Chem Soc Rev



REVIEW ARTICLE

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Cite this: Chem. Soc. Rev., 2018, 47, 2401

Received 24th April 2017 DOI: 10.1039/c7cs00290d

rsc.li/chem-soc-rev

Introduction

A cornerstone of organic chemistry is the synthesis of large, complex molecules from smaller building blocks.¹ These syntheses rely on the preservation of covalent bonds within the

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metal oxides

assembly, and symmetry breaking of layered oxides for electronic applications.



Soft chemistry of ion-exchangeable layered

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Soft chemical reactions such as ion-exchange and acid-base reactions have been extensively investigated to synthesize novel metastable layered inorganic solids, to exfoliate them into individual nanosheets, and to re-assemble them as thin films and nanocomposite materials. These reactions proceed at relatively low temperature and enable the synthesis of a rich variety of structures by stepwise reactions. In recent years, the toolbox of soft chemical reactions has been utilized to rationally design and tailor the properties of functional layered transition metal oxides. Layer-by-layer assembly and intercalation chemistry have provided insight into covalent interactions that stabilize oxide-supported nanoparticle catalysts. In addition, topochemical reactions have been utilized to tune the compositions of layered perovskite oxides in order to break

inversion symmetry, resulting in piezoelectric and ferroelectric properties. This review focuses on the use of soft chemical approaches to design functional layered transition metal oxides with tunable properties.

Soft chemical reactions enable the design of functional materials for diverse applications that include artificial photosynthesis, catalysis, energy storage, fuel cells, optical sensors, ferroics, and high-*k* dielectrics.

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precursor molecules as new bonds are formed, an approach that

has become increasingly popular over the past few decades in the

synthesis of solid state materials with extended lattices.² For

example, metal organic frameworks with predetermined struc-

tures are made in low-temperature reactions that involve coordination of metals by bridging ligands,³ and extended nanoparticle lattices with programmable structures can be made by exploiting

DNA hybridization.⁴ Metastable solid state materials synthesized

under kinetic rather than thermodynamic control are now being

increasingly designed for applications in energy storage, chemical

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sensing, separations, biomedicine, and other areas.

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Layered metal oxides represent a special class of solid state materials that are amenable to low-temperature chemical transformations without disrupting the covalent bonding within the layers. These compounds can contain stacks of electrically neutral metal-oxide layers, but more commonly they are intergrowths of charged layers that are interleaved with cations or anions, or their metal oxide sheets alternate with covalently bonded interlayers. Examples of layered oxides with uncharged sheets include $MoO_3 \cdot 2H_2O$, which contains distorted $MoO_5(H_2O)$ octahedral layers with interlayer water molecules, and V2O5 which consists of O atoms in trigonal bipyramidal coordination around V atoms, which are cross-linked in a zig-zag pattern to form sheets.^{5,6} Ionic intergrowths include A_xMO₂ and A₂MO₃-type structures that have MO₆ edge-sharing octahedra with alkali metal ions inserted between the layers.⁷ In addition, they also include alkali metal niobates such as KNb₃O₈⁸ and K₄Nb₆O₁₇⁹ as well as titanates with the general formulas $M_2Ti_nO_{2n+1}$ $(M = Na, K)^{10-14}$ and $Na_4Ti_nO_{2n+2}$.^{15,16} The titanate structures have layer slabs that are sheared in a direction perpendicular to the plane at every nth octahedron. Ternary oxides of other transition metals, such as Mn, V, and W have also been prepared and some of them are anion-exchangers.^{17–19} Layered quaternary oxides include mixed-metal oxides, perovskite structures and layered double hydroxides and are discussed in detail below.

Layered perovskites represent a special class of layered materials that contain ABX₃ perovskite as their basic building block, where A refers to cations in a cubooctahedral cavity of twelve X anions (where X = O, halogen, N, S, and/or H) and B refers to a cation in a BX₆ octahedron. The two most common structural classes of layered oxide perovskites that contain ion-exchangeable cations are Ruddlesden–Popper (RP) phases, $A_2'[A_{n-1}B_nO_{3n+1}]$, and Dion–Jacobson (DJ) phases, $A'[A_{n-1}B_nO_{3n+1}]$, where *n* represents the number of BO₆ octahedral layers and comprise the covalent perovskite blocks. The key difference between these structural families is that Dion–Jacobson phases

have half the number of interlayer cations as the Ruddlesden– Popper phases, which have a rock salt type AO interlayer (see Fig. 1). Aurivillius (AV) phases, $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$, represent another class of layered perovskites in which a covalent network of $Bi_2O_2^{2+}$ occupies the interlayer galleries. Layered perovskites can have their layers oriented along different crystallographic axes based on the connectivity pattern of BX₆ octahedra and the interlayer orientation. These include (110) layered perovskites in which the octahedra are linked at the edges and (111) layered perovskites with the octahedra connected along the faces.²⁰

Compared to cation exchangers, which are quite common among layered oxides, layered anion exchangers are relatively rare. Layered double hydroxides (LDHs), which contain positively charged metal hydroxide sheets interleaved with anions, were first discovered in 1940s by Feitknecht while studying the co-precipitation of alkali metal cations with bases.²¹ They have a structure analogous to brucite, Mg(OH)₂, and contain the general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]A^{n-}_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent cations, x corresponds to the ratio $M^{3+}/(M^{2+} + M^{3+})$, and *n* represents the anion charge. The choice of M²⁺ and M³⁺ ions used are similar in size to Mg²⁺ ions and can consist of a variety of counter anions such as carbonates, nitrates, and hydroxides. LDHs with the hydrotalcite structure have also been prepared using Li⁺ and Al³⁺ ions.²²⁻²⁴ Layered rare earth hydroxides of general formulas $Ln(OH)_2A^{q-}_{1/q} \cdot mH_2O^{25}$ and $Ln_8(OH)_{20}A^{q-}_{4/q} \cdot nH_2O^{26}$ represent another class of layered anion exchangers, the properties of which have been recently reviewed.27

Layered oxides with cation and anion ordering have been explored for different applications. Brownmillerites are oxygendeficient layered perovskites of the general formula A₂B₂O₅ having alternating layers of oxygen octahedra and tetrahedra and were discovered in the 1920s.²⁸ These structures can also have ordered B-site cations that can exhibit tetrahedral and



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to external stimuli. Alyssa now works with Prof. Thomas Mallouk on the characterization of late transition catalytic metal nanoparticles on early transition metal oxide supports for applications in heterogeneous catalyst design.



Thomas E. Mallouk

Thomas E. Mallouk received his ScB degree from Brown University and PhD from the University of California, Berkeley under the direction of Prof. Neil Bartlett. In 1985, after a postdoctoral fellowship with Mark Wrighton at MIT, he joined the faculty at the University of Texas at Austin. In 1993, he moved to Penn State where he is currently Evan Pugh University Professor. His research interests are in nanoscale and layered inorganic materials and

their applications to problems in chemistry, biochemistry, physics, and materials science.



Fig. 1 Structural motifs of selected layered oxides that are amenable to soft chemical transformations: binary oxides (a) MoO_3 : $2H_2O$ and (b) V_2O_5 ; ternary oxides (c) ABO_2 -type LiCoO₂ structure, (d) layered double hydroxide (LDH), (e) Brownmillerite $Ca_2Fe_2O_5$ structure. Shear structures (f) KNb_3O_8 , (g) $K_4Nb_6O_{17}$, and (h) $Na_2Ti_3O_7$; layered oxide perovskites: (i) Ruddlesden–Popper phase, $A_2'[A_{n-1}B_nO_{3n+1}]$, (j) Dion–Jacobson phase $A'[A_{n-1}B_nO_{3n+1}]$, and (k) Aurivillius phase $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$.

octahedral coordination in the alternating layers. Anion-ordered layered oxides include oxyhydrides, oxychlorides, and oxyfluorides that have been explored for applications as ion conductors and antiferromagnets.^{29–31} The most common families of layered oxide structures are illustrated in Fig. 1.

Unlike layered van der Waals solids that have weak intermolecular forces, most layered transition metal oxides consist of charged sheets with charged species intercalated between them. The presence of electrostatic attractive forces make them amenable to 'host-guest' chemistry, in which the exchangeable intercalant is the guest species and the metal oxide block is the host. The presence of electrostatic attractive forces can enable layered oxides to be pulled apart into two-dimensional monolayer nanosheets and also stack the monolayers back to form three dimensionally bonded perovskites.³²

Solid state synthesis offers a convenient route to synthesize functional layered oxides but the range of compositions accessible are limited by the competition between thermodynamics and kinetics. The key limiting factor in solid state chemistry is often the requirement for diffusion of individual atoms that

necessitates high temperature reaction conditions and thus produces the most thermodynamically stable products.³³ On the other hand, low temperature syntheses of materials enable one to access kinetic metastable phases, often while retaining some or all of the chemical bonding of precursor molecules. The history of this approach can be traced back to sol-gel synthesis, a molecular approach that uses aqueous and organic phase precursors, which was first demonstrated in the mid 19th century by Ebelman who observed that hydrolysis of tetraorthoethylsilicate (TEOS) under acidic conditions formed silica.34 Later, Roy and co-workers expanded the sol-gel method to synthesize several new silicate and ceramic glasses of technological interest.^{35,36} In recent years, sol-gel synthetic techniques have been expanded to include a variety of solid-state structures, including nanostructures.³⁷ The sol-gel method is also closely related to hydrothermal and solvothermal techniques that have been used to synthesize porous materials such as zeolites and MOFs, as well as shape-controlled nanocrystals of a very broad variety of materials, all from molecular precursors.

In contrast to the molecular precursor approach, topochemical solid state chemical reactions convert extended arrays of atoms into other forms, usually with retention of much of the bonding in the precursor material.³⁸ In this way a thermodynamically stable precursor, typically made by a high temperature solid state reaction, can be converted into a related metastable structure that is not accessible by direct synthesis. The earliest examples of these reactions included the dehydration of molybdenum trioxide hydrate, which takes place at 125 °C,³⁹ and the transformation of the layered titanate, K2Ti4O9, to metastable TiO2(B) by acid exchange of K₂Ti₄O₉ in nitric acid followed by dehydration at 500 °C. These kinds of reactions, initially developed by French chemists, were called "chimie douce" - most commonly translated as "soft chemistry" - to signify the gentle conversion of one structure into another with retention of chemical bonding. Soft chemical reactions have since been widely explored for the synthesis of layered oxides and include intercalation, reductive deintercalation, layer expansion, grafting, ion-exchange, exfoliation, pillaring, and substitution reactions. Multistep synthetic strategies have been employed to demonstrate the retrosynthetic design concept in layered oxides. These processes have been extensively described in earlier reviews^{32,40,41} and some of these approaches will be discussed briefly in light of recent advances.

Layered oxides have been investigated for several technological applications such as ferroelectrics,⁴² solid state ion conduction,⁴³ giant magnetoresistance,⁴⁴ and superconductivity.⁴⁵ In the past few years, this class of materials has been expanded to include several new applications (Chart 1). This is seen by the prolific number of review papers published on this topic ranging from new methods of synthesis to applications in energy storage. 41,46-53 Most reviews focus on either the synthetic aspects of this class of materials, assembly techniques, or specific applications of layered transition metal oxides. A comprehensive understanding of using the stepwise synthetic approach for the rational design of functional materials is lacking. This review aims to bridge the synthetic aspects of layered oxides that are accessible by soft chemical methods with emergent functionalities by highlighting a few new applications of technological relevance. A strong emphasis will be placed on layered perovskite oxides as these are technologically fascinating for different applications, although a few good examples of different structure types will be highlighted as well. A number of reviews have covered applications of other structure types in detail and the interested reader is referred to those reviews.48,54-56

The first section presents an overview of different synthetic strategies used to access a variety of layered oxide compositions by soft chemical techniques that do not disrupt the parent crystal structure. A strong focus will be placed on the use of step-wise synthetic schemes, such as ion-exchange and intercalation chemistry, to obtain different compositions of layered oxides. Novel synthetic techniques, such as microwave-assisted functionalization, will be briefly surveyed. Exfoliation and re-assembly techniques will be presented as effective methods for interconverting between three-dimensionally bonded oxides and unilamellar oxide nanosheets.

The second section will survey key characterization techniques employed to investigate both the structure and physical properties of layered oxides. This section will cover commonly



Chart 1 Key technological milestones in the chemistry of layered metal oxides over the past 35 years.

used techniques, such as X-ray scattering, transmission electron microscopy, atomic force microscopy, and UV-vis spectroscopy to characterize the phase, morphology, and electronic structure of layered oxides in bulk and as nanoscale colloids. The role played by characterization in investigating structure–property relationships for designing functional materials will be explored for each of these techniques.

