offers fertile ground for research at the intersection of multiple fields, in which the preparation, composition, structure, and properties of solid state materials are studied.¹ The properties of a solid state material are not determined solely by its chemical composition but also by its structure.² Note that the structure of solid state materials may be described by four components: electronic structure, which defines interaction among atoms; atomic structure, which includes the bond types and arrangement of atoms; microstructure, which includes micromorphological characteristics

that can be seen using an electron microscope, which hence becomes the most common characterization technique for the solid materials; macrostructure, which includes characteristics that can be seen with the naked eye.³ Meanwhile, it should be noted that the arrangement of atoms in most solid materials is not perfect; the regular patterns of atomic structures are usually

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interrupted by crystallographic defects, which would strongly affect the physical properties of solid materials and have a decisive impact on their performance in applications.⁴ Accordingly, it is concluded that solid state chemistry deals primarily with the clear relationship between atomic, defect, and electronic structure and intrinsic properties of solid materials. As is well-known, solid materials can generally be classified as amorphous, quasicrystalline, and crystalline on the basis of their atomic arrangement, in which crystalline materials can be further divided into single crystals, microcrystals, and nanocrystals. Note that conventional solid state chemistry mainly studies single crystals and microcrystals, while there has been much scientific activity on nanocrystals over the past decade. With the fast development of nanotechnology, more and more nanocrystalline materials have been artificially synthesized, which enables the investigation of nano-solid materials to become a new subdiscipline: solid state nanochemistry. However, solid state nanochemistry, usually shortened to “nanochemistry”, mainly studies the nanomaterial’s microstructures by using electron microscopes and hence investigates their corresponding macroscopic properties for the aggregation states of various nanostructures. Owing to the abundant microstructures such as surface, interface, grain boundary, defects, and capping agents in the nanosolids’s aggregation states, it is very difficult to establish their precise structure–property relationships that are really the concern of solid state chemistry. Hence, the knowledge gained from the corresponding experiments could not be directly applicable to other material systems. To obtain well-defined structure–property correlations, simplifying and bridging the material model with the real material is of crucial importance.

Of note, with the global boom in graphene research, more and more atomically thin two-dimensional inorganic materials have gained significant interest.^{5–8} Besides their promising applications in various nanodevices with ultrathinness, transparency, and flexibility, the ultrathin two-dimensional materials could also serve as one of the ideal models for establishing clear structure–property relationships in the field of solid state nanochemistry. Ultrathin two-dimensional materials with atomic thickness can be homogeneously dispersed without the assistance of capping ligand, while their atomic thickness favors building clear atomic structure.^{9–14} Meanwhile, the more exposed interior atoms inevitably induce the formation of defects on the surfaces, which would have an important affect on their electronic structure. Also, the individual ultrathin two-dimensional material can be fabricated into a nanodevice without grain boundaries,^{15–17} and also it can be assembled into a highly oriented thin film-based nanodevice through a layer-by-layer assembly strategy,^{9,18,19} thus providing an ideal platform to study the correlations between atomic, defect, and electronic structure and intrinsic properties of the atomically thin two-dimensional materials. In contrast, the zero- or one-dimensional nanostructures whose size is in the 1–100 nm regime tend to aggregate to form a bulky mass during their formation processes, in which capping ligands are always required to realize their stability.^{20,21} In addition, it is very difficult to directly measure the properties of an individual 0D material, while its orientation disorder or the presence of capping ligands leads its assembled nanodevices to inevitably generate abundant and complex structural characteristics. Also, the assembly of 1D materials into a nanodevice cannot ignore the presence of abundant grain boundaries and different crystal orientations, which makes it hard to obtain clear structure–

property relationships. Despite the easy synthesis and convenient property measurements for three-dimensional nanostructures, their microstructures are too abundant to build a clear atomic structure, and hence only a simple but imprecise structure–property relationship can be achieved. Notably, although the atomically thin two-dimensional materials possess several clear-cut prerequisites for establishing clear structure–property correlations, characterization of their low-dimensional structures and understanding of their structure–property relationships are still very limited.^{10,22} This is most likely because the lack of long-range order in the third dimension leaves the typical structure characterization techniques, such as X-ray diffraction (XRD) techniques, unable to identify the spatial atomic distribution in ultrathin two-dimensional materials, since they rely on the long-range order of atomic positions in a crystal. We recently utilized a powerful element-specific tool of X-ray absorption fine structure spectroscopy (XAFS) to study the local atomic geometry and the chemical state of the atoms of one specific element in ultrathin two-dimensional materials.^{9,10,18} Owing to the deep penetration of X-rays and atomic species identity, the XAFS technique is the most suitable and adequate tool for determining structures that lack long-range order such as nanomaterials, amorphous materials, highly disordered solids, or even liquids. More importantly, upon reduction of the thickness of two-dimensional solid materials to the atomic-scale regime, more interior atoms can be exposed on the surfaces and hence can be easily escaped from the lattice to form vacancies, which would have non-negligible effects on the physicochemical properties of ultrathin two-dimensional materials. However, despite their great importance, the characterization of defects in ultrathin two-dimensional materials is very difficult, because the different types of defects can only be distinguished by different characterization techniques.

