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Strategies for designing metal oxide nanostructures

Abstract

There has been exponential growth in research activities on nanomaterials and nanotechnology for applications in emerging technologies and sustainable energy in the past decade. The properties of nanomaterials have been found to vary in terms of their shapes, sizes, and number of nanoscale dimensions, which have also further boosted the performance of nanomaterial-based electronic, catalytic, and sustainable energy conversion and storage devices. This reveals the importance and, indeed, the linchpin role of nanomaterial synthesis for current nanotechnology and high-performance functional devices. In this review, we provide an overview of the synthesis strategies for designing metal oxide nanomaterials in zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) forms, particularly of the selected typical metal oxides TiO₂, SnO₂ and ZnO. The pros and cons of the typical synthetic methods and experimental protocols are reviewed and outlined. This comprehensive review gives a broad overview of the synthetic strategies for designing "property-on-demand" metal oxide nanostructures to further advance current nanoscience and nanotechnology.

Keywords

metal, oxide, nanostructures, designing, strategies

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Strategies for designing metal oxide nanostructures

Ziqi Sun^{1*}, Ting Liao² and Liangzhi Kou¹

ABSTRACT There has been exponential growth in research activities on nanomaterials and nanotechnology for applications in emerging technologies and sustainable energy in the past decade. The properties of nanomaterials have been found to vary in terms of their shapes, sizes, and number of nanoscale dimensions, which have also further boosted the performance of nanomaterial-based electronic, catalytic, and sustainable energy conversion and storage devices. This reveals the importance and, indeed, the linchpin role of nanomaterial synthesis for current nanotechnology and high-performance functional devices. In this review, we provide an overview of the synthesis strategies for designing metal oxide nanomaterials in zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) forms, particularly of the selected typical metal oxides TiO₂, SnO₂ and ZnO. The pros and cons of the typical synthetic methods and experimental protocols are reviewed and outlined. This comprehensive review gives a broad overview of the synthetic strategies for designing “property-on-demand” metal oxide nanostructures to further advance current nanoscience and nanotechnology.

Keywords: nanomaterials, synthesis of materials, metal oxide, nanostructures

INTRODUCTION

Metal oxides are known to possess unique functionalities that are absent or inferior in other solid materials. Their nanostructures have emerged as an important class of materials with a rich collection of properties and general potential for various applications, including electrodes, high-mobility transistors, gas sensors, photovoltaics, photonic devices, and non-volatile memories [1–4]. In particular, metal oxide nanostructures have led to a revival of interest in them for wide applications in energy conversion, harvesting, and storage devices, such as lithium-ion batteries [5,6], fuel cells [7–9], solar cells [10,11], nanogenerators [12,13], hydrogen production by water photolysis and its

storage [14–17], water and air purification [18,19]. In all of these new technologies, nanomaterials are increasingly playing a critical role by either increasing the efficiency of the energy storage and conversion processes or by improving device design and performance.

Nanomaterials are defined as materials with at least one external dimension in the size range from approximately 1–100 nanometers [20]. Nanomaterials differ from micro-sized and bulk materials not only in the scale of their characteristic dimensions, but also in the fact that they may possess new physical properties and offer new possibilities for various technical applications. For example, the well-known “quantum-size confinement effect” is found in semiconductor nanomaterials, which leads to an increased band gap, and “surface plasmon resonant absorption” exists in noble metal nanoparticles, which tunes the nanoparticles into size-dependent colours [21–23]. Owing to the advantages that have been discovered in nanostructured materials: offering huge surface to volume ratios, favourable transport properties, altered physical properties, and confinement effects resulting from the nanoscale dimensions, metal oxide nanomaterials have presented superior performance compared to their corresponding bulk materials [24,25]. Previous studies have demonstrated that the morphology, crystallinity, and pore configurations of the nanostructured materials strongly influence the performance of the devices based on them, due to the fact that the surface area, optical effects, electron or ion transport, and electrolyte diffusion paths are strongly dependent on the structural configuration of the nanomaterials [24,25].