The third section will highlight a few recent examples of functionalities that have emerged by utilizing rational design and assembly principles. First, strong interfacial bonding between late transition metal oxide nanoparticles and layered perovskites of early transition metals has recently been discovered. The interfacial bonding stabilizes nanoparticles on the nanosheet supports at high temperatures and provides new insight into strong metal–support interaction (SMSI) in heterogeneous catalysis. Layered oxide nanosheets obtained by soft chemical delamination are useful for imaging supported nanoparticles by electron microscopy and for investigating the strength of interfacial bonding by calorimetry. Similarly, topochemical ionexchange of layered perovskites has been explored as a means of lowering the crystal symmetry for applications in piezoelectrics and ferroics. The resultant properties were dependent on the size and ordering of the A-site and A'-site cations, which can induce and control the cooperative rotation of cornersharing MO_6 octahedra. This section demonstrates that soft chemistry can be utilized as a tool for tailoring the structure and emergent properties of metal oxides for new technological applications.

The fourth section presents an overview of applications to highlight key advances in this field enabled by soft chemistry principles. Soft chemical approaches discussed in the first section have been utilized to fabricate functional materials for applications in artificial photosynthesis, energy storage, fuel cells, photoluminescence and optics, ferroelectric and magnetic applications, and high-k dielectrics (Table 1). The role played by the soft chemistry approaches in tuning the resulting properties

Synthetic approach	Composition	Property exhibited	Ref.
Ion exchange	$A'_{1-x}Na_xCa_2Ta_3O_{10}\cdot nH_2O$ (A' = K, Li)	Photocatalysis	74
	LiHSrTa ₂ O ₇	Piezoelectric	75
	$Cu_3NaIr_2O_6$	Ferromagnetic	77
	$Cu_3LiIr_2O_6$	Antiferromagnetic	77
	$LiRTiO_4$ (R = La-Ho)	Acentric	195
	$HRTiO_4$ (R = La-Ho)	Acentric	196
	$H_2Ti_3O_7$	Energy storage	219
	$Li_2Ti_3O_7$	Energy storage	218
	$Na_{0.8}Ti_{1.73}Li_{0.27}O_{4}$	Energy storage	217
	$H_2La_{1.95-2x}Er_{0.05}Yb_{2x}Ti_3O_{10}$	Photoluminescence	238
Exfoliation/flocculation	Li/MnO ₂	Energy storage	122
	$Rh_2O_3/KCa_2Nb_3O_{10}$	HER active	188
	$Rh(OH)_3/K_4Nb_6O_{17}$	HER active	131
	Pt/KCa ₂ Nb ₃ O ₁₀	HER active	159
	Pt/HCa ₂ Nb ₃ O ₁₀	HER active	214
	$HCa_{2-r}Sr_rNb_3O_{10}$	HER active	213
	$HCa_2Nb_{3-y}Ta_yO_{10}$	HER active	213
	$RuO_{x}/KCa_{2}Nb_{2}O_{10}$	HER and OER active	212
	$H_0Ti_0O_{17}$	Energy storage	223
	HSbP ₂ O ₂	Optical sensors	240
	H ₂ Sh ₂ P ₂ O ₁	Optical sensors	239
	$T_{a}P_{a}O_{a}^{2-}$	Optical sensors	241
	Na _x MnO ₂	Energy storage	224
Topochemical oxidation/reduction	La2BaFe2O5F4	Antiferromagnetic	106
	$La_2SrCr_2O_7F_2$	Antiferromagnetic	107
	$Sr_4Mn_2O_6$ [C]	Antiferromagnetic	103
	$La_2Ni_2O_{\pi}$ = F_2 =	Antiferroelectric	108
	Sr ₂ FeO ₂	Antiferromagnetic	102
	LaCasFesOs	Antiferromagnetic	247
	LasNisOr For	Ferroelectric	108
	$Sr_3(M_{0.5}Ru_{0.5})_2O_7F_2$ (M = Ti, Mn, Fe)	Metal/antiferromagnetic	105
Layer-by-layer assembly	H ₄ Nb ₆ O ₁₇ /PAH	Epitaxial growth	110
	PDDA/Na-TSM	Anion-exchanger	145
	$(rGO/Ti_{0.07}O_{0.052}^{-})_{r}$	Field-effect transistor	142
	$\mathbf{PANI-Ti}_{0.87} \mathbf{O}_2 \qquad \mathbf{j}_n$	Photoelectrode	141
	Al ₄₀ /MnO ₂	Electrochemistry	141
	$Ti_{0.87}O_2/Ca_2Nb_3O_{10}^{-}$	Seed layers for epitaxial growth	140
Langmuir–Blodgett deposition	$Ti_{0.8}Co_{0.2}O_{2}/Ca_{2}Nb_{3}O_{10}^{-}$	Multiferroic	245
	$(HLaNb_2O_7/HCa_2Nb_2O_{10})$	Ferroelectric	154
	$HCa_2Na_{m-3}Nb_mO_{10}$ ($m = 3-6$)/SrRuO ₃	Ferroelectric	249

will be described. A summary of current challenges and new research directions will be addressed in the last section.

1. Synthesis, exfoliation, and assembly of layered oxides

a. Synthesis of layered oxides. Solid state synthesis: the most common route to synthesis of layered oxides is the ceramic method, in which precursor oxides are typically ground and heated to varying temperatures to promote diffusion of atoms. Because refractory intermediates can form at the interfaces between reacting crystal grains, the phase purity of the resulting products often depends on the heating rate, temperature, and pressure. Sol-gel synthetic routes have been utilized to overcome the diffusion barrier in these syntheses by effectively mixing the precursor elements at the molecular level. For example, birnessite KrMnO₂ can be made by reaction of KMnO₄ with a sugar such as glucose. Drying followed by calcination at 450 °C results in the formation of a layered birnessite structure with interlayer potassium cations.⁵⁷ Recently, Ma, et al. showed that a new amorphous layered titanate $Ti_{2-x} \Box_x O_{4-4x}(OH)_{4x}$ could be stabilized en route to making anatase TiO₂ by a sol-gel reaction of titanium isopropoxide in ethanol using water as the hydrolysis agent.58

A popular sol-gel precursor route to layered oxide perovskites is the polymerizable complex method, also known as Pechini method, which is based upon the esterification reaction between a carboxylic acid and an alcohol. This method was originally developed in the 1960s for the synthesis of dielectric films⁵⁹ and has now been extended to many layered oxide perovskites. In this method, a chelating carboxylic acid (such as citric acid) solubilizes metal ions such as Nb(v), Ta(v), and Sr(II), and ethylene glycol promotes the esterification process.⁶⁰ The Dion-Jacobson phase oxide KCa₂Nb₃O₁₀ was synthesized using the Pechini method by polymerizing a mixture of NbCl₅, CaCO₃, and KCl in the presence of ethylene glycol and anhydrous citric acid in methanol followed by calcination in air at 1273 K for 2 h. Pt-Loaded HCa2Nb3O10 nanosheets obtained by this method had improved photocatalytic activity for hydrogen evolution under bandgap irradiation when compared with the solid state synthesis approach as a result of higher surface area of the sheets.⁶¹ The Pechini method has also been utilized in the synthesis of A-site and B-site doped layered oxides, such as a new Ruddlesden-Popper phase K₂CaNaNb₃O₁₀⁶² and two new Dion-Jacobson phases $KCa_{2-x}Sr_{x}Nb_{3}O_{10}$ and $KCa_{2}Nb_{3-y}Ta_{y}O_{10}^{63}$ in which the ratio of metal ions was adjusted to tune the band-edge potentials for photocatalysis. Effective strategies of polymerization can expand the choice of layered oxide compositions that are otherwise inaccessible through solid-state synthesis due to diffusion barriers or the volatility of some of their components.

b. Topochemical synthesis

Ion exchange. Ion-exchange is one of the most popular soft chemistry routes in designing novel metastable phases of layered oxides and utilizes general chemistry principles of charge density and acid-base chemistry. The higher charge-to-radius ratio of smaller cations (or divalent cations) can drive larger cations out by lowering the electrostatic energy, and thus results in isostructures with smaller cations in the interlayer galleries. Acid-base chemistry is also a powerful tool for exchanging protons reversibly with alkali metal cations or with covalent intergrowth layers. Ion-exchange in layered oxides was first demonstrated in the layered titanate, $Tl_2Ti_4O_9$, by reacting it with molten KNO₃-KCl flux to obtain the isostructure $K_2Ti_4O_9$.¹¹ Similarly, acid exchange has been demonstrated in the layered titanates Na₂Ti₃O₇ and $K_2Ti_4O_9$ to convert them into anhydrous $H_2Ti_3O_7$ and hydrated $H_2Ti_4O_9$ ·H₂O respectively. The former could be made to revert to its parent phase by reacting with NaOH.⁶⁴ In recent years, proton exchange has also been demonstrated in layered oxides containing late transition metals such as the layered ruthenic acid $H_{0.22}RuO_{2.11}^{65}$ and the trivalent iridate $K_{0.75}Na_{0.75}IrO_2$, which can be converted to the protonated oxyhydroxide IrOOH.⁶⁶

Ion-exchange has also been used in layered perovskite oxides to replace alkali metal cations in the interlayer galleries with divalent metal cations^{67,68} and with complex metal halides^{69–71} Wiley and coworkers pioneered topochemical exchange in layered perovskites and also studied the metastability of the ion-exchanged compounds with respect to temperature.⁷² They performed monovalent and divalent ion-exchange in a series of two-layer Dion–Jacobson phase ALaNb₂O₇ compounds (A = H, Li, Na, K, NH₄, and Ag) by heating them in molten alkali metal nitrates and recently extended this to ANdNb₂O₇.⁷⁰ Ion-exchange has also been reported in oxyfluorides and oxynitrides such as RbLaNb₂O₆F⁷³ and CsCa₂Ta₃O_{10–x}N_y³⁰ respectively upon treatment with acids.

In recent years, ion-exchange in both layered perovskites and non-perovskite oxides has been observed to modify their resulting properties. Mitsuyama, et al. reported partial ionexchange of triple-layered Dion-Jacobson phases KCa₂Ta₃O₁₀ and $LiCa_2Ta_3O_{10}$ with Na^+ using the mixed molten nitrates $A'NO_3$ (A' = K, Na) and NaNO₃ to tune the interlayer hydration for photocatalysis. Partially ion-exchanged layers showed the highest photocatalytic activity, resulting from the higher hydration enthalpy of Na⁺ ions coupled with the optimum interlayer distance for water intercalation.⁷⁴ Similarly, Galven, et al. were able to ion-exchange one half of Li⁺ ions in Li₂SrTa₂O₇ by reacting with NH₄Cl in the solid-state to form the acentric compound LiHSrTa₂O₇.⁷⁵ Another partial ion-exchange route was reported by Cussen who converted HLaTiO₄ to the solidsolution $H_{1-r}Li_rLaTiO_4$.⁷⁶ Recently, Roudebush, *et al.* synthesized two layered iridates Cu₃NaIr₂O₆ and Cu₃LiIr₂O₆ containing the honeycomb lattice from Na2IrO3 and Li2IrO3 by reaction with CuCl below 450 °C. They found that ion-exchange resulted in vastly different magnetic properties from the parent structure and this difference was attributed to changes in the interlayer spacing of the IrO₆ layers.⁷⁷ Controlled ion-exchange of layered oxides can thus be used for fine tuning of the structure to realize useful properties that are difficult to control by direct high temperature synthesis. Some examples of these properties are summarized in Table 1.

Intercalation chemistry. Intercalation represents another topochemical synthetic approach that introduces different species (cations, anions, polymers, organic ligands) into the interlayer gallery spaces of layered oxides. Intercalation can be driven

quite effectively by acid–base reactions, given the large thermodynamic driving force for neutralization of interlayer protons by strong or weak bases. Intercalation can also be driven electrochemically in cases where the A- or B-site cations, or intercalant molecules, can undergo oxidation–reduction reactions.

Intercalation by acid-base chemistry was first reported in shear-structure layered titanates such as HTiNbO₅ and HTi₂NbO₇·2H₂O, which showed complete intercalation of amines of varying chain lengths.⁴⁰ The electrochemical insertion of lithium ions was first reported for the binary layered oxides MoO_3 and $V_2O_5^{-78}$ and these intial studies opened up the now huge technology of lithium intercalation batteries. Recently, electrochemical intercalation has been extended to divalent alkali metal cations, such as Mg^{2+} , by using incorporated water in the host MnO_2 structure to screen the electrostatic interaction with the host anions.⁷⁹

Intercalation reactions have been extensively studied in lavered oxide structures and include intercalation of neutral species, cations, or co-intercalation of both cations and anions. A variety of guest species, such as alkali metals,⁸⁰ metal hydroxides and chalcogenides,^{81,82} organic compounds,⁸³ and nanoparticles⁸⁴ have been successfully intercalated into layered perovskite oxides. Often this method provides access to metastable compounds that cannot be made by direct solid-state synthesis. For instance, electrochemical intercalation of Na into layered sodium oxide has been utilized to synthesize new phases of Na_xVO₂ that are not obtained by direct synthesis.⁸⁰ Similarly, Montasserasadi, et al. used topochemical intercalation to synthesize the metal hydroxide-intercalated layered perovskites (K2OH)LaNb2O7, (Rb2OH)LaNb2O7, and (Rb2OH)-Ca₂Nb₃O₁₀ by decomposition of calcium oxalate monohydrate followed by oxidative intercalation of hydroxide ions in a sealed tube.⁸¹ This method has also been employed to oxidatively intercalate chalcogenides such as H₂S and H₂Se into Rb₂LaNb₂O₇.⁸² Other compositions synthesized by using this topochemical method include (Li₂Cl)LaNb₂O₇⁸⁵ and (A₂Cl)LaNb₂O₇ (A = Rb, Cs).⁸⁶ Some of the different structures accessible by topochemical intercalation of layered perovskite oxides are illustrated in Fig. 2.