In this Account, we focus on our recent systematic studies utilizing XAFS technique to disclose the well-defined atomic structure in atomically thin two-dimensional inorganic materials, discuss characterization of their different types of structural defects by positron annihilation spectra and electron spin resonance, and also survey their electronic structure variations revealed by density-functional theory (DFT) calculations. Moreover, we highlight the correlation between atomic, defect, and electronic structure variations and the optoelectronic, electrical, magnetic, and thermal properties of ultrathin two-dimensional materials. Finally, we also outline the major opportunities that face solid state nanochemistry.

2. ATOMIC STRUCTURE OF ULTRATHIN TWO-DIMENSIONAL INORGANIC MATERIALS

Atomically thin two-dimensional inorganic materials are a conceptually new class of materials that provide new opportunities to satisfy people’s requirement of high-quality nanodevices.^{9–14} However, the lack of long-range order in the third dimension disables XRD to determine the spatial distribution of real atoms in these ultrathin two-dimensional materials. Intriguingly, XAFS is a particularly useful supplement to the XRD technique and could play a crucial role in studying the two-dimensional ultrathin materials, since it is based on short-range effects and also it can immediately identify the coordination number, bond length, and disorder degree of the atoms surrounding the examined element.²³

Taking the all-surface-atomic SnS sheets as an example,¹⁸ XAFS spectra in Figure 1A,B reveal that the peak intensity for

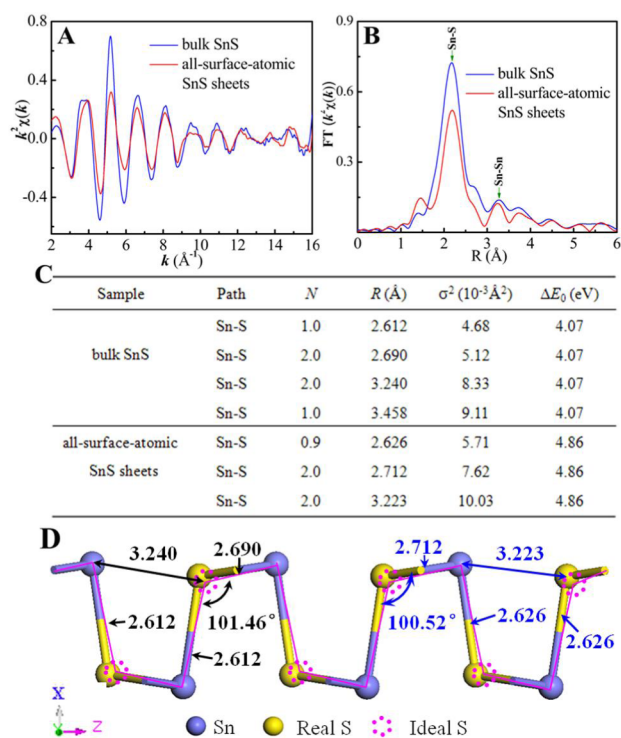


Figure 1. (A) Sn K-edge extended XAFS oscillation function, $k^2\chi(k)$, and (B) the corresponding Fourier transforms for all-surface-atomic SnS sheets and their bulk counterpart. (C) Structural parameters extracted from EXAFS curve-fitting. (D) Structural model for all-surface-atomic SnS sheets. Adapted with permission from ref 18. Copyright 2014 Wiley-VCH.

the all-surface-atomic SnS sheets is decreased and the peak position is shifted by 0.02 Å to the high R direction compared with those of the bulk counterpart. XAFS fitting results in Figure 1C reveal that the interatomic distances of all the Sn–S coordinations in the all-surface-atomic SnS sheets are slightly

elongated and their degrees of disorder are considerably increased. According to these structural parameters, the schematic structure model of two-atom-thick SnS sheets is built and shown in Figure 1D in which the distorted bond lengths and bond angles are labeled. Note that the loss of the neighboring S atom in the adjacent layer does not result in a remarkable change of the monolayer structure but leads to a slight intralayer structural distortion. The distorted atomic structure would endow the all-surface-atomic SnS sheets with peculiar electronic structure and hence benefit for enhanced solar water splitting efficiency. Moreover, in the synthetic pit-confined three-atom-thick CeO₂ sheets,¹⁰ the EXAFS data fitting results reveal that the pit-surrounding Ce–O distances are reduced from 2.327 to 2.302 Å, and their coordination numbers decrease from 6.5 to 4.6, associated with increased degrees of disorder compared with that of the three-atom-thick CeO₂ sheets. This indicates a structural distortion surrounding the pits of ultrathin CeO₂ sheets, which would induce changes in the electronic structure parameters and hence favor their physical properties. Furthermore, in the case of the MoS₂ single layers, XAFS studies reveal short, intermediate, and long Mo–Mo distances, indicating a distortion from the hexagonal parent structure.²⁴ As a result, synchrotron radiation XAFS can clearly detect atomic structure variations of the ultrathin two-dimensional materials, opening new opportunities to uncover their structure–property relationships.

