Surface Chemical-Modification for Engineering Intrinsic Physical Properties of Inorganic Two-Dimensional Nanomaterials

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Complete List of Authors:	Guo, Yuqiao; University of Science and Technology of China, Xu, Kun; University of Sci and Technol of China, Department of Chemistry Wu, Changzheng; University of Sci and Technol of China, Department of Chemistry Zhao, Jiyin; University of Science and Technology of China, Hefei National Laboratory for Physical Science at Microscale Xie, Yi; University of Sci and Technol of China, Department of Chemistry

Surface chemical-modification for engineering intrinsic physical properties of inorganic two-dimensional nanomaterials

Yuqiao Guo, Kun Xu, Changzheng Wu*, Jiyin Zhao, and Yi Xie

Hefei National Laboratory for Physical Sciences at the Microscale,
and Collaborative Innovation Center of Chemistry for Energy Materials,
University of Science and Technology of China,
*Hefei, Anhui 230026, P. R. China. *E-mail: czwu@ustc.edu.cn.*

Abstract

Two-dimensional (2D) nanomaterials especially those inorganic ultrathin nanosheets with single or few-atomic layers, have been extensively studied due to their special structures and rich physical properties coming from quantum confinement of electrons. With atomic-scale thickness, 2D nanomaterials have extremely high specific surface area enabling their surface phase to be as important as bulk counterparts, and therefore provide an alternative way of modification surface phase for engineering intrinsic physical properties of inorganic 2D nanomaterials. In this review, we focus on recent researches concerning surface chemical modification strategies to effectively engineer intrinsic physical properties of inorganic 2D nanomaterials. We highlight the newly developed regulation strategies of surface incorporation, defect engineering, and structure modulation of inorganic 2D nanomaterials, which respectively influences the intrinsic conductivity, band structure, and magnetism while maintaining the primary 2D freestanding structures that are vital for 2D based ultrasensitive electronic response, enhanced catalytic and magnetocaloric capabilities.

Key learning points

(1) Advantages of surface chemical modification for engineering intrinsic physical properties in 2D materials.

(2) Tuning electronic conductivity of inorganic 2D materials by surface incorporation.

(3) Regulation band structure of inorganic 2D materials by defect engineering.

(4) Introducing intrinsic magnetism in 2D materials by surface modulation.

(5) Applications of surface modified inorganic 2D nanomaterials.

1 Introduction

Two dimensional nanomaterials, with the characters of intrinsic quantum confined electrons, demonstrate a vast array of unique physicochemical properties, such as planar conductivity, magnetic anisotropy, tunable band gap, surface activity *etc*[1-6]. Enormous efforts have been made on modifying those intrinsic physical properties for further widening applications in high conductivity electrode, planar spintronic and high-efficient photo-/electro- catalytic. After exfoliating into ultrathin nanosheets, dramatically increased surface areas would not only enhance their chemical and physical reactivity, but also influences a 2D wave function from quantum confinement effects. Such effects entail them to modify the intrinsic physical properties by regulating the electronic band structure. For example, exfoliation bulk MoS_2 into monolayer bringing unique direct bandgap;[7] exerting external pressures on TaS_2 and MoS_2 inducing serial electronic phase transformations;[8,9] internal lattice strain converted semiconducting state to metallic ones in WS_2 and MoS_2,[10,11] zigzag edge state in MoS_2 nanoribbons leads to ferromagnetism.[12] Engineering of intrinsic physical properties of 2D nanomaterials endow them extensive functionalities: 2D-semiconductos with direct bandgap are usually superb photoelectric materials;[13] metallic 2D nanomaterials with chemical reactivity acted as electrocatalysts;[14] spin-regulated 2D nanomaterials emerge large magnetoresistance.[15,16] Besides, a wide variety of layered metal oxides and layered hydroxides have been successfully exfoliated into individual ultrathin nanosheets which show unique physicochemical properties, especially those transitional metal oxide and double hydroxides ultrathin nanosheets which are considered as the excellent 2D ferromagnetic and catalytic candidates.[17,18] Controlling those intrinsic physicochemical properties of 2D materials have born great fascination and potential applications in fields of electronics, energy, and spintronics.[19] Although a few interesting reviews have concerned the significant progresses upon physicochemical properties of 2D nanomaterials,[20-22] there were still present the great expectation that precise regulation of intrinsic physical properties independent of external field and without destroying pristine freestanding lattices, producing controllable and available intrinsic physicochemical behaviors in 2D nanomaterials. In this review, we focus on serial surface modification strategies which lead to effectively engineer intrinsic physical properties of inorganic 2D nanomaterials.