The intercalation of organic molecules into layered oxides produces inorganic-organic hybrid structures. Alkyl chains, amines, alcohols, and carboxylic acids have been intercalated into a variety of layered oxides including layered oxide perovskites.^{87–91} Organic bases, such as pyridine and organoammonium cations, readily intercalate into the interlayer galleries of proton-intercalated Dion-Jacobson phases, such as HLaNb₂O₇ and HCa₂Nb₃O₁₀, through an acid-base reaction in which the protonated layered perovskite acts as the Bronsted acid.^{87,92,93} Alcohols can also be intercalated by the replacement of protons in the interlayer galleries of HLaNb₂O₇^{88,89} and more recently, the Ruddlesden-Popper phase acid $H_2CaTa_2O_7^{90}$ under ambient conditions. Similarly, the layered molybdic acid MoO₃·H₂O has been intercalated with n-octylamine at room temperature.⁹⁴ Sugahara, et al. recently demonstrated the intercalation of triethylphosphine oxide (TEPO) by first intercalating n-decoxy groups into HLaNb₂O₇ and HCa₂Nb₃O₁₀ to expand the interlayer gallery followed by the hydrolysis of n-decoxy groups in the presence of water. Hydrolysis of n-decoxy groups generates hydroxyl ligands in the interlayer spaces that can hydrogen bond with phosphoryl oxygens of TEPO and replace the *n*-decoxy site.⁹¹

Microwave and sonochemical techniques are rapidly emerging as green chemical techniques for intercalating and functionalizing layered perovskites with organic molecules. Microwave heating confers several advantages over conventional heating by increasing reaction rates and thus providing higher yields⁹⁵ Boykin and Smith first reported the microwave-assisted intercalation of *n*-alcohols into the acidic three-layer Dion–Jacobson phase $HSr_2Nb_3O_{10}$ with 40% coverage by heating in a microwave oven with methanol followed by propanol and hexanol. Protons could be completely replaced in the interlayer galleries by hexoxy-groups within 12 h, compared to 7 days with conventional heating.⁹⁶ Recently, Wiley and coworkers extended microwave synthesis to a variety of topochemical reactions by demonstrating cation exchange



Fig. 2 Structures obtained by topochemical ion-exchange and intercalation of the Dion–Jacobson phase $ALaNb_2O_7$ (A = Rb, K). (a) (MCI)LaNb₂O₇ (M = transition metal), (b) (Li₂CI)LaNb₂O₇, (c) (Rb₂CI)LaNb₂O₇, and (Rb₂OH)LaNb₂O₇. (Key: M = small blue spheres; Cl = large violet; La = medium green; oxygen = small red; NbO₆ octahedra = light blue; Li = small dark purple; Rb = large dark purple; H/D = gray.) Adapted with permission from ref. 81. Copyright 2014 American Chemical Society.



Fig. 3 Microwave-assisted click chemistry in Aurivillius phase Bi₂SrTa₂O₉. Adapted with permission from ref. 99. Copyright 2016 American Chemical Society.

and intercalation with both alcohols and amines.⁹⁷ Similarly, microwave reactions have recently been used to protonate and intercalate a new class of amines bearing aromatic groups into Aurivillius phase Bi₂SrTa₂O₉, with post-synthesis modification to demonstrate *in situ* click chemistry by alkyne-azide cyclo-addition (Fig. 3).^{98,99} Ultrasonication has been found to be another effective technique for rapidly intercalating and functionalizing layered perovskites at ambient temperature. Using this technique, Giannici, *et al.* were able to intercalate a variety of organic molecules including imidazole, histamine, and 3-mercaptopropyl-trimethoxysilane into HLaNb₂O₇, which was unreactive to these molecules without sonication.¹⁰⁰

Other topochemical reactions. Topochemical redox reactions have also been demonstrated for Ruddlesden-Popper phase oxides derived from late transition metals, such as Fe, Co, Ni, and Mn, that are not ion-exchangeable but are interesting materials for applications in Li-ion battery anodes, antiferromagnetism, ferroelectrics, and high temperature superconductors. Hayward and co-workers have pioneered rational design principles for topochemical oxidation and reduction by using a combined approach of bond valence sum (BVS) calculations and coordination geometry to deduce the available anion (de-)intercalation sites on reacting with metal fluorides and metal halides, respectively.¹⁰¹ The smallest thermodymanic cost for de-intercalation of oxygen atoms was predicted to be the site that results in the largest decrease in BVS of B-site cations (resulting from reduction of B-site cations) but the smallest change in BVS of the A-site cations. The largest difference in the BVS of B-site and A-site cations was used as a strategy to predict the site of oxygen de-intercalation. This concept was verified experimentally for reduction of a variety of layered oxides such as Ruddlesden-Popper oxide Sr₂FeO₃¹⁰² and the layered oxychloride, Sr₄Mn₃O_{6.5}Cl₂,¹⁰³ by using CaH₂ as the reducing agent at 350 °C. Recently, topochemical fluorination has been investigated in a variety of layered oxides by reacting with metal fluorides such as CuF₂ or CaF₂ in the presence of O₂.

Topochemical fluorination generally resulted in the intercalation of fluorine atoms into the rocksalt layers with concomitant oxidation of the B-site cations, but it also sometimes resulted in partial ion-exchange with O-atoms at the apical sites. The positions of the inserted F atoms were determined by calculating bond valence sums to determine the local bonding environment. The choice of intercalation *vs.* ion-exchange was dependent upon the stability of the oxidation state of the B-site cation.^{104–108} The rational design of metastable layered oxides by topochemical oxidation and reduction approaches have been covered in detail in other recent reviews.^{101,109}

Exfoliation and flocculation. The exfoliation of layered perovskites was initially reported by Treacy, et al., who intercalated amines into the Dion-Jacobson phase KCa2Nb3O10 and observed the formation of individual nanosheets by electron microscopy.93 Keller, et al. later demonstrated that anionic nanosheets produced by reaction of the acid-exchanged nanosheets with tetrabutylammonium hydroxide (TBA⁺OH⁻) could be grown layer-by-layer on surfaces by dipping suitably primed substrates alternately in suspensions of the nanosheets and solutions of cationic polymers.¹¹⁰ In 1996, Sasaki, et al. used TBA⁺OH⁻ used to swell a layered protonic titanate, $H_x Ti_{2-x/4} \Box_{x/4} O_4 \cdot H_2 O$ (x ~ 0.7; \Box , vacancy). In the same report, they coined the single-layer particles in the suspension as "nanosheets" because of the subnanometer thickness and micrometer lateral dimensions of the individual sheets.¹¹¹ Since these early reports, TBA⁺OH⁻ has been widely used to produce stable colloidal suspensions of oxide nanosheets from acidic oxide precursors. However, other exfoliating agents have recently been studied, including tetrabutylphosphonium hydroxide (TBP⁺OH⁻), which was more effective for completely exfoliating the layered titanate, H_{0.8}[Ti_{1.2}Fe_{0.8}]O₄·H₂O.¹¹² The trirutile-like structure of HNbWO₆ can be exfoliated using triethanolamine.¹¹³ Well-crystallized layered double hydroxide (LDH) structures can be treated with formamide to achieve the swelling necessary for exfoliation.¹¹⁴

The conversion of layered metal oxides into layered hydrated solid acids is achieved by treating the parent compound with an acidic solution. Some examples of these solid acids include $HCa_2Nb_3O_{10}$ ·1.5H₂O, $H_{0.8}[Ti_{1.2}Fe_{0.8}]O_4$ ·H₂O, and $H_{0.13}MnO_2$ ·0.7H₂O. These solid acids react by intercalating organophosphonium ions, organoamines, or organoammonium ions, from basic solutions, but only a fraction of the acid groups can be neutralized because of the large size of these cations.^{113,115,116} The reaction also introduces a large volume of water into the interlayer galleries, which results in gigantic osmotic swelling.

The general mechanism of exfoliation relies upon the osmotic swelling of the layers to produce unilamellar nanosheets; a schematic of the mechanism is shown in Scheme 1. As the swelling increases, the interlayer spacing increases and the intermolecular forces of neighboring layers are weakened and the structure is prone to delamination, or exfoliation. The difference in osmotic pressure between the interlayer gallery and the surrounding solution determines the degree of osmotic swelling. The osmotic pressure is independent of the exfoliating agent used but depends on its concentration, and the optimal



Scheme 1 Schematic representation of the general mechanism of exfoliation. Reproduced with permission from ref. 117. Copyright 2014 American Chemical Society.

concentration has been found to be 30–40% of the cation exchange capacity of the layered solid acid.¹¹⁷ Higher concentrations are less effective because excess salt in solution lowers the osmotic pressure difference between the bulk solution and the interlayer galleries.

The chemical characteristics of the exfoliating agent affects the stability of the resulting swollen layered oxide. For example, layered titanates intercalated with 2-(dimethylamino)ethanol (DMAE) produced a stable and reversible 100-fold expansion within the interlayer gallery.¹¹⁵ Intercalation of layered oxides with small, polar ions tends to yield stable swollen structures whereas intercalation of larger, less polar ions decreases the stability of the swollen structures, which are more susceptible to complete delamination.²⁷ The most commonly used cation is the bulky relatively low polarity TBA⁺ ion, which produces a relatively unstable swollen structure and that can be delaminated by mechanical shaking.^{118,119}

Layered oxide nanosheets are charge-bearing two-dimensional nanomaterials, unlike their electroneutral parent compounds. Colloidal suspensions of negatively charged nanosheets can be restacked, or flocculated, by addition of cations/polycations at high ionic strength where the total charge is in excess of the nanosheets.^{120,121} The flocculation of nanosheets results in microand mesoporous randomly restacked lamellar materials in which the crystallinity of the individual two-dimensional oxide layers is preserved. These layers are oriented irregularly and are misaligned in the *z*-direction in the flocculated materials.¹²¹ Fig. 4 illustrates the restacking of charged nanosheets. Anionic nanosheets often restack rapidly upon introduction of cations and can be readily collected through filtration. The flocculated materials have higher porosity than their ordered lamellar parent structures, which can be used to tailor functionality. Flocculation can also be used as a tool to introduce guest species that may be more difficult to intercalate through typical ion-exchange reactions or other impregnation methods. As an example, Li^+ was incorporated into MnO_2 by flocculation of the delaminated oxide nanosheets. Electrochemical analysis of the flocculated-LiMnO₂ showed smoother charge/discharge of Li^+ for lithium-ion battery applications.¹²²

While these restacked materials are typically disordered, when flocculation occurs slowly enough and under specific conditions, it can be possible to restack the sheets with registry to recover the structure of the original material. For example, $Ca_2Nb_3O_{10}^{-}$ nanosheets can be restacked when dialyzed with KCl; Rietveld refinement of X-ray powder diffraction patterns coupled with microscopic imaging suggested the re-establishment the parent compound, KCa_2Nb_3O_{10}, with small domains of three-dimensional ordering.¹²³

Nanoscrolls and nanotubes. Colloidal oxides nanosheets can also restack by rolling up into scrolls and tubules. Complete proton exchange of $K_4Nb_6O_{17}$, followed by exfoliation with TBA^+OH^- and re-acidification produces nanoscrolls because this compound (and its Ta relative) contains asymmetric nanosheets that are stacked as dimer pairs in the parent solid.¹²⁴ Hexaniobate nanoscrolls were converted to Nb_2O_5 nanotubes by thermal



Fig. 4 Flocculation, or restacking, of a colloidal nanosheet suspension can be achieved through the addition of a counterion to yield a randomly restacked lamellar material. Reproduced with permission from ref. 121. Copyright 2010 Wiley-VCH.

dehydration at 400–450 °C.¹²⁵ Ma, *et al.* explored the scrolling behavior of other layered oxide compositions that contain symmetric nanosheets, including $Ti_{0.91}O_2$, MnO_2 , and niobate layer perovskites. Nanoscrolls of all these compounds were prepared by restacking exfoliated the nanosheets in NaOH followed by de-intercalation of Na⁺ ions in water. The exchange of Na⁺ ions by H⁺ and water replaced the ionic interactions with covalent O–H bonding, reducing electrostatic repulsion so that scrolling occurred instead of sheet restacking.¹²⁶

Recently, nanoscrolls have been combined with nanoparticles to fabricate multicomponent assemblies with novel optical, magnetic, and catalytic properties. Wiley and coworkers have demonstrated that metal and metal oxide nanoparticles such as Co,¹²⁷ Au,¹²⁸ and ferrites¹²⁹ can be encapsulated within nanoscrolls to fabricate nanopeapod structures that show enhanced coupling of magnetic dipoles and a red-shift in the surface plasmon resonance. The nanopeapods were made by solvothermal treatment of pre-formed ferrite or Au nanoparticles with H₄Nb₆O₁₇ and TBA⁺OH⁻ in a sealed autoclave heated to 220 °C. Nanoparticles of diameters between 9 and 14 nm could be encased within the nanoscrolls in high yields and were found to segregate by size. The authors speculated that preformed nanoparticles selectively oriented along a step-edge of the H₄Nb₆O₁₇ surface before the sheet curled up. Alternatively, nanopeapod formation could be a result of capture of nanoparticles into the curved region of the sheets as they begin to form scrolls.¹²⁸ Nanopeapods containing both Au and ferrite nanoparticles could also be prepared by filling the voids with Au nanoparticles synthesized by reduction with oleylamine (Fig. 5). Nanoparticle-decorated nanosheets are another kind of multicomponent assembly that have been fabricated by techniques such as solvothermal treatment at 150 °C,¹³⁰ exfoliationrestacking,131,132 and electrodeposition.133 The resulting assembly incorporating Rh(OH)₃ nanoparticles also displayed high photocatalytic activity for the hydrogen evolution reaction.¹³¹ Effective strategies for fabricating multicomponent assemblies



Fig. 5 In situ growth of Au NP in hexaniobate nanoscrolls containing partially-filled Fe_3O_4 NPs. Adapted with permission from ref. 129. Copyright 2014 Wiley-VCH.

by combining nanoparticles with nanoscrolls thus expand the choice of available compositions and can enable one to tune their electronic, optical, magnetic, and catalytic properties.