3. DEFECT STRUCTURE OF ULTRATHIN TWO-DIMENSIONAL INORGANIC MATERIALS

Compared with those in the bulk materials, the more exposed interior atoms in the atomically thin two-dimensional inorganic materials can easily escape from the lattice to form vacancy defects, which would have a non-negligible effect on the materials' electronic structure and physicochemical properties. In addition, the different types of defects would have distinct influences on the properties of ultrathin two-dimensional materials. In this case, to gain deep insights into the

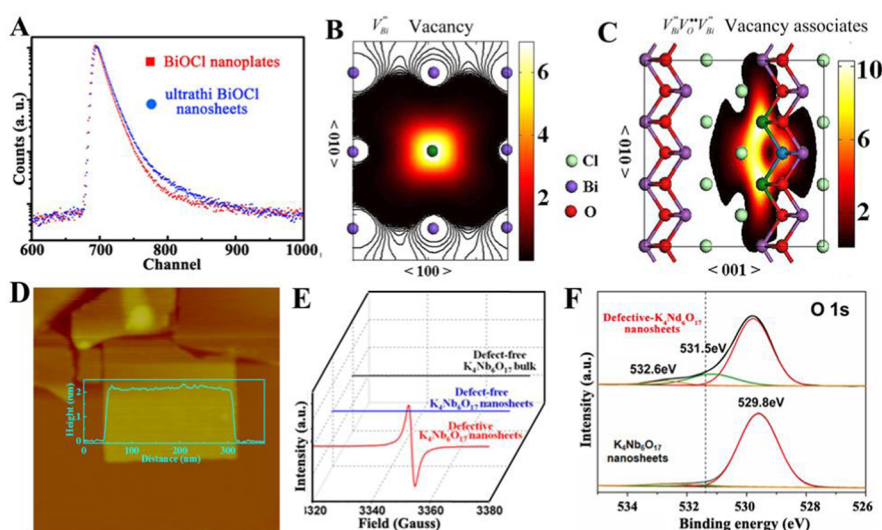


Figure 2. (A) Positron lifetime spectrum of ultrathin BiOCl sheets and BiOCl nanoplates. (B, C) Schematic representations of trapped positrons of triple Bi³⁺-oxygen vacancy associates and isolated bismuth vacancies. Adapted with permission from ref 27. Copyright 2013 American Chemical Society. (D) AFM image and the corresponding height profile of the defective K₄Nb₆O₁₇ nanosheets. (E) ESR spectra of defective and defect-free K₄Nb₆O₁₇ nanosheets and bulk. (F) O 1s region of defect-free and defective K₄Nb₆O₁₇ nanosheets. Adapted with permission from ref 29. Copyright 2014 Wiley-VCH.

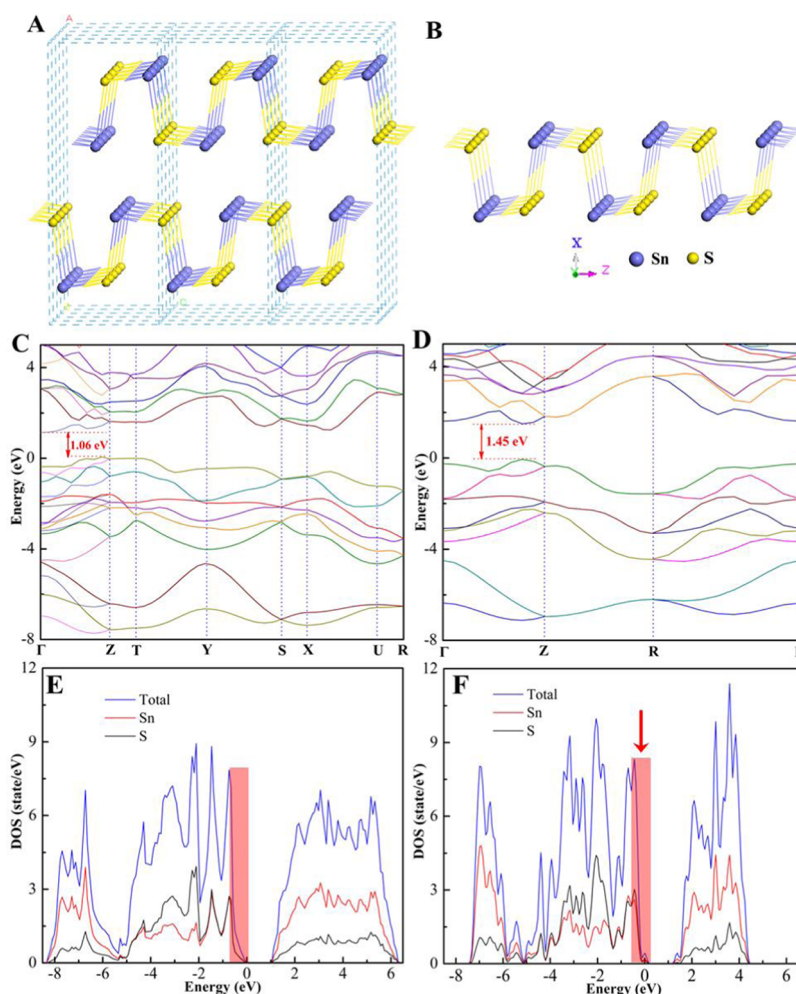


Figure 3. (A) Crystal structure for orthorhombic SnS and (B) monolayer SnS. Calculated band structure for (C) bulk SnS with an indirect band gap of 1.06 eV and (D) SnS monolayer with a direct band gap of 1.45 eV. Calculated density of states for (E) bulk SnS and (F) SnS monolayer; shaded in panel F denotes the increased state density compared with that in panel E. Adapted with permission from ref 18. Copyright 2014 Wiley-VCH.

fundamental properties and promising applications, it is highly desirable to identify the different types of defects in the as-obtained atomically thick two-dimensional materials.