With atomic-scale thickness, 2D nanomaterials have extremely high specific surface area enabling their surface phase is as important as bulk counterparts. And therefore chemical modification on surface-facet atoms provides an alternative way for engineering intrinsic physical properties of inorganic 2D nanomaterials. Although in 3D bulk solids, surface treatment techniques have been traditionally applied for improving reactive activity and biocompatibility *etc.*, artificial manipulation of surface phase is found hard to influence their intrinsic physical properties of whole bulk crystals. Unlike that in bulk form, when dimensionally confined into 2D scale with thin enough, for example, epitaxial thin film or surface coating layer, the surface engineering techniques such as, gate electric field in transistor, different chemical solution/gas environments such as ionic liquid on surface, were able to effectively tune their intrinsic physical properties ranging from electronic, magnetic and even structural aspects. In this view point, inorganic 2D nanomaterials provide an idea platform for regulating intrinsic physical properties via surface modification, expecting to precisely regulate physicochemical properties in 2D ultrathin nanosheets. Detailedly, owing to dimensionally reduction, most of atoms are exposed on surface, chemical modifications of which would regulate carrier concentrations and band gap of inorganic 2D nanomaterials by engineering their electronic structure. The regulation of electrical conductivity and band structures were vital for performance promotion of electrode applications and catalysis capability.[23] In addition, for inorganic 2D nanomaterials with transition metal elements in its lattice framework, unique electrical behaviors such as superconductivity, charge density wave and Mott transition[8] were observed which indicated the strong electron-electron correlation effect, therefore, their surface chemical modification would trigger electron transfer or atomic lattices variation for bringing readjustment of the whole electronic state covering from superconducting, metal, semimetal to semiconducting. More importantly, those chemical modifications with surface electron transfer or local lattices distortion are non-destroyable to the main 2D structure. As listed in Table 1, applicable surface modification strategies without changing the layered frameworks, have been employed as facile approach to tune the intrinsic physical properties of inorganic 2D nanomaterial. In a word, surface chemical modifications, including incorporation, absorption, and defect engineering, paved a new effective strategy to modulate the intrinsic physical properties while maintain the 2D freestanding structure that are vital for mitigating fundamental problems at current stage for diversely practical applications of 2D nanomaterials (as illustrated in Fig. 1).

Table 1 A concise List of surface chemical modification for engineering physical properties of inorganic 2D nanomaterials.

Surface-modification Methods		***2D Inorganic Materials***	**Intrinsic physical Properties**	**Ref.**
Incorporation	Hydrogen,	TiS_2,	Electronic mobility,	26
	Water,	VS_2,	Carrier concentration,	29
	Dangling bonds	C_3N_4,MoS_2	Spin polarization	44,45
Defect	Pit,	CeO_2,	Photo-/electro- chemical reactivity	34
	Vacancy,	$K_4Nb_6O_{17}$, In_2O_3		35,36
	Disorder	MoS_2		37
Structural engineering	Strain	VSe_2,NbS_2,$NbSe_2$	Intrinsic magnetism Bandgap	40,41
	Superlattice	Graphene/VO_2		43,
	Grain boundary	$Zn_{1-x}Cd_xS$		32

We focus on our recent researches concerning surface chemical modification strategies to engineer intrinsic physical properties of inorganic 2D nanomaterials. We emphasize chemical modifications on the surface facet atoms of 2D nanomaterials including surface incorporation, defect engineering and modulation, which have shown effective capability for tuning intrinsic conductivity, band structure, and magnetism properties, respectively, while maintaining the pristine 2D lattice framework. The chemically modified 2D structures significantly expanded fascinatingly application in nanoelectronics and efficient clean-energy applications.

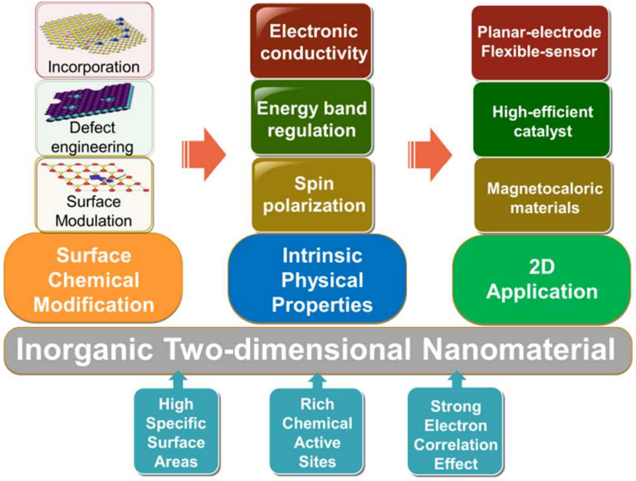

Fig. 1 Schematic illustration of surface chemical-modification for engineering intrinsic physical properties of inorganic two-dimensional nanomaterials towards 2D applications.

2 Engineering intrinsic physical properties by surface chemical modification

As well known, intrinsic electronic properties and magnetic properties are fundamentally determined by the charge and spin degrees of freedom of their confined electrons. Unlike that in bulk samples, 2D nanomaterials with atomic thickness show ultrahigh specific surface area, enabling surface state to be as important as that in the bulk inside. And therefore, chemical modification on the charge, spin, and coordination of surface atoms in 2D nanomaterials has become an effective way to influence their intrinsic physical properties. In this dimensional confinement system, surface engineering methodologies, such as molecular absorption, heteroatom incorporation, and defect introduction on the surface atoms would actively regulate intrinsic properties of electrical conductivity, magnetic behavior, and band structure, opening new window for applications in planar-electrode, sensor, magnetocaloric and high efficient catalyst devices.

2.1 Tuning electronic conductivity by incorporation

The intrinsic conductivity in metallic inorganic 2D nanomaterials is mainly determined by their carrier concentration and in-plane mobility. Surface incorporation strategies such as hydrogen incorporation and molecule implantation that can respectively inject electrons and block the electron migration are available for tuning the intrinsic conductivity. Hydrogen, the lightest element, when incorporation into external lattice framework, not simply doping, could be an electron donor that has been successfully used to tune carrier concentration in bulk material systems such as VO_2[24] and TiO_2.[25] For 2D case, we have recently developed an intermediate precursor assistant approach to realize atomic-thin hydrogen incorporated TiS_2 nanosheets.[26] In the formation process of H_yTiS_2, the chemical reaction forming the non-uniform electron distribution in the S-Ti-S sandwich donates the extra electrons into the S-Ti-S layers to enhance carrier concentration in the 2D lattice framework, thus leading to the great conductivity enhancement with the hydrogen involved (as seen in Fig. 2a and 2b). Using this facile modification, the assembled $H_{0.515}TiS_2$ film with highest hydrogen concentration realized an excellent planar electrical conductivity 6.76×10^4 S/m at 298 K, recording the best value in the solution assembled 2D thin films of both graphene[27] and inorganic graphene analogues[28], even superior to ITO reported so far.