Assembly of nanosheets. A key advantage offered by the exfoliation of oxide nanosheets is their re-organization into hierarchical structures that are not accessible by direct thermal synthesis. For example, nanosheets of different compositions can be assembled in a specific sequence to obtain superlattices, or assembled to a precise thickness for use in coatings, electronics, and other applications.

Layer-by-layer assembly. Oxide nanosheets, which bear either negative or positive charge, can be assembled layer-by-layer (LbL) on both planar and high surface area substrates by alternately adsorbing them and oppositely charged polyelectrolytes. The assembly process is similar to the polymer LbL method developed by Decher and coworkers,¹³⁴ but the use of colloidal nanosheets prevents the interpenetration of sequentially grown layers that invariably occurs with linear polyelectrolytes.135 This method was originally developed with colloidal and layered silicates136,137 and then extended to nanosheet films of exfoliated H₄Nb₆O₁₇ and CsTi₂NbO₇ by adsorbing positively charged electrolytes such as polyallylamine hydrochloride (PAH). This technique, referred to as 'molecular beaker epitaxy', resulted in well-controlled growth of nanosheet multilayers that alternate with polycations as confirmed by ellipsometry.¹¹⁰ The LbL assembly method was later extended to assemble other layered oxide nanosheets, such as Ti_{0.87}O₂^{138,139} and MnO₂,¹⁴⁰ onto a variety of substrates. The adsorbed polycations could be decomposed by using UV light, decreasing the inter-nanosheet distance by forming positivelycharged NH4⁺ cations.¹³⁹ More recently, LbL assembly has been used as a fabrication tool for combining different nanosheets to design photoelectrodes for enhanced light absorption¹⁴¹ and channel materials for field-effect transistors.142 For example, heteroassemblies of (PDDA/GO/PDDA/Ti_{0.87}O₂^{0.52-})_n superlattice films have been fabricated on quartz substrates by adsorbing polydiallyldimethylammonium chloride (PDDA) as a cationic layer between the layers of anionic nanosheets (Fig. 6). Photocatalytic reduction of graphene oxide to reduced graphene oxide (rGO) and decomposition of PDDA formed $(rGO/Ti_{0.87}O_2^{0.52-})_n$ superlattice films that lowered the nanosheet resistance by six orders of magnitude.142

The rational design of multilayer LbL assemblies involves the tuning of electrostatic interactions between the anionic nanosheets and polyelectrolytes. In contrast to the restackinginduced flocculation process discussed above, LbL assembly of nanosheets maintains nanosheets in the unilamellar state by inverting the surface charge with each adsorption step. High molecular weight coiled polymers, such as PDDA, are ideally suited as counterions for anionic nanosheets as they can maximize the nanosheet distance and prevent the restacking process. Similarly, external pH and solvent ionic strength can affect the assembly process as it can control the number of ionic groups present on the polycation.¹⁴³ Cai, *et al.* recently characterized surface charge modification of anionic nanosheets in bulk by mixing



Fig. 6 Fabrication of (PDDA/GO/PDDA/Ti_{0.87}O₂)_n superlattice films by layer-by-layer assembly. Adapted with permission from ref. 142. Copyright 2014 Royal Society of Chemistry.

high molecular weight polyelectrolytes used in layer-by-layer assembly with nanosheets added dropwise in water. They found that the resulting sheets had a positive zeta potential, thus indicating a positive surface charge.¹⁴⁴ Similarly, charge inversion of a layered synthetic fluoromica has been achieved by re-stacking with a positively charged polymer of low charge density that can coil up in the interlayer galleries. The resulting assembly could be used as an anion-exchanger to intercalate negatively charged dye molecules and nanoparticles.^{145,146} The charge inversion mechanism enables LbL assembly and can also expand the range of anion-exchangers available for fabricating multilayer assemblies.

Langmuir-Blodgett deposition. Langmuir-Blodgett (LB) deposition, originally developed for layer-by-layer transfer of surfactant monolayers to solid surfaces,¹⁴⁷ is another powerful method for fabricate multilamellar nanosheet films. This technique utilizes the surface tension at the solvent-air interface to create well-packed monolayer films by compression of barriers. This technique has an advantage over layer-by-layer adsorption of colloids from suspensions in that the deposited sheets are wellpacked with >95% coverage and also show minimal overlaps. Muramatsu, et al. first used LB deposition to transfer layered metal oxide nanosheets onto different substrates without the use of amphiphilic additives. Tetrabutylammonium cations used as the exfoliating agent adsorbed onto the nanosheet surface and possibly acted as amphiphiles to enable subsequent depositions.¹⁴⁸ This method was later extended to perform LB deposition of MnO2 nanosheets exfoliated using tetramethylammonium hydroxide (TBA⁺OH⁻).¹⁴⁹ LB deposition of titanate nanosheets (up to 10 layers) was performed at a surface pressure of 10 mN m^{-1} by using large nanosheets (10-30 µm) that yielded well-packed monolayers and multilayers. Cross-sectional TEM images of the deposited films on SrRuO3 revealed the homogeneous thickness of the individual sheets thus indicating good coverage and minimal overlap between the sheets.¹⁵⁰ More recently, Yuan, et al. found that densely packed titanate nanosheets could be obtained by using both tetrapropylammonium and tetrabutylammonium hydroxide as exfoliating agents and that the packing was

independent of nanosheet concentration.¹⁵¹ Shorter exfoliation times (~1 day) and higher TBA⁺/H⁺ ratios resulted in a higher concentration of nanosheets at the liquid–air interface, possibly because the adsorbed TBA⁺ ions conferred hydrophobicity to the nanosheets.¹⁵²

Over the past few years, Langmuir-Blodgett deposition has been explored as a synthetic tool to obtain oriented crystal growth of perovskite oxides on different substrates. Thin film growth technologies that require vacuum, and solution-based deposition techniques that deposit ABO₃ perovskite thin films, require high temperature annealing and limit the deposition to crystalline inorganic substrates. LB deposition, on the other hand, uses the soft chemistry approach to fabricate ultrathin seed layers of nanosheets derived from layer perovskites and other oxides at room temperature, resulting in epitaxial growth of oxides. The choice of metal oxides deposited onto the seed layers depends on the degree of epitaxy in their in-plane lattice constants. For instance, Shibata, et al. first reported the oriented growth of SrTiO₃ and TiO₂ films on HCa₂Nb₃O₁₀ nanosheets and ZnO films onto MnO2 nanosheets by sol-gel synthesis. X-ray diffraction patterns revealed intense (h00) reflections thus indicating crystal orientation along the [100] axis, which was absent when the films were directly deposited without the seed layer.¹⁵³ LB deposition has also been used to grow perovskite superlattices of $(HLaNb_2O_7/HCa_2Nb_3O_{10})_n$ by using two different kinds of nanosheets as building blocks (Fig. 7).¹⁵⁴ More recently, the in-plane and out-of-plane crystal orientation was tuned to obtain [100], [110], and [111] oriented growth by selectively varying the choice of seed layer and the deposited oxide layer¹⁵⁵⁻¹⁵⁷ as well as by van der Waals heteroepitaxy¹⁵⁸ to optimize the lattice mismatch. Langmuir-Blodgett deposition has thus expanded the variety of films that can be produced by epitaxial growth using nanosheet seed layers and has resulted in a variety of interesting properties that are described in detail below.

2. Characterization of layered oxides

X-ray scattering. X-ray diffraction (XRD) refers to the scattering of monochromatic X-rays by successive planes of atoms within



Fig. 7 Fabrication of $(LaNb_2O_7/Ca_2Nb_3O_{10})_n$ superlattice films by Langmuir–Blodgett deposition. Adapted with permission from ref. 154. Copyright 2010 American Chemical Society.

a crystal and is a key analytical tool for determining the crystal structure of a bulk material or thin film. XRD has been used to study the course of intercalation, exfoliation and restacking processes discussed above. Sasaki, et al. first reported a detailed in situ XRD study of exfoliation and re-assembly processes for the layered titanate $H_x Ti_{2-x/4} \Box_{x/4} O_4 \cdot H_2 O$ (\Box : vacancy). They found that exfoliation of layered titanates by TBA⁺OH⁻ resulted in the loss of the original Bragg diffraction peaks, and that several sharp reflections appeared in the low angle region, indicative of a spacing >10 nm. They were able to track changes in layer spacing by exposing the powder to varying degrees of relative humidity, thus revealing a stepwise hydration process.¹¹¹ Restacking of nanosheets by the addition of acid or an alkali metal ions results in the appearance of (hk0) and (00l)reflections in the XRD patterns. The absence of (hkl) reflections was attributed to the loss of three-dimensional structure and orientational disorder when the nanosheets were restacked turbostratically.159

Small angle X-ray scattering (SAXS) is emerging as a powerful tool for tracking long-range order resulting from swelling of layered oxides by introducing different intercalants. SAXS is a reciprocal space scattering technique typically used to study materials with large interplanar distances (i.e., nanometer length scale) by scattering X-rays at low angles. SAXS uses a 2D detector that collects the scattered X-rays from the sample, which can be averaged to give a 1D scattering curve plotted against the scattering vector $q = 4\pi \sin(\theta)/\lambda$.¹⁶⁰ Recently, Geng, et al. used SAXS to follow osmotic swelling of a layered titanate H_{0.8}[Ti_{1.2}Fe_{0.8}]O₄·H₂O^{112,115,117} upon intercalation with bases such as TBA⁺OH⁻ and tetra-(*n*-butylphosphonium) hydroxide (TBP⁺OH⁻) at different base/H⁺ ratios. Interlayer spacings of up to 90 nm were measured by SAXS and correlated with the amount of base intercalated (Fig. 8). The absence of SAXS peaks signaled the complete exfoliation of the layered oxides into isolated nanosheets.151,152

In recent years, synchrotron powder X-ray and neutron diffraction have also emerged as key techniques for probing subtle symmetry differences in bulk layered oxides. Synchrotron X-ray sources have an advantage over laboratory scale X-ray diffractometers as they offer higher beam brightness, a high degree of collimation, and variable monochromatic X-ray wavelengths. These methods have been used to study subtle structural changes in layered materials, including the cooperative tilting and rotation of oxygen octahedra in layer perovskites that break inversion symmetry, leading to piezoelectric and ferroelectric properties. Akamatsu, *et al.* re-investigated the structures of the series n = 1 RP NaRTiO₄ (R = rare-earth element) by synchrotron X-ray diffraction and found low-temperature, acentric phases that are piezoelectric. Earlier studies had reported these compounds to be centrosymmetric.¹⁶¹



Fig. 8 (a) SAXS profiles of TBPOH-swollen samples plotted as $l \times q^2$ with a scattering vector, q. (b) Interlayer spacings of swollen samples as a function of the reciprocal of the square root of base concentration. (c) The amount of intercalated base with respect to starting concentration. Reproduced with permission from ref. 112. Copyright 2014 Royal Society of Chemistry.