Taking the negatively charged vacancy defects generated in ultrathin two-dimensional materials as an example, they can be detected by positron annihilation spectroscopy, which is based on the detection of γ radiation after annihilation of positron with an electron in the studied sample.^{25,26} For instance, in the synthetic ultrathin BiOCl sheets and BiOCl nanoplates,²⁷ positron annihilation spectrometry in Figure 2A–C clearly reveals that the ultrathin two-dimensional BiOCl sheets predominately possess the triple Bi³⁺–oxygen vacancy associates, while the BiOCl nanoplates mainly display isolated bismuth vacancies. In other words, as the thickness of BiOCl reduces to atomic thickness, the predominant vacancies change from isolated vacancy to triple vacancy associates.

Moreover, the single-electron-trapped vacancy-type defects in ultrathin two-dimensional materials can be identified by electron spin resonance (ESR),²⁸ which is based on the absorption of microwave radiation by an unpaired electron when it is exposed to a strong magnetic field. For example, in the synthetic ultrathin K₄Nb₆O₁₇ nanosheets (Figure 2D,E),²⁹ ESR reveals that a sharp signal at $g = 2.004$ is detected only in the defective-K₄Nb₆O₁₇ nanosheets, which verifies the successful introduction of oxygen vacancies,³⁰ further demon-

strated by their X-ray photoelectron spectroscopy (XPS) measurements. The O 1s XPS in Figure 2F shows a new peak located at 531.5 eV in the defective-K₄Nb₆O₁₇ nanosheets, which can be assigned to the oxygen vacancies.^{29,31} Also, in another case of the synthetic ultrathin In₂O₃ porous sheets,³¹ their ESR signal at $g = 2.004$ also demonstrates the presence of single-electron-trapped oxygen vacancies, further confirmed by the corresponding XPS and photoluminescence spectra. Moreover, Casiraghi and co-workers have utilized Raman spectra to identify the sp³-type, vacancy-like, and boundary-like defects in graphene through fitting the D and D' Raman peaks.³² Also, Jin et al. have used an aberration-corrected high-resolution transmission electron microscopy to resolve atomic defects in a BN monolayer, in which boron monovacancies are found to be preferably formed and the dominating zigzag-type edges are proved to be nitrogen terminated.³³

In brief, although the defect structure plays an important role in affecting the electronic structure and properties of the ultrathin two-dimensional materials, the characterization of these defects is still very limited, since the different types of defects can only be identified by unique characterization techniques.

4. UNIQUE ELECTRONIC STRUCTURE OF ULTRATHIN TWO-DIMENSIONAL INORGANIC MATERIALS

As is well-known, electronic structure refers to the arrangement of electrons in an atom in different shells and subshells. The number of electrons in their outermost shell primarily determines the physical properties such as band gap, electrical conductivity, carrier concentration and mobility, melting point, boiling point, hardness, and mechanical strength. Thus, studying and understanding the electronic structure is of vital importance for the design and synthesis of functional materials with controllable properties. In this regard, ultrathin two-dimensional inorganic materials could serve as an ideal platform for investigating the changes of electronic structure, owing to the obvious atomic and defect structural variations relative to bulk counterpart.

To disclose the electronic structure of atomically thin two-dimensional materials, DFT calculations are carried out based on their atomic structural parameters obtained by synchrotron radiation XAFS. Taking the synthetic all-surface-atomic SnS sheets as an example (Figure 3A,B),¹⁸ their calculated band structures in Figure 3C,D reveal that the exfoliation of bulk SnS into SnS monolayer results in the change from an indirect semiconductor to a direct semiconductor, suggesting enhanced light-harvesting capability. In addition, Figure 3E,F clearly shows that the SnS monolayer possesses increased DOS at the valence band edge in comparison with the bulk counterpart, which gives it with higher carrier transport efficiency. Moreover, in the case of synthetic ultrathin VO₂(M) sheets,³⁴ the DFT calculations reveal that atomic structural variations can bring unprecedented electronic structure features. The calculated DOS shows that the bulk VO₂(M) is a semiconductor with a band gap of about 0.65 eV, while the spin-down states of the ultrathin VO₂(M) sheet show a band gap of about 0.41 eV and the spin-up states are gapless. This suggests that the ultrathin VO₂(M) sheet possesses a new half-metallic conductive nature, holding great promise for applications in spintronic devices. Similar results also appear in synthetic ultrathin Co₉Se₈ sheets with four atomic thicknesses;³⁵ their calculated DOS shows that the spin-down states have a band gap of ~1.5 eV and the spin-up states are gapless, indicating the half-metallic nature of the ultrathin Co₉Se₈ sheets. This behavior is distinctly different from the semiconductor behavior of their bulk counterpart.