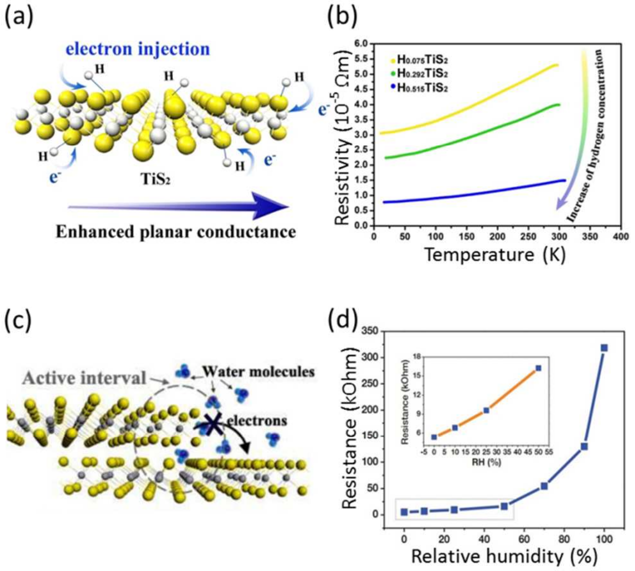

Fig. 2 (a) Schematic illustration of carrier concentration regulation in metallic ultrathin TiS_2 by surface hydrogenation, (b) Temperature-dependent electrical resistivity for ultrathin TiS_2 samples with gradient hydrogenation, Adapted with permission from ref. 26 copyright 2013 American Chemical Society; (c) Schematic illustration of the mechanism for the conductivity decreasing with the increasing of surface water adsorption, (d) The derived humidity-dependent resistance changes, Adapted with permission from ref. 29 copyright 2011 Wiley-VCH.

Beside the enhancement of conductivity by increasing surface carrier concentration, the surface molecule implantation can further be used to reversibly regulate the conductivity in 2D nanomaterials through the control of carrier migration. Water, one the most accessible molecules in our living environment, was utilized as the implantations to modify the planar transport of the metallic 2D VS_2 nanosheet.[29] As shown in Fig. 2c, in VS_2 nanosheets assembled thin film the electric conducting mechanism is that electrons are transmitted from the side-exposed V atoms of an individual nanosheet toward another nanosheet covered below. In this sense, if the side-exposed V atoms were covered by poor conducting water molecules, the migration of the carriers would be suppressed, and thus the electric resistance will be substantially increased. In the experiments, we demonstrated that the electric conductivity of this oriented film was highly sensitive to environmental humidity, *i. e.* water absorption, which has a resistance change of almost two orders of magnitude from the relative humidity of 0% to that of 100% (as seen in Fig. 2d).

2.2 Regulation band structure by defect engineering

Defects exist widely in materials and are well-accepted to tailor the intrinsic properties of materials, even with an extremely low concentration. For example, the intrinsic magnetic and electronic properties in magnetoresistance manganites can be readily regulated by their oxygen-defect concentration.[30] Our recent research on serial 2D nanomaterials including single-layer SnO_2[31], $Zn_{1-x}Cd_xS$[32], and ZnSe[33] *etc.*, demonstrated that the existence of surface structural defect can enhance the orbital hybridization, and substantially lead to an obvious increase in density of states (DOS). Benefiting from the increased DOS near Fermi level, atomic-thin nanomaterials possess higher conductivity in comparison with the defect-poor counterparts. Inspired by these experimental results, we anticipated that artificially surface defect engineering such as pits digging, oxygen-vacancy controlling, and heteroatom substitution can effectively optimize electronic structure of inorganic 2D nanomaterials.

The introduction of pits provides a feasible approach to enhance the degree of surface defect via bringing more dangling bonds and unsaturated coordination atoms to the nanosheets (as seen in Fig. 3a). We developed an ‘ultrafast open space transformation’ strategy and successfully synthesize three-atom-layer thin CeO_2 sheets with about 20% pits occupancy.[34] As expected, the presence of coordination-unsaturated cerium sites in pits-rich CeO_2 nanosheets not only increases the density of states, but also leads to the formation of a defect state near the Fermi level (as seen in Fig. 3b), both of which resulted in an obvious increase of hole carrier concentration with respect to the ultrathin CeO_2 sheets and bulk counterpart.

Oxygen vacancy, owing to its ubiquity in oxide materials, provides another available approach to engineer the degree of surface defects in 2D materials.[35] For example, through a mesoscopic-assembly strategy, we realized the fabrication of 5-atom-thick In_2O_3 porous sheets with O-vacancies via a fast-heating process.[36] The presence of oxygen-vacancies confined in atomically thin In_2O_3 nanosheets endows the 5-atom-thick In_2O_3 slab with obviously increased DOS at valence band maximum(as seen in Fig. 3c and 3d). More importantly, oxygen-defects render a new defect donor level near the conduction band minimum, hence contribute to shifting the onset light absorption from the UV regime (2.90 eV) to visible region (2.18 eV). In this case, the electrons can easily be excited into the conduction band under irradiation of solar light, thereby achieving higher photoconversion efficiency.