Similarly, Pitcher, *et al.* used powder neutron diffraction to characterize the cooperative tilting of the oxygen octahedra along three different crystallographic axes in the n = 2 Ruddlesden–Popper layered perovskite $(Ca_ySr_{1-y})_{1.15}Tb_{1.85}Fe_2O_7$ as neutrons have higher sensitivity than X-rays to oxygen atomic positions. This compound was found to exhibit simultaneous electrical polarization and magnetization within the same material.¹⁶²

Transmission electron microscopy. Transmission electron microscopy (TEM) is a powerful tool for directly imaging individual nanosheets as well as for gaining insights into the nanosheet structure and dimensions at atomic resolution. Selected area electron diffraction (SAED) patterns can be used to distinguish between single crystal and polycrystalline samples. The SAED patterns of individual nanosheets show a spot pattern indicating that they are single crystals,¹⁶³ whereas restacked layered oxides show concentric rings indicative of polycrystalline structure.¹²² Additionally, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) techniques have been utilized to visualize the quality of films obtained by layer-by-layer assembly. This technique collects electrons scattered at high angles and the signal intensity is directly proportional to Z^2 , where Z represents atomic number. Ziegler, et al. characterized the superlattices obtained from alternating assembly of HCa2Nb3O10 nanosheets and LDHs by HAADF-STEM at atomic resolution and were able to map out the elemental distribution. This study confirmed that the two kinds of nanosheets alternated in the film, with the bright atoms representing perovskite blocks that contained strongly scattering niobium atoms and the darker regions representing lighter element LDH nanosheets. The authors also noted that the morphology of the nanosheets could be selectively modified by the choice of solvent in which they were dispersed.¹⁶⁴

Recently, HAADF-STEM has been used to gain atomiclevel insights into the doping of layered oxide nanosheets for photocatalytic applications. Nanosheets derived from layered oxides are particularly amenable to visualization of atomic scale features by electron microscopy as they are crystalline and uniform in thickness. Ida, et al. imaged Tb³⁺-doped Ca₂Ta₃O₁₀ nanosheets and could distinguish the dopant atoms by quantifying the signal intensity. The photoluminescent properties of the doped nanosheets enhanced their photocatalytic activity.¹⁶⁵ In another study, the size of the smallest co-catalyst clusters that could be loaded onto layered oxide nanosheets for photocatalysis was elucidated by doping titanate nanosheets with Rh³⁺. HAADF-STEM images of Rh³⁺-doped single-crystal titania nanosheets revealed isolated single Rh atoms (Fig. 9a). Rh atoms were found to be three times brighter than Ti atoms as shown in a magnified STEM image (Fig. 9b). Single-atom Rh atom dopants enhanced the rate of H₂ evolution by simultaneously acting as reaction and recombination centers.¹⁶⁶ Similarly, high resolution TEM and HAADF-STEM images of Bi2MoO6 combined with EDX mapping revealed both the crystal orientation as well as the atomic positions of Bi, Mo, and O atoms. These techniques provided structural information about the exposed facets, where structural disorder and defects dominate the electrochemical properties.167



Fig. 9 (a) HAADF-STEM (200 kV) image of Rh (x = 0.026)-doped Ti_{1.86-x}Rh_xO₄ nanosheets. (b) Magnified HAADF-STEM image (80 kV) of Rh-doped nanosheets. Reproduced with permission from ref. 166. Copyright 2015 American Chemical Society.

Atomic force microscopy. Atomic force microscopy (AFM) is a complementary imaging technique to TEM as it can visualize the packing density of nanosheets as well as determine the nanosheet thickness. AFM reports on the local force between a cantilever tip and the substrate and can thus map out the topography of the surface at high resolution. AFM is particularly useful for imaging and measuring the monolayer sheet thicknesses as it can measure step heights with sub-nanometer precision. The typical sample preparation technique for AFM involves coating a substrate such as quartz or a Si wafer with a positively charged polymer, such as polyethyleneimine, followed by adsorption of the nanosheet. Ebina, et al. used AFM to precisely determine the thicknesses of higher order $Ca_2Na_{n-3}Nb_nO_{3n+1}$ nanosheets for n = 4-6. They found thicknesses of 2.7 nm (*n* = 4), 3.1 nm (*n* = 5), and 3.6 nm (*n* = 6) for the three kinds of nanosheets, respectively (Fig. 10).168 In addition, AFM can be used to image the lateral packing of nanosheets obtained by varying deposition parameters in the LbL or LB deposition processes. Li, et al. used AFM to verify that LB deposition of layered titanate nanosheets showed >95% coverage on a variety of substrates when deposited at a surface tension of 10 mN m⁻¹.¹⁵⁰ Recently, conducting-tip AFM has been utilized to probe the dielectric and insulating properties of layered oxide nanosheets as a function of temperature. This technique can map out both topography and conducting properties of layered oxides as will be discussed in more detail below.¹⁶⁹

UV-visible absorption and emission spectroscopy. UV-visible spectroscopy is a simple but powerful tool for the characterization of suspended nanosheets and thin films derived from them. It has been used to follow exfoliation of layered titanates, where the absorbance of the exfoliated nanosheets is slightly blue-shifted relative to the parent layered oxide.^{116,170} The shift in absorbance is a result of quantum effects at the nanoscale. UV-visible spectroscopy has also been employed to characterize LbL assembled and LB-deposited nanosheets on different substrates. For instance, Li, *et al.* were able to distinguish $LaNb_2O_7^-$ and $Ca_2Nb_3O_{10}^-$ nanosheets by noting their absorbances at wavelengths of 206 nm and 232 nm, respectively.¹⁵⁴ The subsequent deposition of multilayer nanosheets can be followed by noting a linear increase in the absorbance value. The strong distance dependence of fluorescent resonant energy



Fig. 10 AFM images and height profiles for $Ca_2Na_{n-3}Nb_nO_{3n+1}$ nanosheets: (a) n = 4, (b) n = 5, (c) n = 6. Reproduced with permission from ref. 168. Copyright 2012 American Chemical Society.

transfer (FRET) between luminescent donor and accept molecules was used to determine the degree of interpenetration of polycation layers in LbL assemblies of nanosheets,¹³⁵ and was also used as a means of extending the wavelength response in electron donor-acceptor LbL films for artificial photosynthesis.¹⁷¹

Electronic structure. The electronic structure of nanosheets is an important input into the rational design of layered oxide materials and assemblies for applications that include photocatalysis, photovoltaics, energy storage, and ion conduction. The flat-band potential (the onset potential at which charge depletion occurs in a semiconductor) and the band gap energy have been measured by several techniques for semiconducting nanosheets derived from the delamination of layered oxides.^{63,172–175} Sakai, *et al.* determined the flatband potentials of titania nanosheets deposited onto indium-tin oxide (ITO) substrates by cyclic voltammetry. The redox processes of Li^+ insertion/extraction in electrolyte containing $LiCO_4$ /propylene carbonate were followed by UV-vis spectroscopy. An increased

absorbance at λ > 323 nm and loss of intensity at λ < 323 nm upon applying a bias negative of -1.3 V vs. Ag/Ag⁺ indicated electron accumulation in the conduction band. The measured flatband potential value was correlated with photoelectrochemical measurements, which showed an onset photocurrent potential of -1.27 V vs. Ag/Ag^{+,172} More recently, Maeda, et al. investigated the effect of doping on the band-edge potentials of layered oxides and found that substitution of larger A-site cation resulted in less octahedral tilting and effectively lowered the bandgap energy, an effect attributed to greater delocalization of electron density.63 The flatband potentials of layered metal oxide nanosheets in aqueous media have also been measured by electrochemical impedance spectroscopy (EIS). The EIS data were analyzed by using the Mott-Schottky equation, which relates the inverse square of capacitance $(1/C^2)$ to the applied potential. The flatband potentials for all nanosheets showed the expected pH dependence of -59 mV per pH and correlated directly with their bandgap energies (Fig. 11).¹⁷⁴



Fig. 11 (a) Flatband potentials of layered oxide nanosheets assembled onto fluorine-doped tin oxide glass substrate. (b) DFT calculated band gaps, valence band minima, and conduction band maxima of layered oxide nanosheets. Reproduced with permission from ref. 174. Copyright 2016 American Chemical Society.

3. Rational design and functionality

Soft chemical synthesis and assembly of layered oxides can be utilized in a strategic manner to design compositions and structures that exhibit interesting functionality. These properties impact applications in catalysis and photocatalysis, ferroics, chemical sensing, energy storage, and electronics, as will be described below. In this section, the role of soft chemistry for tuning emergent properties in layered oxides will be explored with a focus on two recent developments, namely the immobilization of nanoparticles onto oxide nanosheets as models for the metal-support interaction in heterogeneous catalysis, and lifting of inversion symmetry in layer perovskites to realize piezoelectric and ferroelectric properties. The design rules illustrated in this section converge on the theme of soft chemical approaches to materials design. This approach enables a comprehensive understanding of structure, bonding, and reactivity that facilitates the rational design of new materials.

a. Tailoring interfacial chemistry for catalysis

Sintering of nanoparticle catalysts. The metal-metal oxide interface is of great interest in both basic science and in applications that include microelectronics, catalysis, surface chemistry, and fuel cells. The field of heterogeneous catalysis relies on such interfaces for metal-support interactions that modulate the stability, activity, and selectivity of catalytic reactions. The coarsening of nanoparticles at working temperatures limits the lifetime of heterogeneous catalysts used in steam reforming, automotive exhaust treatment, catalytic combustion, selective oxidation reactions, and other applications.¹⁷⁶ There are two principal mechanisms of nanoparticle coarsening: particle migration and coalescence (PMC) and Ostwald ripening. PMC results from the diffusion of individual particles on supports, which results in their aggregation and coalescence, whereas Ostwald ripening results from the movement of individual atoms from smaller to larger particles. In both cases, the process minimizes the surface energy.¹⁷⁶ The key to designing a durable catalyst is to inhibit the coalescence of nanoparticles under operating conditions; this in turn requires fundamental insights into the interactions that stabilize catalytic nanoparticles on their supports. For example, Liu, et al. were recently able to suppress Au nanoparticle sintering by using a mesoporous silica support that had an abundance of micropores. By using in situ heating TEM, they were able to track particle movement between the mesoporous channels and found that it was driven by gravitational forces.¹⁷⁷ Another method of stabilizing catalyst nanoparticles is to create yolk-shell nanostructures in which the shell allows the diffusion of reactant and product molecules but inhibits the coalescence of the catalyst particles.¹⁷⁸

Strong metal-support interaction (SMSI). Chemical specific interactions between metal nanoparticle catalysts and oxide supports have been shown to prevent particle coarsening, and also to modulate the catalytic activity and selectivity of the supported particles. Plausible explanations for the stabilization of late transition metal such as Pt, Pd Rh, and Co on high surface area oxide support surfaces have been evolving in the surface science literature over the past four decades.



Fig. 12 Schematic illustration of (left) outward migration of Ti^{3+} ions driven by work function differences and (right) encapsulation of metal atoms by TiO_x to minimize surface energy. Reproduced with permission from ref. 182. Copyright 2005 American Chemical Society.

The 'strong metal-support interaction' (SMSI) was first proposed by Tauster and Fung^{179,180} to explain the suppression of H₂ and CO chemisorption on transition metal nanoparticles supported on reducible oxides, such as TiO2, under reducing conditions at high temperatures. They postulated that chemical interactions, possibly metal-metal bonding or formation of intermetallic compounds, between titanium cations and the transition metal suppressed chemisorption.179 Subsequent molecular orbital calculations by the same group suggested that electron transfer from the oxide support to supported metal atom clusters stabilized the latter and conferred negative charge on it, thus forming a polar support-metal bond.¹⁸⁰ Nuzzo and Dubois subsequently observed the encapsulation of metal nanoparticles by a thin oxide layer upon oxidation.¹⁸¹ These earlier models and observations led Fu, et al. to propose a physical model based on the difference in work functions (ϕ) between the TiO₂ oxide support and the more electronegative supported metal ($\phi_{\text{metal}} > \text{TiO}_2$). In that model, the electric field that develops between the oxide and the supported metal drives the migration of titanium cations and results in encapsulation of the metal to minimize its surface energy (Fig. 12).¹⁸² The most widely accepted observations of the SMSI involve the encapsulation of the metal by the supporting oxide layer, which is thought to modulate the metal's catalytic activity and selectivity by blocking sites for adsorption of reactant gas molecules.