Due to the fact that the properties of the materials vary with their shapes, sizes, and reduced dimensions, which then boost the performance of the nanomaterial-based devices, nanomaterials and nanotechnologies have now be-

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come the hottest research areas. Many excellent perspectives and reviews on the preparation and the new physical and chemical properties of nanomaterials have been published recently [21–32]. In general, the synthesis of nanomaterials and the creation of nanostructures are achieved mainly through two complementary approaches, identified as top-down synthesis and bottom-up synthesis. Fig. 1 gives a general overview of the top-down and bottom-up synthesis of nanoscale structures with zero, one, two and three dimensions (0D, 1D, 2D, and 3D). The top-down approaches involve whittling down the size of materials from the bulk, thin films, or microscale mesoporous structures to nanometer scale, for example, via lithography, mechanical milling, exfoliation, chemical intercalation, severe plastic deformation, etc. [32–36]. The bottom-up approaches, on the contrary, involve assembly of the nanostructures atom-by-atom or molecule-by-molecule from atoms, molecules, and sometimes proteins, by techniques including molecule self-assembly, layer-by-layer deposition, template-assisted synthesis, etc. [37–40].

In this review, we concentrate on drawing a map of the preparation methods for the most commonly used wide-gap metal oxide semiconductors, TiO_2 , SnO_2 , and ZnO , for example. The synthetic strategies for approaching TiO_2 , SnO_2 , and ZnO free-standing or isolated nanomaterials

in 0D, 1D, 2D, and 3D forms are outlined. Table 1 summarizes the typical synthetic methods for fabricating metal oxide nanostructures. We hope that this critical review will provide a general understanding of the possible synthetic strategies for the design of “property-on-demand” metal oxide nanostructures to further advance current nanoscience and associated technologies.

SYNTHETIC STRATEGIES FOR 0D METAL OXIDE NANOSTRUCTURES

The term “0D nanostructures” indicates that the particles have sizes with all three spatial dimensions below 100 nm. 0D nanomaterials include nanocluster materials and nanodispersions, i.e., materials in which nanoparticles are isolated from each other. If the 0D nanoparticles possess sizes small enough that the electrons or carriers are confined in all three spatial dimensions, they are a specific class of 0D nanostructures—quantum dots (QDs) [41]. Fig. 2 presents the commonly used methods for fabricating typical 0D metal oxide nanostructures. 0D metal oxide nanostructures have to be synthesized under confined conditions, i.e., within the branches of dendrimers, from reverse surfactant micelles and capping agents, or within the pores of hard templates such as zeolites. Besides the confined synthesis of 0D nanoparticles, there is a surface patterning technique, in which the nanoisland arrays can be created on the substrates relying on utilizing the Asaro-Tiller-Grinfeld (ATG) instability [42,43]. Owing to their high surface energy, the 0D nanomaterials are usually highly active and thermodynamically unstable, which makes them easily grow larger or aggregate into big particles. The key factor in the synthesis of 0D nanomaterials is to retard the growth of nanocrystals and to prevent the aggregation of the nanoparticles. The synthesis of 0D nanomaterials with well-controlled sizes and shapes usually needs a complex process, stringent synthesis parameters, and expensive raw materials, but still suffers from a low production yield, the use of non-environmentally friendly chemicals and processes, etc.

Dendrimer-encapsulated synthesis of 0D nanostructures

The use of well-defined polymers known as dendrimers as templates is one of the most widely applied approaches to the synthesis of 0D nanoparticles with controlled size and narrow particle size distribution [44,45]. Fig. 2a presents the strategy for the synthesis of 0D nanoparticles from highly branched dendrimers. Dendrimers are repetitively branched molecules, such as poly(propyleneimine) (PPI) and poly(amidoamine) (PAMAM), typically symmetric

Figure 1 Approaches to the synthesis of nanoscale structures.