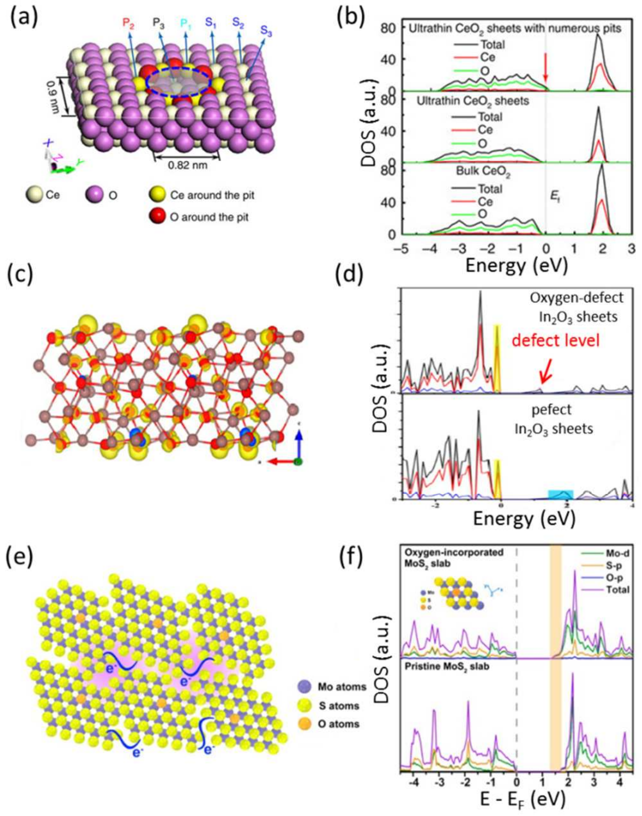

Fig. 3 (a) Overhead view of schematic representation of the CeO_2 sheets with surface pit defect, (b) Calculated DOS for the ultrathin CeO_2 sheets with numerous surface pits, perfect ultrathin CeO_2 sheets and bulk CeO_2, respectively, Adapted with permission from ref. 34 copyright 2013 Nature Publishing Group; (c) Plots of oxygen-defect 5-atom-thick In_2O_3 slab, (d) Calculated DOS of oxygen-defect 5-atom-thick In_2O_3 (top) and perfect 5-atom-thick In_2O_3 (bottom), Adapted with permission from ref. 36 copyright 2014 American Chemical Society; (e) Schematic illustration of the disordered structure in oxygen-doped MoS_2 ultrathin nanosheets, (f) Calculated DOS of the oxygen-doped MoS_2 slab (top) and the pristine 2H-MoS_2 slab (bottom), Adapted with permission from ref. 37 copyright 2013 American Chemical Society.

Besides vacancy, oxygen as heteroatom substitution with controllable disorder can also realize the electronic structure regulation of the 2D nanomaterials. A controlling insufficient crystallization process was developed to realize the oxygen doping in MoS_2.[37] We found that the band gap of ultrathin MoS_2 can be readily reduced by surface oxygen doping thus realizing the electronic modulation (as seen in Fig. 3e and 3f). Further study showed that although the reduced band gap was attributed to the enhanced hybridization between Mo d-orbital and S p-orbital, the surface doped oxygen atom significantly contributes to the charge density for both valence band and conduction band to improve the intrinsic conductivity confirming the significant effect of surface doping on the electronic structure.

2.3 Introducing magnetism by surface modulation

The 2D magnetic materials have wider applications of 2D-based magnetocaloric and spintronic devices. Typically, the giant magnetoresistance effect was first discovered in the sandwich Fe-Cr-Fe structure, which was made up by layered ferromagnetic and non-magnetic thin films. Moreover, as most of the ferromagnetism diluted magnetic semiconductors (DMS) can only be prepared in its thin-film form, there are many 2D magnetic materials that are DMSs thin-films.[38] The atomic precision of magnetically doped semiconducting film deposition has allowed ferromagnetic signatures persisting at high temperatures. For the freestanding 2D ferromagnetic materials, exfoliation of the layered transitional metal oxides/hydroxides provides a direct potential strategy for 2D ferromagnetism. Recently, we have developed an atomic-scale topochemical transformation ensures the formation of 2D δ-FeOOH ultrathin nanosheets which present a robust ferromagnetic behavior with unprecedented high saturation magnetization.[39] However, most of other two-dimensional materials such as graphene and transition metal dichalcogenide are lack of robust intrinsic ferromagnetic behavior. As a traditional method, magnetic ion doping into nonmagnetic matrix was an effective way to tune magnetic properties, and it has proven the significance in the case of DMS thin films for boring spin ordering. However, directly employing magnetic cation doping in 2D transition metal dichalcogenide is not the most desirable answer from microstructural and synthetic viewpoint. In layered sandwich structure, negatively charged chalcogen anions are exposed on outer surfaces. When external positive magnetic cations doped, they tend to gather in the interlayer space by the electrostatic attraction between doped cations and surface chalcogen anions, thus forming intercalated compounds that are very difficult to be exfoliated to the two-dimensional nanomaterials. Therefore, developing surface modification strategies to regulate the spin structure is critical to develop those nonmagnetic 2D nanosheets for next-generation spintronics.

2D nanomaterials have the advantages of enormous exposed surface atoms that are convenient for chemical reactions, as well as 2D quantum confinement caused the strong electrons correlation results in the coupling among spin, charge and crystal structure in inorganic 2D nanomaterials. Therefore, surface chemical modification, such as interface strain, irradiation, and absorption which lead to structure distortion, dangling bond, and electron injection, respectively, are promising approaches of spin modulation to induce magnetism.