'Anomalous' cases. In recent years, a number of theories have emerged to describe the fundamental chemistry of SMSI that differed from the classical models described above. Some of these theories suggest not only insight into the SMSI mechanism but also provide a prescription for achieving enhanced catalytic activity. Rodriguez, *et al.* identified a new type of SMSI, referred to as the electronic metal–support interaction (EMSI), in Pt/CeO₂ that produced large electronic perturbations of Pt₈ clusters by partial charge transfer to the ceria support. The electronic perturbations tuned the chemical properties of the Pt clusters and enhanced their ability to dissociate water and adsorb the water dissociation products, which are steps in the production of H₂ *via* the water–gas shift reaction.¹⁸³ In a related study, Wang, *et al.* found suppressed CO oxidation in the Au/TiO₂ system when the supported catalyst was pretreated under strongly

reducing atmospheres and the activity recovered after long periods of time (~1200 min). The loss of catalytic activity was attributed to electronic modification of Au nanoparticles by the formation of bulk oxygen vacancies in TiO₂ that initially suppressed CO adsorption. This phenomenon was reversed over time due to the presence of O_2 in the atmosphere, which slowly refilled the oxygen vacancies.¹⁸⁴ Similarly, recent SMSI investigations on Au/ZnO¹⁸⁵ and Au/hydroxyapatite¹⁸⁶ showed SMSI characteristics under oxidizing conditions, suggesting that electron transfer occurred from the metal to support, in contrast to the SMSI model shown in Fig. 12. More recently, Matsubu, et al. discovered a novel adsorbate-induced SMSI (A-SMSI) on Rh/(TiO₂ or Nb₂O₅) and found an overlayer of the reactant (CHO–) $_x$ species that is permeable to reactants. The permeability of the overlayer enabled selective tuning of the CO₂ reduction products, to form CO rather than C-H bonded molecules, by regulating the catalytic activity of Rh.¹⁸⁷

Further insights into the chemistry of metal-support interface have recently been enabled by studying the chemistry of well-dispersed nanoparticles of late transition metal hydroxide nanoparticles onto layered oxide nanosheets. While studying charge inversion and intercalation of anionic nanosheets by metal and metal oxide nanoparticles, Hata, et al. observed the unusual stability of Rh(OH)₃ onto layered Nb oxide nanosheets.¹⁸⁸ The anomalous stability of the Rh(OH)₃ nanoparticles was attributed to covalent bonding between the metal and the support. This model was supported by calorimetric measurements that showed that the binding of Rh(OH)₃ nanoparticles to the nanosheet surface was an exothermic process.¹⁸⁹ In contrast to field-driven migration model for the SMSI, where the supporting oxide is reduced (Fig. 12), X-ray absorption measurements showed that Rh(OH)₃ nanoparticles were reduced to Rh at high temperatures, whereas the oxidation state of Nb in the nanosheet support remained unchanged. Nanoparticles of other late transition metal oxides were also stabilized by binding to HCa2Nb3O10 nanosheets, and their stability against coalescence at high temperature was correlated with the exothermicity of the nanoparticle-support interaction.¹⁹⁰ The exothermicity of the nanoparticle-support interaction was linearly correlated with metal oxide bond strengths, but the slope of the correlation was different for silicate and niobate nanosheets, with the latter showing much stronger bonding interactions and, experimentally, much greater stabilization of the supported nanoparticles (Fig. 13a and b). Electronic structure calculations revealed a partial charge transfer from late transition metal to the metal oxide support indicated metal-metal bond formation by the overlap of d-orbitals (Fig. 13b). The strength of binding interaction could thus be tuned by optimizing the d-band energy level. Charge transfer from the more electronegative transition metal (Pt, Rh, Ir, etc.) to the less electronegative metal (Nb) was found to be consistent with Brewer's investigations of d-orbital mixing that stabilized early-late transition metal intermetallic alloys such as ZrPt₃,¹⁹¹ exactly as postulated in the initial 1978 report of the SMSI effect by Tauster, et al.179

Implications for catalysis. In recent years, a number of studies have emerged that investigated the role of SMSI in supported

catalytic systems. These studies found that the SMSI can influence catalysis by stabilizing nanoparticle catalysts against sintering as well as by controlling oxidation states that can confer selectivity to reaction products. Tian, et al. utilized the advantages conferred by SMSI to design a novel, low-cost electrocatalyst using a titanium nickel binary nitride as the support. This system was tested for the oxygen reduction reaction (ORR) and showed improved stability and mass activity even after 10 000 cycles. The authors attributed the high stability/ durability of the electrocatalyst to donation of d-electrons from Pt to Ti atoms.¹⁹² In another study, Freakley, et al. reported enhanced selectivity for the direct synthesis of H₂O₂ from H₂ and O₂ by using Pd-Sn alloy nanoparticle catalysts. The main challenge in the selective synthesis of H2O2 has been degradation of H₂O₂ due to the presence of smaller Pd-rich nanoparticles (Pd-rich NPs). However, degradation of H2O2 could be prevented by an oxidation-reduction-oxidation (O-R-O) process that encapsulated smaller Pd-rich NPs by a secondary SnOx thin film (Fig. 14). The calcination step resulted in the formation of an amorphous SnOx films on TiO2 as well as oxidized Pd-Sn alloy nanostructures, and the reduction step caused encapsulation of smaller Pd-rich NPs by the SnO_x film. The final re-oxidation step further restored Pd²⁺ as the dominant surface species that suppressed hydrogenation of H₂O₂.¹⁹³ Similarly, Ma, et al. were able to tune the hydrogenation products of CO₂ in the Ir/CeO₂ catalyst system by varying the loading concentration of Ir. The selective formation of CO vs. methane was attributed to control of the Ir oxidation state by the ceria substrate at different loadings.¹⁹⁴ Thus, new insights into SMSI mechanisms gained from model studies with metal oxide nanosheets can be exploited to establish design rules, providing a prescription for stabilizing catalytic nanoparticles and for controlling the selectivity of the reaction products.

b. Tuning the composition of layered perovskite oxides to lift inversion symmetry. The soft chemistry approach has opened up avenues for studying layered perovskites that have exotic symmetry-driven properties such as hybrid improper ferroelectricity.^{161,195-197} The best known ferroelectric perovskites that have been commercialized for piezoelectric applications are lead-based compounds like PZT, PMNPT and PbTiO₃, and the mechanism by which these compounds become ferroelectric is second-order Jahn-Teller effect (SOJT).198,199 The high piezoelectric coefficient coupled with efficient synthesis approaches have made these compounds indispensible for applications in actuators and electronic devices. Nevertheless, the presence of Pb poses two problems. Firstly, lead is toxic and the use of lead based products is becoming more tightly controlled worldwide. Secondly, the volatility of Pb results in composition changes at processing temperatures above about 400 °C. Hence, synthetic methods and applications are limited for lead-based compounds. Also, until recently, ferroelectricity and piezoelectricity have relied almost exclusively on d⁰ transition metal compounds, which have low electronic conductivity but are typically diamagnetic.^{199,200} The versatility of layered perovskite chemistry, including soft chemical transformations, has created a paradigm shift as new mechanisms can be explored to lift inversion symmetry and



Fig. 13 (a) Electron microscopy images showing nanoparticle diameters of late transition metals on $HCa_2Nb_3O_{10}$ nanosheets. (b) Thermochemical measurements of heats of interaction between metal oxide/hydroxide nanoparticles and supports for layered Nb oxide (blue diamonds) and high surface area silica (red). The *x*-axis represents M–O bond strength. (c) Cartoon illustrating charge transfer from transition metal clusters to Nb. Reproduced from ref. 190. Copyright 2015 American Chemical Society.

look beyond SOJT transitions for ferroelectric and multiferroic applications. Soft chemical approaches to structure tuning of layered oxide perovskites have recently been explored by Akamstsu, *et al.*¹⁶¹ Sen Gupta, *et al.*^{195,196} and Strayer, *et al.*²⁰¹ The convergence of theory and experiments have shown that soft chemical reactions can be used to drive cooperative oxygen octahedral rotations (OORs),²⁰² a mechanism that can break inversion symmetry in layered perovskites to realize piezoelectric and ferroelectric properties.

Before we further describe the way in which OORs can break inversion symmetry, it is important to note that OORs of various types are already abundantly present in ABO₃ perovskites, but that they do not remove the inversion centers from these compounds.^{203,204} Benedek, *et al.*²⁰⁵ have noted that 70% of all the known natural and synthetic ABO₃ perovskites have OORs in their crystal structures in the centric *Pnma* space group. Moreover, ABO₃ compounds that are ferroelectric by virtue of the SOJT do not have OORs.²⁰⁵ As shown in Fig. 15a, the Glaser notation of OORs can explained by two simple examples. When two adjacent layers undergo OORs in opposite directions, it is called an out-of-phase rotation. If we represent the OOR rotation axes in the three orthogonal directions *x*, *y* and *z*, and the out-of-phase rotation occurs only in the *z*-direction, then this OOR is represented by $a^0a^0c^-$. Here the superscript of zero denotes no rotation, whereas the negative sign indicates the out-of-phase rotation along that axis. Similarly, $a^0a^0c^+$ denotes an OOR with in-phase rotation along the *z*-axis only. The pie-chart represents the distribution of OORs present in ABO₃ perovskites (Fig. 15b). The majority of these compounds have OORs represented by $a^-a^-c^+$, and remain in the centric space group *Pnma* (orthorhombic).^{203,204}

In order to elucidate how OORs do not lift inversion symmetry in ABO₃ perovskites, it is helpful to look at OORs in a single layer of BO₆ octahedra. In Fig. 15c, a two-dimensional representation of the BO₆ octahedra in a ABO₃ perovskite is shown. If we imagine that the BO₆ octahedron at the center of the plane rotates in a clockwise direction about the out-of-plane axis, then the nearest neighbor octahedra rotate in the counter clockwise direction. This leads to the retention of the inversion center at the B site of the BO₆ octahedra, which is highlighted by the symbol 'i'. Now, if this two-dimensional



Fig. 14 (A) Suppression of H_2O_2 degradation by small Pd-rich NPs through a strong metal support interaction (SMSI). (B and C) STEM-EELS mapping of a 5 wt% Pd/SnO₂ model catalyst at the (B) oxidized and (C) O-R-O stages, showing partial encapsulation of Pd (red) by SnO_x (green). Reproduced with permission from ref. 193. Copyright 2016 American Association for the Advancement of Science.

octahedral layer is expanded to infinity along both the *x* and *y* axes, then the inversion centers at all the B sites of the individual BO_6 octahedra are retained. This makes the entire ABO_3 structure centrosymmetric, as shown by the rotated octahedra in Fig. 15c.

By comparing ABO_3 perovskites to the layered perovskites in the Ruddlesden-Popper,² Dion-Jacobson⁸ and Aurivillius¹² structural families, we observe a key distinction, which is the discontinuity of the BO₆ octahedra along the stacking axis.



Fig. 15 Schematic drawings of (a) octahedral rotation in a ABO_3 perovskite block seen along the *z* (or c) axis. (b) Pie chart showing all the possible rotations found in naturally occurring and synthetic perovskites before 2001. (c) Schematic showing oxygen octahedral rotation (ORR) in BO_6 octahedra of an ABO_3 perovskite. Reproduced with permission from ref. 203 and 204. Copyright 1997 International Union of Crystallography.



Fig. 16 Schematic drawings of (a) the ABO₃ perovskite structure (also considered as $n = \infty$ layering), and Ruddlesden–Popper structures (b) n = 1 A₂BO₄, (c) n = 2 A₃B₂O₇ and (d) n = 1 AA'BO₄ with red and blue A and A' cations in alternating layers. The inversion centers are highlighted in the crystal structures by the letter 'i'. Adapted with permission from ref. 206. Copyright 2012 Elsevier.

In Fig. 16(a) and (b), an ABO₃ perovskite is compared with its single-layer Ruddlesden-Popper relative A2BO4. Both the structures have high symmetry with inversion centers 'i' at the B-atom sites that center the BO₆ octahedra.²⁰⁶ In ABO₃, inversion centers also exist at the A sites, but in A_2BO_4 these exist between the A sites. Interestingly, when these structures are compared with the two-layer A3B2O7 structure shown in Fig. 16(c), we see that the inversion center is absent at the B-site, although inversion centers are retained midway between the A sites, as in the single-layer compound. Furthermore, as seen in Fig. 16(d), when the cations on half the A-sites are replaced by different cations A' in an ordered fashion (as would occur, *e.g.*, in the compound NaRTiO₄, R = rare earth), the inversion centers are lost at the B-sites but they still exist at the midpoints between the A- and A'-cation sites. This maintains the overall centrosymmetry of this compound, and for AA'BO₄, the space group symmetry is P4/nmm.

Now, in order to completely remove all the inversion centers in an AA'BO₄ compound, OORs need to be introduced, as has been shown by Akamatsu, *et al.*¹⁶¹ Introduction of OORs can remove the inversion centers between the A-sites and also between the A'-sites (Fig. 17a). The appropriate OORs thus render the compounds non-centrosymmetric. DFT calculations performed by Akamastu, *et al.*¹⁶¹ and Sen Gupta, *et al.*¹⁹⁵ predicted that AA'BO₄ compounds such as NaRTiO₄ and LiRTiO₄ can undergo a phase transition from the centrosymmetric *P*4/*nmm* space group to noncentrosymmetric *P*42₁*m* (Fig. 17b). Their calculations predicted centrosymmetric structures with larger rare earth ions La and Nd. With smaller ions (Sm–Ho), the rare earth is underbonded by oxygen and this triggers a rotation of the octahedra such that the coordination environment around the oxygen is satisfied.¹⁶¹

Recently, soft chemistry has opened a new route for accessing compositions that can break inversion symmetry in layered oxides.



Fig. 17 (a) The AA'BO₄ structure with OOR. (b) Total Energy vs. Ionic Radius for LiRTiO₄ (R = La–Ho). Adapted with permission from ref. 161 and 195. Copyright 2014 American Chemical Society and 2015 Wiley-VCH.

Following the first report on NaRTiO₄,¹⁶¹ ion-exchange was used to synthesize LiRTiO₄¹⁹⁵ and HRTiO₄.¹⁹⁶ Second harmonic generation (SHG) experiments in combination with synchrotron powder X-ray diffraction (SXRD) have helped in understanding the phase transition behavior of these compounds. Both SHG and SXRD have confirmed noncentrosymmetry at room temperature for various members of the AA'TiO₄ family which are piezoelectric. This suggests the possibility that ferroelectric and multiferroic oxides, which have already been synthesized in the layered perovskite structural family with divalent A and A' cations,^{162,207} might be made by similar soft chemical methods.