Moreover, the defects also play a vital role in affecting the electronic structure, which could be demonstrated in the synthetic five-atom-thick In₂O₃ sheets with oxygen vacancies.³¹ DFT calculations for the five-atom-thick In₂O₃ slab display that the oxygen vacancies not only endow it with increased DOS at the valence band maximum but also benefit the formation of a new defect level near the conduction band minimum, which ensures a narrowed band gap and higher carrier concentration, hence facilitating visible light harvesting and carrier separation efficiency.

Briefly, the DFT calculations demonstrate that the unique atomic structures as well as the defect structures could endow the ultrathin two-dimensional materials with peculiar electronic structures and hence ensure improved physical properties.

5. STRUCTURE–PROPERTY CORRELATION OF ULTRATHIN TWO-DIMENSIONAL INORGANIC MATERIALS

Over the past decade, nanoscale solids have been demonstrated to possess a wealth of intriguing properties and promising

applications in various fields. However, up to now, only a simple but imprecise structure–property relationship could be achieved, owing to the presence of abundant microstructures in the previously synthesized nanosolids. To gain in-depth understanding of the structure–property correlation, atomically thin two-dimensional materials are proposed as an ideal material model to study the correlation between their atomic, defect, and electronic structures and intrinsic properties.

5.1. Optoelectronic Properties of Ultrathin Two-Dimensional Inorganic Materials

Benefiting from the unique atomic structure and defect structure, ultrathin two-dimensional materials could achieve enhanced solar light harvesting, hence ensuring promoted optoelectronic properties. Taking the synthetic ultrathin BiOCl nanosheets as an example,²⁷ they possess a defect type of triple Bi³⁺-oxygen vacancy associates, which is distinctly different from the isolated Bi³⁺ vacancies in the BiOCl nanoplates (Figure 2B,C). UV/vis absorption spectra and XPS valence spectra in Figure 4A–C show that the ultrathin BiOCl

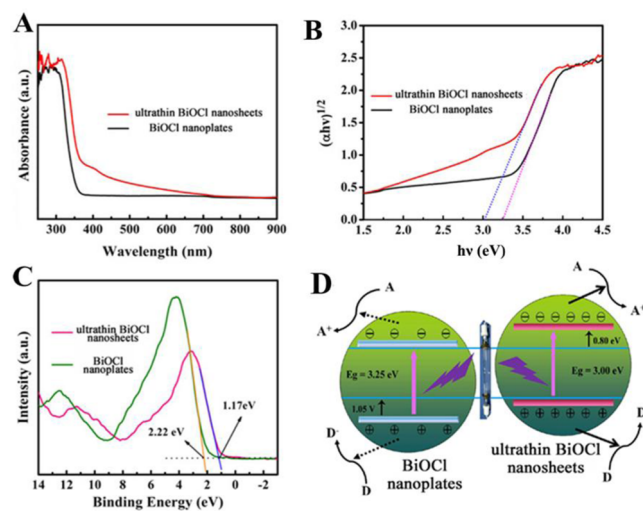


Figure 4. (A, B) UV/vis absorption spectra, (C) valence-band XPS spectra, and (D) schematic illustration of the band structure for the ultrathin BiOCl nanosheets and BiOCl nanoplates. Adapted with permission from ref 27. Copyright 2013 American Chemical Society.

nanosheets possess a narrowed band gap from 3.25 to 3 eV, an up-shifted valence band (VB) maximum energy by 0.12 eV, and an up-shifted conduction band (CB) minimum energy by 0.8 eV compared with those of the BiOCl nanoplates. Thus, the band structure variations not only help the ultrathin BiOCl nanosheets to harvest more solar light but also facilitate electron transport, thus achieving higher photocatalytic activity than the BiOCl nanoplates. Synthetic ZnSe single-layers also possess obviously increased UV light absorption,⁹ while the fabricated all-surface-atomic SnS sheets and SnS₂ single-layers exhibit remarkably improved visible light absorption,^{13,18} which contributes to their increased solar water splitting efficiency compared with bulk counterparts. Furthermore, in another case of the ultrathin g-C₃N₄ nanosheets,³⁶ UV/vis absorption spectra reveal that their absorption spectra extend to the whole visible light region and even the infrared region, which enhances the absorbance of light, thus producing increased photocatalytic activity with respect to the bulk g-C₃N₄. Therefore, their peculiar electronic structures endow the ultrathin two-dimensional sheets with better optoelectronic