Theoretical calculation had shown that the monolayer VSe_2 exhibited ferromagnetism, with V and Se atoms carrying small magnetic moment. Moreover, it was predicted that the magnetic moments and the strength of the magnetic coupling in NbS_2, VS_2 and VSe_2 could be tuned by strain (as seen in Fig. 4a and 4b).[40,41] Recently, we have developed an experimental realization of VSe_2 ultrathin nanosheets with 4-8 atomic layers through liquid exfoliation of their bulk crystal in formamide solvent (as illustrated in Fig. 4c).[42] As expected, ultrathin VSe_2 nanosheets manifested the features of both charge density wave behavior and room-temperature ferromagnetism as shown in Fig. 4d.

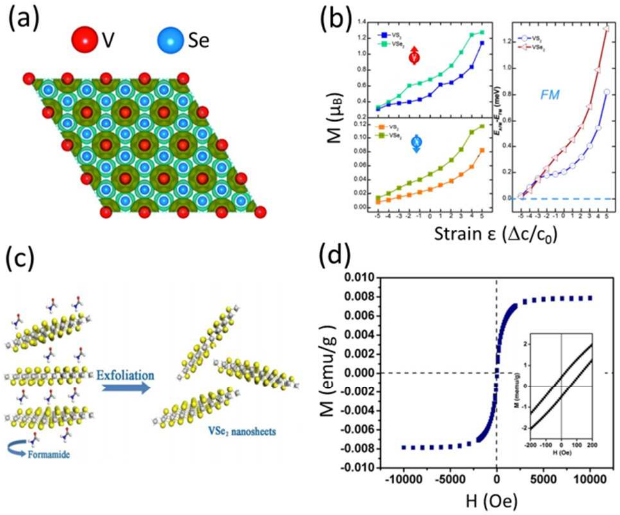

Fig. 4 (a) The calculated spin-resolved charge density isosurface of VSe_2 monolayers in ferromagnetic state, (b) Strain dependence of the magnetic moment and the energy difference between FM and AFM order of VX_2 monolayers, Adapted with permission from ref. 41 copyright 2012 American Chemical Society. (c) Schematic illustration of surface formamide assisted liquid-exfoliation process from bulk VSe_2 to VSe_2 ultrathin nanosheets; (d) Field-dependent magnetization curves of the obtained VSe_2 ultrathin nanosheets at 300 K. Adapted with permission from ref. 42 copyright 2013 Wiley-VCH.

Based on theoretical prediction that strain can regulate the magnetic moments, we further proposed that introduction of structural lattice perturbation by an additional substance would also provide an effective way to modulate the magnetic structure. We developed a space-confined method to synthesize graphene-based 2D vanadium oxide superlattices in which the graphene layers provided not only a space confined nanoreactor to direct the growth of monolayered vanadium oxide frameworks, but also served as an electron donor to reduce the formation energy for highly symmetrical vanadium oxide frameworks.[43] As illustrated in Fig. 5a, these graphene-based 2D vanadium oxide superlattices were formed by the interlayers of reduced graphene oxides. The electron transfer and stress field at the interface of the superlattice lead to the structural rearrangements of the vanadium-oxide frameworks, which endow the superlattice nanosheets with magnetism property. Due to the orientation of sharing V d-orbit electrons in a V–V chain, the magnetism of the space-confined synthesized superlattice nanosheets showed progressive increases with increasing temperature at about 252K, presenting a step-like behavior in the temperature range covering the phase transition (as seen in Fig. 5b). The field dependence of magnetization for the as-obtained superlattice nanosheets, as seen in Fig. 5c, also confirmed the magnetism and step-like features which were favorable to magnetocaloric effects.

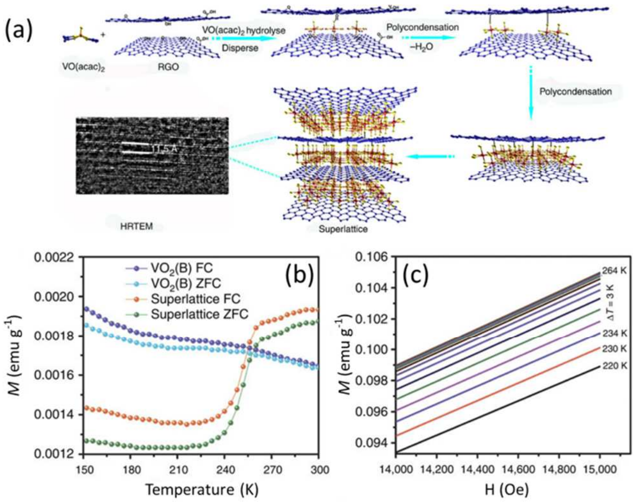

Fig. 5 Schematic illustration of the formation process for the superlattice through space-confined nanoreactor strategy; (b) Zero field cooling and field cooling M-T curves for the superlattice nanosheets and VO_2(B); (c) The field-dependent magnetization plots at transition temperatures. Adapted with permission from ref. 43 copyright 2014 Nature Publishing Group.