4. Overview of applications

Artificial photosynthesis. Soft chemical reactions can be used to create oxide semiconductor-based nanostructures that compartmentalize the functions of light absorption, charge separation, and electron transfer catalysis, which are essential functions in artificial photosynthesis. Fig. 18 shows a general design of a dye-sensitized photocatalytic system based upon a nanosheet framework.



Fig. 18 General design of a dye-sensitized HER photocatalytic system based upon a nanosheet framework. Reproduced with permission from ref. 213. Copyright 2015 American Chemical Society.

Catalytically active metal nanoparticles can be incorporated within the interlayer gallery of layered perovskites through flocculation of nanosheets. The micro- and mesoporous semiconducting materials can incorporate these nanoparticles to catalyze hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Layered perovskites are attractive candidates for HER and OER because intercalation and exfoliation enable one to achieve tunable layer thickness, high surface area, anisotropy, and a high degree of crystallinity, which are all factors that influence the performance of photocatalytic systems.²⁰⁸ In addition, the crystallinity and uniform thickness of oxide nanosheets are conducive to atomic-scale analysis by electron microscopy. This feature has been used successfully in photolabeling experiments to image the separation of electron-hole pairs by observing the photocatalytic deposition of oxidation and reduction products on the nanosheets.²⁰⁹

Photocatalytic activity can be improved upon in semiconducting perovskite nanosheets by direct deposition of metal nanoparticles, synthesis of solid solutions of doped perovskites through solidstate synthesis, and by incorporation of catalytic metal nanoparticles through an exfoliation–flocculation reaction.

Well-dispersed catalytically active nanoparticles can also be incorporated into perovskite structure by direct deposition onto nanosheets. As noted above, there is an interfacial electronic interaction associated with the stability of later transition metal particles on layered niobate supports.^{189,190} Subnanometer Rh(OH)₃ particles were directly deposited onto HCa₂Nb₃O₁₀ nanosheets. Flocculation with K⁺ ions produced Rh(OH)₃/ KCa₂Nb₃O₁₀, which was calcinated to dehydrate Rh(OH)₃ to Rh₂O₃. The photocatalytic activity of these materials for HER was tested under UV light using methanol as a sacrificial electron donor. The Rh-O-Nb covalent interaction contributes to the uniform dispersion of the rhodium trihydroxide nanoparticles, which results in an increase in photocatalytic activity.¹⁸⁸ Similarly, the photocatalytic activity of K₄Nb₆O₁₇ nanoscrolls increases when they are functionalized with subnanometer Rh(OH)₃ particles by the exfoliation-flocculation procedure. K4Nb6O17 and KCa2Nb3O10 intercalated with Ni and Pt nanoparticles have also been shown to be active for the photolysis of water under UV irradiation.^{159,210,211}

Nanosheets of layered perovskites can themselves act as co-catalysts in HER or OER. Solid solutions with tunable band gaps and band edge energetics, for example $HCa_{2-x}Sr_xNb_3O_{10}$ and $HCa_2Nb_{3-y}Ta_yO_{10}$, have been obtained by solid-state synthesis of layered perovskites, and were studied as HER photocatalysts under UV irradiation with methanol as an electron donor, where $HCa_2Nb_2TaO_{10}$ exhibits a high quantum yield of 80% at 300 nm.⁶³ Water-splitting catalyzed by $KCa_2Nb_3O_{10}$ nanosheets has been reported to produce stoichiometric amounts of hydrogen and oxygen whereas $K_4Nb_6O_{17}$ does not, despite the fact that both materials have a band gap of 3.44 eV.^{173,212}

Catalytic metal nanoparticles can be synthetically incorporated within the interlayer galleries of layered oxide perovskites by exfoliation followed by flocculation. This route is an alternative to the more traditional impregnation methods and is more attractive because a larger concentration of particles can be loaded within the micro- and mesoporous networks as opposed to the near-edge and other surface sites available through impregnation. The incorporation of the trinuclear complex, ruthenium red ([$(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5$]Cl₆) within the interlayer galleries of HCa₂Nb₃O₁₀ nanosheets *via* exfoliation– flocculation was shown to be promote photocatalytic activity for the HER. Upon oxidation of the trinuclear Ru complex to RuO_x, the system stoichiometrically produces hydrogen and oxygen under UV radiation. In contrast, impregnation of the parent compound, KCa₂Nb₃O₁₀ with RuO_x did not result in water splitting activity.²¹²

Nanosheets of $HCa_{2-x}Sr_xNb_3O_{10}$ and $HCa_2Nb_{3-y}Ta_yO_{10}$ show HER photocatalytic activity under visible light following photodeposition of platinum nanoparticles and sensitization with Ru(II) polypyridyl complexes.²¹³ Nanoscrolls made by exfoliation of $H_4Nb_6O_{17}$, which were functionalized with $Ru(bpy)_2(4,4'-(PO_3H_2)_2bpy)^{2+}$ (bpy = 2,2-bipyridine) and Pt nanoparticles, showed quantum yields of 20–25% for the HER under visible light in the presence of EDTA. The high quantum yield was attributed to rapid electron transfer between the dye and the catalyst particles, mediated by the single crystal nanoscrolls.²¹⁴

Energy storage. Energy storage technologies have been pursued aggressively over the past few decades with the goal of providing portable and stationary power to meet the planet's growing needs. The broader utilization of rechargeable lithium-ion batteries for vehicles and grid storage are, however, limited by their storage capacity, current density, capacity fading, stability and cost. A key problem with lithium metal-based batteries are the reactions that occur upon charging to form insulating phases and metal dendrites, which can compromise the capacity, lifetime, and safety of the battery.²¹⁵ Two main approaches, namely alloying and intercalation chemistry, have been investigated to address these issues. Layered transition metal oxides have been extensively investigated as electrode materials as they are amenable to intercalation/de-intercalation of cations while preserving their parent structure with minimal volume expansion.²¹⁶ Their interlayer distances can also be tuned by optimizing the choice of cations between the nanosheets which can affect their resulting energy storage properties.

Intercalation compounds, especially layered titanates, have received significant interest as battery anode materials. Layered titanates have the advantages of being abundant, nontoxic, and possessing high energy densities and low insertion voltages.²¹⁷ The zig-zag layered oxide Na2Ti3O7 containing corner-sharing TiO_6 octahedra (Fig. 1) and its isostructural phases H₂Ti₃O₇ and Li2Ti3O7 obtained through topochemical ion-exchange have been investigated as anode materials for both Li-ion and Na-ion batteries.²¹⁸⁻²²¹ The three structures displayed significantly different storage capacities for Li⁺ insertion (Table 2). However, H₂Ti₃O₇ showed a higher capacity retention for the insertion of Na⁺ ions when compared with Na₂Ti₃O₇ due to retention of the structure by forming the solid solution H₂Na_xTi₃O₇ with up to 0.6 Na⁺ per formula unit.²²¹ Similarly, a comparison between the layered titanate K_{0.8}Ti_{1.73}Li_{0.27}O₄ and its ion-exchanged derivative Na_{0.8}Ti_{1.73}Li_{0.27}O₄ revealed that the specific capacity for both Na⁺ and Li⁺ ions was improved significantly. The improved capacity was attributed to the smaller ionic radius of sodium compared to potassium and a change in symmetry that allows reversible insertion of more alkali cations.²¹⁵ More recently, nanosheets of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ were hybridized with reduced graphene oxide (rGO) to combine the advantages of electrochemical activity with electrical conductivity to obtain higher capacity.222

Layered metal oxides confer the added advantage of tunability of their interlayer distances and nanosheet thicknesses by exfoliation/reassembly techniques that have been explored for energy storage applications. For instance, Suzuki, et al. found that re-assembled layered octatitanates showed enhanced energy density and cyclability for lithium intercalation resulting from greater surface area when compared to octatitanates that were prepared directly.²²³ Similarly, the interlayer cation sizes act as another tuning knob to alter the symmetry of the material and can control the energy densities of Li and Na ions. Lu, et al. investigated sodium and lithium storage capacities in a series of manganese oxide nanosheets containing alkali metal and divalent metal cations and found that the energy densities were proportional to ionic size for monovalent cations.²²⁴ However, high energy densities were not observed with divalent metal cations, presumably due to Coulombic repulsions with the

Anode composition	Capacity ^{<i>a</i>} (mA h g^{-1})		Capacity retention (%)/current density (mA g^{-1})		
	Li^+	Na ⁺	Li^+	Na ⁺	Ref.
Na ₂ Ti ₃ O ₇	50	200		_	218 and 221
H ₂ Ti ₃ O ₇	175	56	_	_	219 and 220
Li ₂ Ti ₃ O ₇	147	_	50/10	_	218
$K_{0.8}Ti_{1.73}Li_{0.27}O_4$	100	25	$25/0.2^{d}$	$60/0.2^{d}$	217
$Na_{0.8}Ti_{1.73}Li_{0.27}O_4$	200	100	$50/0.2^{d}$	$50/0.2^{d}$	217
$Na_{0.8}Ti_{1.73}Li_{0.27}O_4$ (with PAA binder) ^b	_	140	_	$60/0.2^{d}$	217
$H_2 Ti_8 O_{17}$	170	_	91/100	_	223
Li _r MnO ₂	118	75	50/200	32/200	224
Na _r MnO ₂	137	145	58/200	40/200	224
K _r MnO ₂	155	113	61/200	38/200	224
Mg_rMnO_2	97	65	48/200	21/200	224
Co _x MnO ₂	87	46	45/200	19/200	224
$Na_{2}Ti_{3}O_{7}NP-NS^{c}$	_	150	_	$95/500^{d}$	225

Table 2 Comparison of the electrochemical performance of different layered oxide compositions for lithiated and sodiated cells

^a Maximum reported reversible capacity. ^b PAA: polyacrylic acid. ^c NP–NS = mixture of nanoplatelets and nanosheets. ^d Current density units in mA cm⁻².

incoming cations.²²⁴ More recently, the electrochemical properties of the layered trititanate Na₂Ti₃O₇ were improved by controlled exfoliation that resulted in the formation of a mixture of monolayer nanosheets and trilayer nanoplatelets. The two different morphologies could be obtained by partial exchange of Na⁺ with H⁺ followed by ultrasonication and centrifugation at different speeds (2000 rpm for nanoplatelets *vs.* 5000 rpm for nanosheets). The mixture containing nanosheets and nanoplatelets expanded the electrochemical window for Na⁺ insertion and resulted in enhanced energy storage. The nanosheets displayed capacitor-like behavior whereas nanoplatelets showed diffusion-controlled behavior by providing sites for cation intercalation.²²⁵

Fuel cells. The conversion of chemical energy directly into electrical energy has emerged as another viable option for the production of energy from fuels. Fuel cells operate by an electrochemical reaction with oxidation of fuel occurring at the anode and reduction oxygen (typically from air) at the cathode. The free energy of the chemical reaction is efficiently converted to electrical energy because the cell avoids Carnot cycle losses. However, the performance of fuel cells is limited by several factors, most importantly by electrode overpotentials and electrolyte resistance.²²⁶ In recent years, efforts have been undertaken to incorporate metal oxide nanosheets into nanocomposites of Pt-reduced graphene oxide (Pt-rGO) in batteries and fuel cells to increase the surface area and enhance the electrical conductivity.^{227,228} The addition of titantia nanosheets to Pt-rGO composites resulted in weakening of the π - π interactions between rGO nanosheets and allowed access to the pore structure that resulted in enhanced electrocatalytic activity and lower onset potential.²²⁷ The performance of fuel cells can also be enhanced by using proton conducting electrolytes. The Dion-Jacobson phase HLa2TiTa2O10 prepared by esterification of tantalum citrate and titanium isopropoxide was found to be a mixed conductor under reducing conditions. Interestingly, the same phase prepared by direct solid state synthesis was less conductive, presumably because it lacked the high surface area conferred by the polymerized complex synthetic method. Although this material could not be utilized as a solid electrolyte in fuel cells because of its residual electronic conductivity, these experiments demonstrated that transport properties could be enhanced by the polymerized complex route.²²⁹

Optical properties. Photoluminescent nanomaterials have attracted interest in recent years for the development of optical devices and sensors. A key principle in the design of optical sensors is the controlled absorption and emission of light as well as the ability to distinguish between vapors of similar and dissimilar materials optically. Photoluminescence of a semiconductor typically involves excitation by light of energy above the band gap energy, followed by relaxation, often involving trap states. Another kind of relaxation process is upconversion luminescence, in which excitons combine to produce a higher energy excited state. The relaxation of this excited state can result in higher-energy photon emission.²³⁰ Upconversion luminescence has been observed using lanthanide ions as activators and oxides as host materials.²³⁰ Over the past decade,

layered oxides with lanthanide cations have been explored for their photoluminescent properties. The emitted light can be tuned by varying the choice of lanthanide cations anchored to the oxide nanosheets.^{231–235} Layered perovskite oxides are ideally suited as host materials for exhibiting high quality photoluminescence properties as the corner-sharing octahedra are electronically isolated but doping with rare-earth elements can modify the electronic structure of the surrounding octahedra. Thus, certain octahedra can act as luminescence centers by confining the electronic transitions to the perovskite lattice.²³⁶