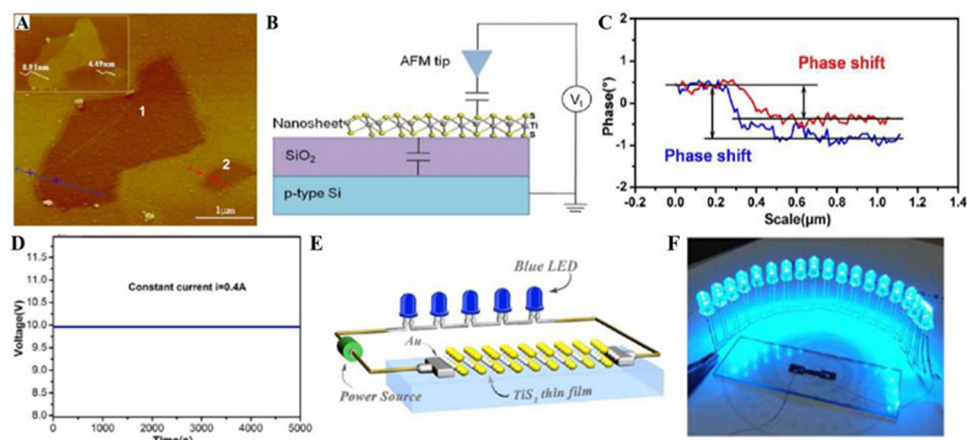


Figure 5. (A) Scanning conductance microscopy for ultrathin hydric TiS_2 sheets, (B) schematic illustration of scanning conductance microscopy, and (C) the corresponding line profiles along the blue and red line shown in panel A), (D) time-dependent voltage value curve of the assembled ultrathin hydric TiS_2 sheets film, (E) schematic illustration of working model for an endurance test, and (F) digital photograph of the stability testing setup. Adapted with permission from ref 37. Copyright 2013 American Chemical Society.

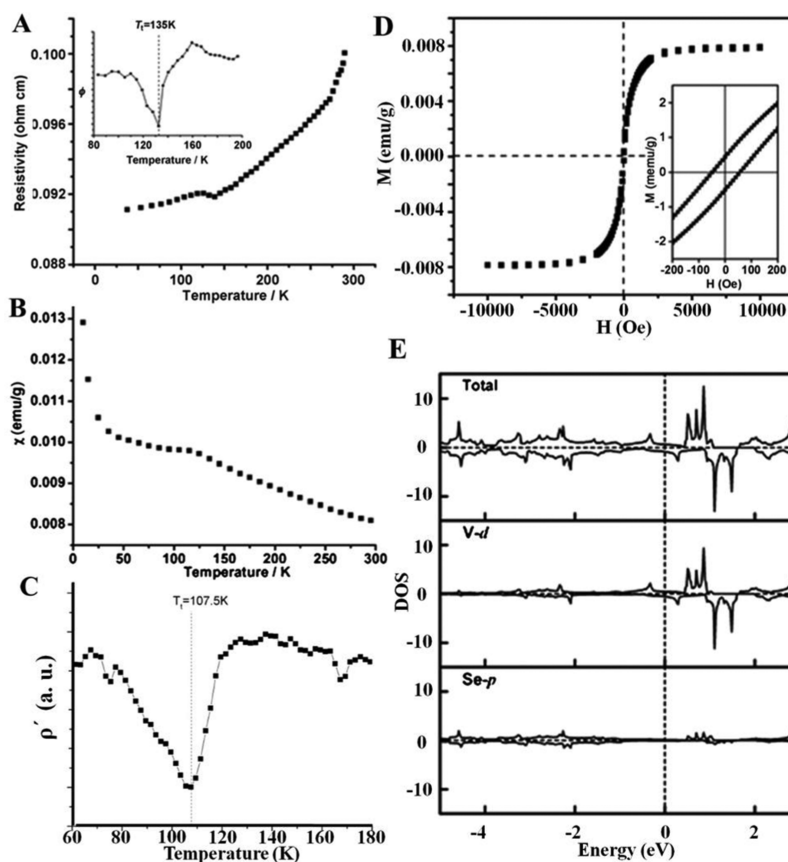


Figure 6. (A) Temperature-dependent resistance; inset gives the differential resistivity versus temperature. (B) Temperature-dependent ZFC magnetization of ultrathin VSe_2 nanosheets. (C) Differential resistivity versus temperature plot. (D) $M-H$ curves of ultrathin VSe_2 nanosheets at 300 K; inset gives the enlarged central section. (E) DOS of VSe_2 monolayer. Adapted with permission from ref 39. Copyright 2013 Wiley-VCH.

properties, hence helping to improve their photocatalytic properties.

5.2. Electrical Properties of Ultrathin Two-Dimensional Inorganic Materials

Ultrathin two-dimensional materials play an increasingly crucial role in new-generation electronics. For instance, our recent work demonstrates the synthesis of metallic hydric TiS_2 ultrathin sheets,³⁷ thin films of which have an electrical

conductivity of $6.76 \times 10^4 \text{ S/m}$ at 298 K, superior to indium tin oxide ($1.9 \times 10^4 \text{ S/m}$) and graphene ($5.5 \times 10^4 \text{ S/m}$). In this regard, atomic force microscopy in the interleave mode further demonstrates the high conductance of the ultrathin hydric TiS_2 sheets from a microscopic viewpoint (Figure 5A–C).³⁸ In addition, the as-assembled ultrathin hydric TiS_2 sheets film shows very good electrical endurance when 10 V is applied for 4800 s in ambient atmosphere, while the film also serves as an electrical wire when it is connected in series to 19 blue light-