Surface absorption and irradiation were alternative strategies to provide itinerant magnetism due to the defect-induced extended states while maintaining the freestanding structure.[44] Theoretical studies have suggested that, although MoS_2 is a diamagnetic material, the MoS_2 becomes ferromagnetic when absorbed nonmetals atoms such as H, B, C, N, and F or irradiated by proton.[45] Experimentally, the significant ferromagnetism was obtained in nanosheets with a high Curie temperature by those two effective methods.[46] Fig. 6 exhibits the spin density and magnetic hysteresis loops of the hydrogenated and proton irradiated MoS_2 samples, respectively. The pristine MoS_2 shows the negative slope of the hysteresis loop, supporting the diamagnetic property. This diamagnetic property of the MoS_2 changed to ferromagnetic behavior either by hydrogenation or irradiation of proton. As compared with the weakly induced ferromagnetism on the graphene by the formation of defects, MoS_2 is more efficient to induce the ferromagnetic state by surface modification due to the smaller diamagnetism.

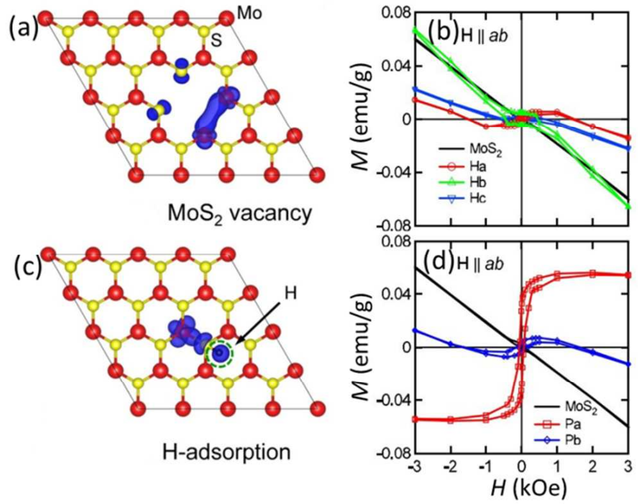

Fig. 6 Top views of the isosurface plot of the spin density for MoS_2 after surface irradiation (a) and hydrogen-adsorption (c); Magnetic hysteresis loops of the surface hydrogenated (b) and proton irradiated (d) samples at 300 K. Adapted with permission from ref. 46 copyright 2013 American Physical Society.

3 Applications of surface modified 2D nanomaterials

As mentioned above, taking advantage of surface chemical modifications, the intrinsic electronic and magnetic properties of inorganic 2D nanomaterials can be engineered to a large extent. Given the inherent stability and non-destructive of chemical modification process, those surface modified 2D nanomaterials with tunable conductivity, magnetism and band structure allow advances to design nanoelectronics and energy related applications.

3.1 2D nanomaterials with tunable conductivity for nano-electrode and sensor materials

Electron injection in 2D TiS_2 by surface hydrogen incorporation successfully achieved the unprecedentedly high electrical conductivity in inorganic ultrathin nanosheets. Together with its synergic advantages of the excellent flexibility, high stability, and stamp-transferrable properties, the hydrogen modified TiS_2 nanosheets showed promising capability for being next generation conducting electrode material in the nanodevice.[26] As shown in Fig. 7a, the as-assembled hydrogen modified TiS_2 film transferred onto the glass by substrate dry-transfer technique based on polydimethysiloxane (PDMS) stamp showed very good electrical endurance when applied 10 V for 4800 s in the ambient atmosphere, verifying its remarkably great stability over high voltage and long electrically applied time. Afterward, the aforementioned film were connected in series to blue light-emitting diodes with a 3.2 V lowest working potential. Apparently, the tandem unit worked well where the film played the role of electrical wire.

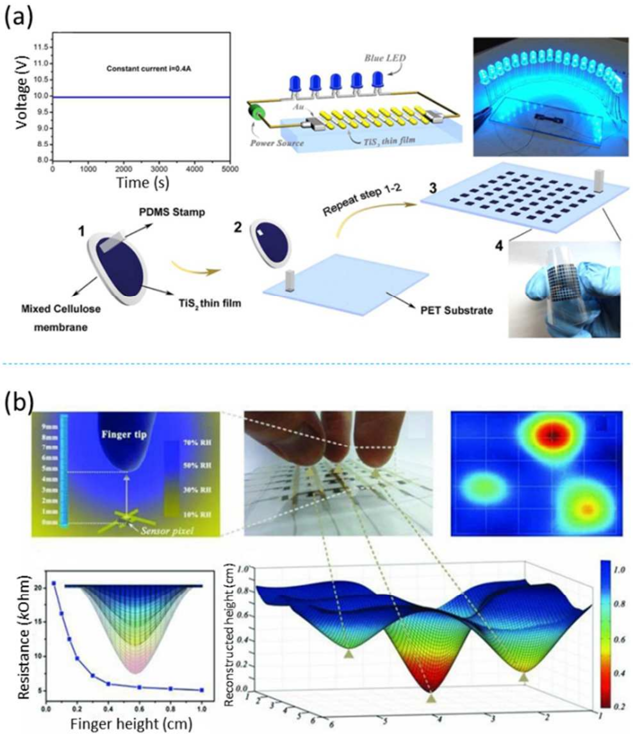

Fig. 7 (a) High-voltage endurance and dry-transfer method for assembled surface hydrogen incorporated TiS_2 film as an excellent electrode material that could be incorporated in various nanodevices, Adapted with permission from ref. 26 copyright 2013 American Chemical Society; (b) The touchless positioning device based on three-dimensional mapping of moisture distribution that was benefited from high surface moisture responsiveness of VS_2 ultrathin nanosheets, Adapted with permission from ref. 29 copyright 2011 Wiley-VCH.