In recent years, the photoluminescence emission properties of layered perovskite oxides have been modulated by optimizing the choice of rare-earth element present in the structure as well as by utilizing ion-exchange and exfoliation-restacking processes. For instance, Qin, et al. found rich luminescence behavior in a series of new triple-layered Dion-Jacobson layered oxides, $CaRNb_3O_{10}$ (R = rare-earth element), and also observed that the emitted light could be tuned to selectively produce blue (La, Yb, Y, or Gd), white (Sm, Er, or Dy), or red (Eu) emitted light. The authors noted that the blue emission was a result of charge-transfer (CT) absorption in NbO₆ octahedra under UV light excitation (*i.e.*, Nb \rightarrow O transition) whereas the white and red emitters showed both NbO6 CT absorption and emission from the rare-earth cations.²³⁷ In a related study, Taniguchi, et al. studied the combined effect of co-doping Eb³⁺ and Y³⁺ and host-guest interactions on the photoluminescence properties of K₂La₂Ti₃O₁₀. They found a green-to-red color transition of the emitted light upon proton exchange. The marked difference in the luminescence behavior was attributed to O-H vibrations in the protonated layered oxide that quenched the population of highest energy levels, thus resulting in lower energy (longer wavelength) emission.²³⁸ Recently, Ozawa expanded the choice of lanthanide dopants by utilizing a flocculation approach that incorporated the guest counterions Ho³⁺, Yb³⁺, and Y³⁺ into the interlayer galleries. They found that samples heated to 500 $^\circ\mathrm{C}$ retained the bulk perovskite structure and also showed photoluminescence behavior.¹²⁰ Thus, host-guest chemistry can be utilized as an effective tuning knob to selectively control the luminescent properties of layered oxide perovskites.

Two-dimensional oxide nanosheets have recently gained attention as photonic sensors by using host-guest chemistry to modulate their optical properties. The sensing mechanism involves the intercalation of solvent molecules into the interlayer galleries, which alters the refractive index of the material and thus results in a visible color change. Lotsch and coworkers designed optical sensors from a variety of phosphate and niobate nanosheets. Nanosheets of layered phosphatoantimonates H₃Sb₃P₂O₁₄ and HSbP₂O₈ were integrated with TiO₂ and SiO₂ nanoparticle layers to make 1D photonic crystals and were used to differentiate vapors of water and alcohols.^{239,240} The absorption of water molecules onto TiO₂ nanoparticles increased the refractive index by filling the pores whereas the intercalation of water molecules into nanosheet galleries decreased the refractive index due to swelling, thus causing a refractive index contrast.²³⁹ The nanosheet response to solvent vapors of different polarities was also found to depend on the exchangeable counterions



Fig. 19 (a) Illustration of the exfoliation process of $HTaP_2O_8$ nanosheets. (b) Time lapse of the optical responses of $H_{3-x}Sb_3P_2O_{14}$ nanosheets exfoliated with and without TBA⁺ cations toward ethanol. (c) Responses of the nanosheet films to solvents of different polarities (RH = relative humidity) given as $(\lambda_x - \lambda_{43})/\lambda_{43}$. Reproduced with permission from ref. 241. Copyright 2017 Wiley-VCH.

between the nanosheets. Ganter, et al. recently demonstrated that tantalum phosphate (HTaP2O8) nanosheets exfoliated using quaternary ammonium (TBA⁺ and TBP⁺) ions had increased sensitivity to water vapor and other solvents when compared with H₃Sb₃P₂O₁₄ nanosheets that had been exfoliated using water (Fig. 19). The authors attributed the faster time response of the nanosheets to the large surface area accessible to vapor molecules resulting from layer expansion by the TBA ions.²⁴¹ More recently, the sensing mechanism of nanosheets to alcohols was coupled with their photocatalytic properties to pattern features at the micron scale. Ganter and Lotsch used HCa2Nb3O10 nanosheets as photoresists by selectively exposing certain parts of the film to UV light to decompose the TBA⁺ cations and reduce the nanosheet thickness. The unexposed regions were washed with polar solvents (acetone and water), resulting in swelling of the layers and formed the pattern of interest.²⁴²

Ferroic and magnetic properties. Layered perovskites and heterostructures with novel ferroic properties is an area that is being actively explored by researchers. The Ruddlesden–Popper phases $(Ca,Sr)_3Ti_2O_7$,²⁰⁷ $Ca_3Mn_2O_7$,²⁴³ $Ca_3Ti_2O_7$,²⁴³ and Dion–Jacobson phases $ALaB_2O_7$ (A = Cs, K/B = Nb/Ta)²⁰¹ have been shown to exhibit ferroelectricity, and $(Ca_xSr_{1-x})_{1.15}Tb_{1.85}Fe_2O_7$,¹⁶² has been studied for magneto-electric coupling. The fact that large families of layered perovskites have yet to be explored by synthesis, and are amenable to structural tuning by ion exchange and other soft chemical reactions creates a broad scope of opportunity in this area of research.²⁴⁴

In one aspect of this research, vapor-phase growth techniques such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD), as well as single-crystal and solid state synthetic routes are helping to identify new materials. In another, metastable materials that are difficult or impossible to synthesize by high temperature techniques have been made accessible by soft chemistry routes. An example of how magnetoelectricity can be achieved in layered perovskites by the soft chemistry route is illustrated by the case of $Ti_{0.8}Co_{0.2}O_2/Ca_2Nb_3O_{10}/Ti_{0.8}Co_{0.2}O_2$ hetero-structured thin films. Li, *et al.* reported layer-by-layer two-dimensional engineering of the nanosheets. Magnetoelectric coupling was achieved when ferromagnetic $Ti_{0.8}Co_{0.2}O_2$ sheets were stacked alternately with high-*k* dielectric HCa₂Nb₃O₁₀ nanosheets.²⁴⁵

To add a new dimension to the use of LB deposited layered perovskites, a new area being explored is the integration of soft chemical LB deposition with the vapor phase thin film deposition technique PLD to realize novel ferroic materials. Recently, Yuan, *et al.*²⁴⁶ reported that PLD deposition of SrRuO₃/PbZr_{0.52}Ti_{0.48}O₃/SrRuO₃ films on a LB deposited buffer layer of HCa₂Nb₃O₁₀ on silicon substrates resulted in high longitudinal piezoelectric d_{33} values ranging from 72–100 pm V⁻¹ and enhanced transverse d_{31} values around –100 pm V⁻¹. Along similar lines, Nguyen, *et al.*¹⁵⁷ have reported that LB deposition of HCa₂Nb₃O₁₀ and Ti_{0.87}O₂ nanosheets on silicon substrates leads to highly oriented growth of PZT films.

On a third front, the topochemical oxidation of the layered oxide $LaCa_2Fe_3O_8$ has led to the synthesis of the triple



Fig. 20 (a) $Ca_2Nb_3O_{10}$ perovskite blocks with octahedral rotations highlighted. The space group is *Cmcm*. (b) Schematic of the LB technique for synthesizing layered perovskite films as high-*k* dielectrics. (c) TEM images of a cross-section of the LB film and SrRuO₃ substrate. Reproduced with permission from ref. 250. Copyright 2012 Wiley-VCH.

perovskite LaCa₂Fe₃O₉, which has a remarkably high valence state of +3.67 for Fe in an oxygen octahedral coordination environment.²⁴⁷ This leads to charge disproportionation of Fe³⁺ and Fe⁵⁺ ions, which results in an antiferromagnetic transition below 170 K.²⁴⁷ Also, as discussed above, the n = 1 Ruddlesden–Popper compounds LiRTiO₄ (R = rare earth), which were synthesized by ion exchange of Na*R*TiO₄, undergoes a structural transition from centrosymmetric *P*4/*nmm* to the piezoelectric phase *P*42₁*m*.¹⁹⁵ Another n = 2 Ruddlesden–Popper compound, La₃Ni₂O_{5.5}F_{3.5}, which was synthesized by topochemical fluorination of Li₃Ni₂O₇, has been reported to be ferroelectric due to the change in the OOR pattern from $a^{-}a^{-}c^{0}$ to $a^{-}a^{-}c^{+}$ upon fluorination.¹⁰⁸ These examples illustrate the complementarity of soft chemistry with vapor-phase or high temperature in the synthesis of layered oxides for ferroic applications.

High-*k* **dielectrics.** Layered oxide perovskites have also been explored as high-*k* dielectrics, using soft chemical approaches to prepare thin films. In order to avoid the problem of the dead-layer interface on the properties of thin-film dielectrics, researchers have made significant progress in LB deposition.^{169,245,248,249} Osada, *et al.*²⁵⁰ reported dielectric constants in the range of 150 to 210 for thin films of $(Ca/Sr)_2(Nb/Ta)_3O_{10}$ deposited by the LB technique from a colloidal suspension of nanosheets onto a SrRuO₃ substrate. This work has been followed up in recent years to investigate the dielectric properties of layered oxides.^{169,248,249}

Fig. 20a shows the crystal structure of $(Ca/Sr)_2(Nb/Ta)_3O_{10}$ with the perovskite blocks highlighted to form the frame of the layered perovskite. The space group is orthorhombic $Cmcm^{251}$ and hence centrosymmetric. Fig. 20b highlights the steps of LB deposition and shows how the nanosheets are deposited onto the substrate. The films were found to have sharp interfaces and a dead-layer of defects at the film-substrate interface could be avoided. Dielectric measurements on a wide range of layered oxide perovskite thin films revealed high dielectric constants

scaling with the number of layers, as reported by Li, *et al.*²⁴⁹ Low leakage currents can be achieved because the deposition of multiple nanosheet layers eliminates leakage pathways through the thin film. For example, $Ca_2Nb_3O_{10}$ films had a leakage current density of only about 10^{-7} A cm⁻² for a ~7.5 nm thick film.²⁵⁰ Thus the LB deposition technique described by Osada, *et al.*²⁵⁰ can be a potent tool for obtaining very thin high-*k* dielectric oxide films.

Summary and outlook

The role of soft chemistry in designing functional materials from layered oxides has been elaborated in this review. Over the past three decades, soft chemical approaches including topochemical ion-exchange, redox reactions, dehydration, anion replacement, acid-base reactions, exfoliation, and flocculation have been utilized to synthesize a rich variety of layered transition metal oxide-based materials that are not accessible by direct thermal synthesis. Similarly, two-dimensional nanosheets can be stacked together layer-by-layer with alternating surface charges or by using Langmuir-Blodgett deposition techniques. Characterization techniques such as X-ray scattering and electron microscopy have great value in understanding the morphological and structural changes that accompany soft chemical processes such as ion-exchange or exfoliation. These techniques also provide useful information about structure-property relationships for energy storage applications. Additionally, the soft chemical design of functional layered transition metal oxides is a powerful tuning knob in the context of understanding and tailoring their functionality. The examples presented above include new insights into strong metal-support interaction (SMSI) that stabilizes nanoparticle catalysts, and the tuning compositions in ferroic oxides to lift inversion symmetry. The implications of utilizing

soft chemistry approaches for the design of functional materials are already evident in fields such as artificial photosynthesis, energy storage, optical sensing, ferroics, and high-*k* dielectrics.

There are several new directions and challenges that are emerging in the field of layered oxides. First, most nanosheets of transition metal oxides are electronically insulating which makes their utilization challenging for energy storage applications in batteries or fuel cells. An effective strategy for overcoming this limitation is to hybridize nanosheets with highly conducting reduced graphene oxide. Topochemical fluorination⁷³ and other anion replacement techniques that result in mixed-valence transition metal ions can potentially provide another route to electronically conductive bulk oxides. On another front, layer expansion by osmotic swelling should be investigated to probe the effects of intercalation and exfoliation reactions on electronic structure. Second, soft chemical reactions have primarily been developed for layered oxides containing early transition metals. However, late transition metal oxides are very interesting for studying strongly correlated electronic phenomena. The primary challenge with designing ion-exchangeable late transition metal oxides is the low oxidation state that necessitates highly charged cations for charge balance in the interlayer galleries. This could be overcome by direct synthesis of oxyfluoride perovskites. Third, multicomponent assemblies made by LB deposition should be considered as an alternative strategy to vapor-phase techniques such as oxide molecular beam epitaxy, which are available in only a few specialized laboratories, for creating superlattices of different materials with control of layer registry. This could expand the range of materials that can be grown on to a wide variety of substrates. Finally, controlled exfoliation techniques that yield nanosheets with homogeneous sizes and controlled shapes are lacking. Effective reagents that would selectively delaminate layered oxides with minimal shear could be explored to produce homogeneous colloids nanosheets. This would enable more precise arrangement of nanosheets by LbL assembly and LB deposition techniques.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the students and postdoctoral coworkers who have contributed to our understanding of the soft chemistry of layered metal oxides and oxide nanosheets. This research has been supported by the National Science Foundation under grant DMR-1306938.

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