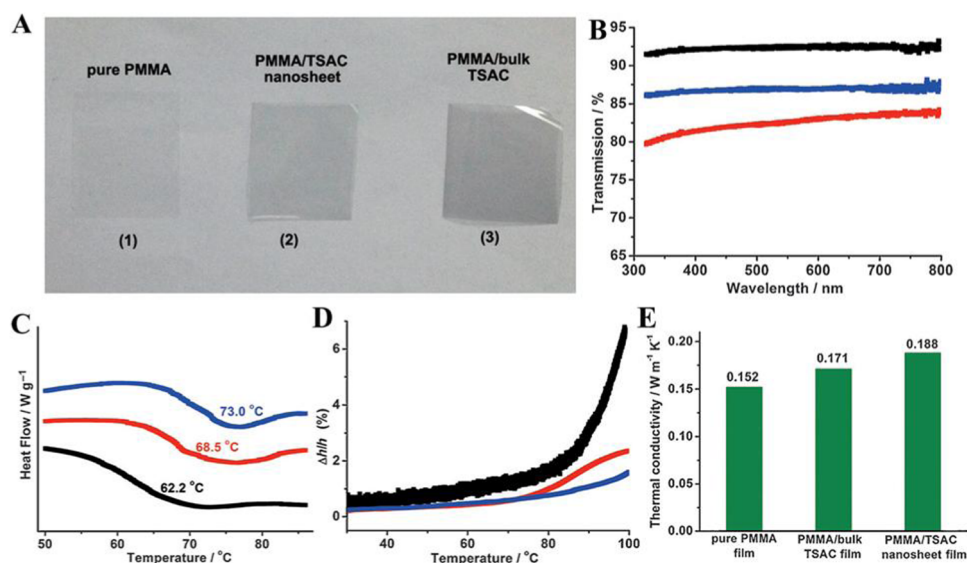


Figure 7. (A) Photograph, (B) UV/vis transmittance spectra, (C) DSC curves, (D) thermal expansion curves, and (E) thermal conductivity for pure PMMA film, PMMA/bulk TSAC composite film, and PMMA/TSAC nanosheet composite film. TSAC stands for $\text{Ti}_3\text{Si}_{0.75}\text{Al}_{0.25}\text{C}_2$; PMMA refers to poly(methyl methacrylate). Adapted with permission from ref 44. Copyright 2013 Wiley-VCH.

emitting diodes, further demonstrating its superior electrical properties with great stability (Figure 5D–F). Moreover, synthetic Bi_2Se_3 single-layers with five-atom thickness¹¹ possesses increased DOS at the conduction band edge compared with its bulk counterpart, indicating the fascinating superiority of the single-layer structure. Actually, the Bi_2Se_3 single-layer-based composite, fabricated from the atomically thick single layers, exhibits a >2-fold increase in electrical conductivity relative to the bulk material at 400 K, demonstrating its improved electrical properties. Furthermore, the synthetic three-atomic-layer thin CeO_2 sheets and the five-atomic-layer SnO_2 sheets possess increased state densities near their Fermi level and hence exhibit lowered CO diffusion barrier, which contributes to lower overall activation energy and finally improves their CO oxidation activity.^{10,12} Accordingly, the atomic thickness, large surface area, and high fraction of coordinated unsaturated surface atoms enable the ultrathin two-dimensional sheets to possess superior electrical properties, which would contribute to the innovation of new-generation electronic devices.

5.3. Magnetic Property of Ultrathin Two-Dimensional Inorganic Materials

Magnetic materials are one of the hottest topics in materials science and condensed matter physics for their practical and theoretical value. In this regard, ultrathin two-dimensional materials may produce novel magnetic properties owing to their exotic electronic structure. Taking the synthetic ultrathin VSe_2 sheets as an example,³⁹ the V^{4+} – V^{4+} strong electron correlation effect and the V^{4+} $3d^1$ odd electronic configuration endow it with unique electrical and magnetic properties. The temperature-dependent electrical resistivity curve for ultrathin VSe_2 sheets also brings an abnormal resistivity bump around 135 K, corresponding to the charge-density-wave transition of VSe_2 nanosheets, which fairly correlates with the result observed by zero-field cooling (ZFC) magnetization (Figure 6A,B). Note that the charge-density-wave transition temperature of the ultrathin VSe_2 sheets is much higher than that of their bulk counterpart (107 K, Figure 6C), which could be ascribed to the dimensional reduction of two-dimensional

ultrathin structure. Also, the M – H curve in Figure 6D for the ultrathin VSe_2 sheets exhibits a clear hysteresis loop, which provides a solid evidence of their room-temperature ferromagnetism, further verified by the DFT calculations in Figure 6E. Moreover, in the case of the synthetic ultrathin Co_9Se_8 sheets,³⁵ their ZFC and FC curves display obvious divergence even at room temperature, while the M – H curve shows a coercivity of ~ 300 Oe and a saturation magnetic moment of ~ 1.7 emu/g, indicating that they are robust ferromagnets, which is further demonstrated by their spin-polarization DFT calculations. Furthermore, the synthetic ultrathin δ - FeOOH nanosheets exhibit a high saturation magnetization value of 7.5 emu/g at room temperature,⁴⁰ which is the highest value among graphene and graphene analogues. Consequently, the exotic magnetic properties of the ultrathin two-dimensional sheets will offer promising opportunities for constructing magnetic response data storage and spintronic devices.