Furthermore, inspired by ultrasensitive surface water sensitivity behavior with a maximum conductivity response of almost two orders of magnitude in assembled transferable c-oriented VS_2 nanosheets thin film,[29] we successfully constructed a novel proof-of-concept fully flexible device, i.e. a 3D positioning interface via spatial mapping of moisture distribution of human fingers, representing a new concept of touchless ultrathin sensor (as seen in Fig. 7b). The new-concept positioning interface model shows promising signs to be scaled up and generalized to fabricate practical real-time moisture mapping matrix or non-contact control interfaces for smart nanodevice in the coming investigations.

3.2 Surface defect modified 2D nanomaterials for high efficient catalysts

The band structures of semiconductors directly influence their ability to absorb light as well as efficiency of carrier transfer and separation. By surface defect engineering in inorganic 2D nanomaterials, coupling regulating band structures with increased edge active sites lead to more efficient light absorption, carrier separation, and increased catalytically activity, which are favorable for photo-/electron- catalytic applications.

Aforementioned, engineering oxygen vacancies in atomically thin In_2O_3 nanosheet successfully narrowed the band gap that evoluted from the ultraviolet regime to visible regime.[36] These advantages can facilitate the visible light harvesting and the carrier separation efficiency (as illustrated in Fig. 8a and 8b). As such, the photocatalytic devices made by oxygen vacancies-engineered ultrathin In_2O_3 porous sheets endow 15 times larger photocurrent in comparison with that assembled with the vacancies-poor bulk In_2O_3. The predominant defects in BiOCl can change from isolated Bi-vacancy to triple vacancy associates Bi-O-Bi vacancy as the thickness of the nanosheets reduces to atomic scale. The triple vacancies associate in ultrathin BiOCl nanosheets not only narrow the band gap but also make surface negatively charged, which effectively separates the photo induced electron-hole pairs(as in illustrated in Fig. 8c).[47] These two factors significantly improved the photocatalytic performances as compared to the isolated Bi-vacancy BiOCl (as seen in Fig. 8d).

In addition, the heteroatom substitution has demonstrated it role in realization band structure engineering in the case of oxygen incorporated MoS_2[37] By virtue of the narrowed energy gap as well as the surface disorder-induced additional active edge sites, the oxygen-incorporated MoS_2 ultrathin nanosheets exhibited an excellent hydrogen evolution reaction (HER) activity with small onset overpotential of 120 mV, and small Tafel slope of 50 mV decade^{-1}. (as illustrated in Fig. 8e and 8f).

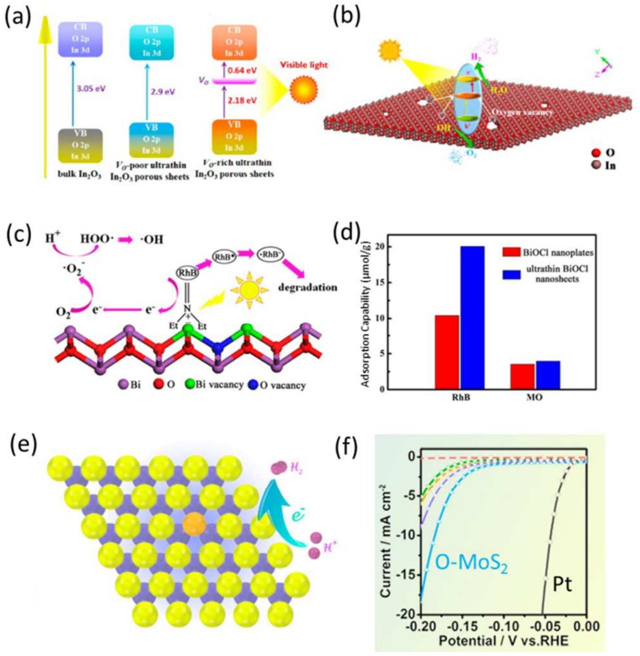

Fig. 8 (a) Schematic energy band structure of bulk, oxygen-vacancy poor, and oxygen-vacancy rich ultrathin In_2O_3, (b) Schematic solar water splitting of surface oxygen-vacancy rich ultrathin In_2O_3 sheets, Adapted with permission from ref. 36 copyright 2014 American Chemical Society; (c) Schematic adsorption and photosensitization of ultrathin BiOCl nanosheets with surface triple vacancies, (d) Comparison of adsorption capability between BiOCl with triple vacancies(blue) and BiOCl with isolated defects(red), Adapted with permission from ref. 47 copyright 2013 American Chemical Society; (e) Constructed model of an individual oxygen-incorporated MoS_2 nanodomain and the illustration of the HER process at the active sites, (f) Polarization curves of oxygen-incorporated MoS_2 ultrathin nanosheets. Adapted with permission from ref. 37 copyright 2013 American Chemical Society.

The above experimental results provide new and deep-seated insights for understanding mechanism of surface defect engineering in optimizing the catalytic property from band structure, surface charge, and active site aspects. Surface modified 2D nanomaterials revealed important guidelines for improving conversion efficiency in clean energy-related field.

3.3 2D magnetic superlattice for enhanced magnetocaloric effects

Magnetic material show magnetocaloric effect in a reversible magnetic susceptibility change experience through adiabatic magnetization or demagnetization, which can be used as an environmental-friendly and highly efficient cooling technology by spin entropy.[48] In our previous work of vanadium oxide, we developed a controlled oxidation reaction to realize the direct solution-based synthesis of VO_2(M) nanorods which feature a step-like behavior of the magnetization-temperature curves. The rapid change of magnetization resulted in substantial magnetic entropy change(as seen in Fig. 9a and 9b).[49] Here, for graphene-based vanadium oxide superlattices, we found that the magnetization increases progressively with increasing temperature, presenting even more sharp step-like behavior in the temperature range which would lead to larger magnetocaloric effect. The temperature dependent magnetic entropy change (ΔS) of vanadium oxide superlattice was calculated by the field dependence of magnetization and plotted in Fig. 9c. The maximum value of ΔS is about 0.4 J $kg^{-1}K^{-1}$, which is remarkably larger than that of the VO_2(M) phase transition-driven magnetocaloric effect.[43] Compared with other magnetic refrigerants, vanadium oxide superlattice possesses quite a number of advantages, such as rare-earth-free element constitution and good oxidation resistance. More interestingly, the layered 2D feature, as shown in Fig. 9d, make it possible for further constructing magnetic-cooling and waste heat utilization units in 2D devices.

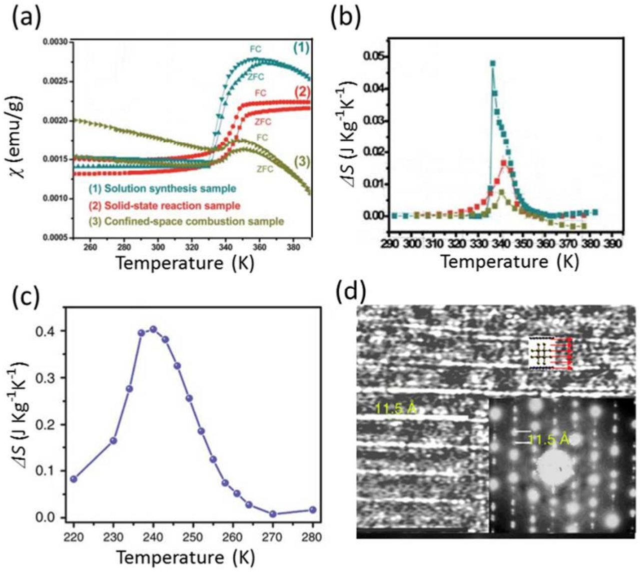

Fig. 9 (a) Temperature dependence magnetization in VO_2(M) samples, (b) Magnetic entropy change of the VO_2(M) samples; Adapted with permission from ref. 49 copyright 2011 The Royal Society of Chemistry; (c) Magnetic entropy change of the vanadium oxide superlattice; (d) HRTEM image of the cross-section edge of the superlattice nanosheets confirms the layered feature. Adapted with permission from ref. 43 copyright 2014 Nature Publishing Group.

4 Conclusion and perspectives

With the rapid growth of 2D nanomaterials research during past decade, a wide range of inorganic 2D nanomaterials covering from inartificial transition metal dichalcogenides and metal halides to exfoliated lamellar hybrid intermediate have attracted great interest for its superior intrinsic physical properties that enable promising applications for electronics and energy-related applications. In the process of exploiting those 2D nanomaterials, finding chemical strategies that can effectively engineer their intrinsic physical properties is the decisive factor that determining what extent the application prospects can be achieved.

With atomic-scale thickness, 2D nanomaterials have extremely high specific surface area enabling their surface phase to be as important as bulk counterparts, and therefore provide an alternative way of modification surface phase for engineering intrinsic physical properties of inorganic 2D nanomaterials. The surface effect of 2D nanomaterials is quite different from that in traditional bulk nanomaterials counterparts. Although surface modification of bulk solids is vital for reactions and biocompatibility etc., artificial manipulation of surface atom configurations is hard to influence the intrinsic physical properties of whole bulk crystals. Unlike that in bulk counterparts, surface chemical modification on the surface facet atoms greatly influences intrinsic physicochemical properties arising from 2D unique characteristic. Owing to dimensionally reduced structure where most of atoms are exposed on surface with high chemical activity, regulating carrier concentrations and band gap of inorganic 2D nanomaterials were achieved by surface chemical modifications, which is vital for performance promotion of electrode applications and catalysis capability. More importantly, as electrons confined at 2D scale are correlated strongly, any surface chemical modification could trigger electron transfer or atomic lattices variation for bringing readjustment of the whole electronic state, and it thus leads to a wide range of regulation of conductivity, magnetism, and energy band structures which are urgently needed in nano-electronic and clean energy related fields. Therefore, chemical modification strategies are critical to engineering physical properties in 2D nanomaterials while maintaining their freestanding 2D lattice framework which shows promising sign in electronics and energy-related devices.

In this review, we outline recently-developed surface chemical modification strategies to engineering intrinsic physical properties of inorganic 2D nanomaterials, including tuning conductivity in 2D nanomaterials by surface incorporation, regulation band structure by surface defect structure, and introducing magnetism by surface modulations. From our own and other research groups' results, proper choice of surface modification effectively regulate intrinsic physical properties for requirements of proof-of-concept applications.

Overall, the inherently superior physical properties in 2D nanomaterials coupled with recent advances in engineering those properties by surface chemical modification inspire a growing excitement for truly 2D applications. More effect was urgently needed to further improve reliable stability and repeatability, which is vital for in-depth understanding of physical behavior mechanism as well as boosting them into practical industrial applications. We are anticipating and optimistic that surface modification progress continued will lead to broader application and deeper understanding of physicochemical properties in 2D nanomaterials.

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Footnotes

The authors declare no competing financial interest.

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SYNOPSIS TOC.

Table of Contents

This tutorial review summarizes the recent advances of engineering intrinsic physical properties of inorganic two-dimensional nanomaterials by surface chemical modification.