5.4. Thermal Properties of Ultrathin Two-Dimensional Inorganic Materials

Recently, the rapidly increasing power densities in electronic, optoelectronic, and photonic devices make enabling efficient heat removal a critical issue for progress in information, communication, and energy storage technologies.⁴¹ Thus, it is highly desirable to pursue a novel material with high thermal conductivity for quickly removing the waste heat from the work devices. In this regard, graphene and ultrathin boron nitride nanosheets show remarkable in-plane thermal conductivity of 3000 and 2000 $\text{W m}^{-1} \text{K}^{-1}$,^{42,43} which are much higher than their corresponding bulk materials. This result suggests that the ultrathin two-dimensional materials could exhibit enhanced thermal properties, which could be further confirmed by our recent works. Taking the synthetic ultrathin $\text{Ti}_3\text{Si}_{0.75}\text{Al}_{0.25}\text{C}_2$ (TSAC) films as an example,⁴⁴ their peculiar two-dimensional structure and metallic characteristics with increased DOS near the Fermi level would endow them with increased thermal properties. In effect, differential scanning calorimetry shows that the PMMA/TSAC nanosheet film possesses a glass-transition temperature (T_g) of 73.0 °C, which is 5 and 10 °C higher than that of the PMMA/bulk TSAC film and pure

PMMA (Figure 7A–C). Figure 7D also reveals that the PMMA film has the highest thermal expansion, while the PMMA/bulk TSAC film and PMMA/TSAC nanosheet film show negligible thermal expansion below the T_g . Benefiting from more electrons than the bulk sample near the Fermi level, the PMMA/TSAC nanosheet film exhibits thermal conductivity of $0.188 \text{ W m}^{-1} \text{ K}^{-1}$ (Figure 7E), which is a 23% and 10% increase compared with that of pure PMMA ($0.152 \text{ W m}^{-1} \text{ K}^{-1}$) and PMMA/bulk TSAC composite ($0.171 \text{ W m}^{-1} \text{ K}^{-1}$). Thus, the superior thermal properties of the ultrathin two-dimensional materials may lead to improvements in the performances of electronics and optoelectronics and renewable energy generation.

6. CONCLUSIONS AND PERSPECTIVES

With the rapid development in nanoscale science and technology, solid state nanochemistry has become a new and

Table 1. Summary of the Properties and Measurement Techniques for the Investigated Ultrathin Two-Dimensional Inorganic Sheets

materials	properties	measurement techniques	
ultrathin BiOCl sheets ²⁷	increased UV light absorption	UV/vis absorption spectra, XPS valence spectra	
	up-shifted valence band maximum		
ZnSe single-layers ⁹	up-shifted conduction band minimum		
	increased UV light absorption		
SnS single-layers ¹³	increased visible light absorption		
SnS ₂ single-layers ¹⁸	increased visible light absorption		
ultrathin g-C ₃ N ₄ sheets ³⁶	increased visible light absorption		
ultrathin hydric TiS ₂ sheets ³⁷	high conductivity of $6.76 \times 10^4 \text{ S/m}$		PPMS
Bi ₂ S ₃ single-layers ¹¹	>2 fold increased electrical conductivity		
ultrathin CeO ₂ sheets ¹⁰	CO catalytic oxidation (lowered CO diffusion barrier)		intelligent CO detector
ultrathin SnO ₂ sheets ¹²			
ultrathin VSe ₂ sheets ³⁹	room-temperature ferromagnetism	SQUID	
	higher charger-density-wave-transition temperature		
ultrathin Co ₉ Se ₈ sheets ³⁵	robust ferromagnets; a high coercivity of $\sim 300 \text{ Oe}$		
ultrathin δ -FeOOH sheets ⁴⁰	high saturation magnetization value of 7.5 emu/g		
graphene ⁴²	high thermal conductivity		noncontact Raman optothermal method
	higher thermal conductivity	thermal conductivity system	
ultrathin Ti ₃ Si _{0.74} Al _{0.25} C ₂ sheets	negligible thermal expansion below T_g	thermal mechanical analyzer	
	higher glass-transition temperature	differential scanning calorimetry	

important subdiscipline in the field of solid state chemistry. However, up to now, it has been very difficult to establish a precise correlation between atomic, defect, and electronic structures and intrinsic properties of nanosolids, that is really the concern of solid state chemistry, due to the abundant microstructures in the aggregation states of the nanosolids. This stimulates us to pursue a suitable material model for building

well-defined structure–property relationships, in which ultrathin two-dimensional inorganic materials could be an ideal material model in the field of solid state nanochemistry, owing to their homogeneous dispersion without assistance of capping ligand and clear atomic and defect structures.

In this Account, we highlight our recent progress in the solid state nanochemistry, including atomic and defect structure characterization, electronic structure calculation, and the corresponding relationship between atomic, defect, and electronic structure and optoelectronic, electrical, magnetic and thermal properties of ultrathin two-dimensional materials (Table 1). Despite the significant advances described in this Account, both opportunities and challenges still remain in the field of solid state nanochemistry. An interesting challenge may be the development of various novel techniques to characterize the defect type and concentration in the ultrathin two-dimensional sheets. An additional challenge is to fabricate the single ultrathin two-dimensional sheet-based nanodevice and hence investigate the effect of atomic, defect, and electronic structure variations on its physicochemical properties. We anticipate that progress continued at this pace will bring additional big leaps in the establishment of clear structure–property relationships in solid state nanochemistry.

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Notes

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