Table 1 Summary of synthetic methods and key technique points for the synthesis of metal oxide nanostructures

Synthetic method	Key technique points	Shapes and configurations
Vapour deposition synthesis	Metal oxide crystals grow from atoms or molecules via a vapour-solid or vapour-liquid-solid process	1D nanowires, nanorods, nanoribbons/belts; 2D nanosheets; 3D hierarchically-ordered micro-nanostructures
Dendrimer-encapsulated synthesis	Highly branched dendrimers are used as template and stabilizer	0D nanoparticles
Surfactant-assisted synthesis	Surfactants in the forms of micelles, microemulsions, single-layer molecular structural agents, etc. are used as templates	0D nanoparticles; 1D nanowires, nanorods, nanoribbons, and nanotubes; 2D nanosheets; 3D nanospheres, hollow spheres, hierarchically-ordered micro-nanostructures
Hard-template assisted synthesis	Mesoporous structures, AAO, CNT, graphene, etc. are used as templates	0D nanoparticles; 1D nanowires, nanorods, nanoribbons, and nanotubes; 2D nanosheets; 3D nanospheres, hollow spheres, hierarchically-ordered micro-nanostructures
Electrochemical synthesis	Synthesis of nanostructures by anodic oxidation or electrodepositions	1D nanofibers, nanowires, nanorods, nanotubes; 3D nanoflowers
Exfoliation synthesis	Delaminating layered host materials into ultrathin nanosheets	2D nanosheets

Figure 2 Strategies for synthesizing 0D metal oxide nanostructures. (a) 0D nanoparticles grown within the branches of dendrimers, (b) soft templates such as reverse micelles, and (c) hard templates such as mesoporous structures.

around the core, and they often adopt a spherical 3D morphology, serving not only as a template but also to stabilize the nanoparticle [46]. These highly branched macromolecules have well-defined structures that enable them to bind metal ions to generate precursors that can be converted into nanoparticles with diameters of 1–2 nm, with a standard deviation of 0.3–0.6 nm [47,48]. The growth of nanoparticles from dendrimers can take the full advantage of them: (i) dendrimers are of uniform composition and structure for yielding well-defined nanoparticle repli-

cas; (ii) dendrimers prevent agglomeration of nanoparticles; (iii) the encapsulated nanoparticles are confined primarily by steric effects and their surface is unpassivated; (iv) the terminal groups on the dendrimer periphery can be tailored to control solubility of the nanocomposites, etc. [44]. There are some drawbacks for this approach as well: some reactions require large excess of dendrons and provide rather poor process control; some cases using ligand exchange reaction suffer from a low exchange rate; and sometimes it is a problem to separate the encapsulated reactants, etc. [46]. Moreover, it is a challenge to control the shape as well as the size of nanoparticles using dendrimer templates [47]. It is worth noting that dendrimers can also serve as surfactants, which leads to the opportunities for the synthesis of nanocomposites with controlled solubility, functionality, and morphologies, owing to their structures differing significantly from that of conventional surfactants [46].

Satoh *et al.* [49] described the sub-nanometre size control of both anatase and rutile forms of TiO_2 particles with phenylazomethine dendrimers, leading to samples with very narrow size distributions. In this synthesis, a fourth-generation phenylazomethine dendrimer (DPA G4) was used, which allowed the complexation of 30 metal ions and enabled the number and locations of the metal ions to be finely controlled. A stepwise addition of $\text{Ti}(\text{acac})\text{Cl}_3$ (acac = acetylacetonate) into the DPA G4 templates resulted in complexation at different radii. The

quantum size TiO_2 was then obtained by either hydrolysis of the Ti-assembled DPA G4 in HCl solution to form rutile TiO_2 or thermolysis of the Ti complexation at 500°C for 1 h in air to produce anatase TiO_2 . The sizes of the TiO_2 QDs fabricated via this method ranged from around 1.47 ± 0.16 nm to 1.70 ± 0.20 nm based on transmission electron microscopy (TEM) observation, or 0.7 ± 0.09 nm to 1.24 ± 0.11 nm based on atomic force microscopy (AFM) characterization.

Compared to the widely studied II–VI semiconductor 0D QDs, ZnO QDs have received little attention, owing to the fact that the conventional ZnO QDs are not stable in water. Moussodia *et al.* [50] reported the synthesis of stable ZnO QDs by employing siloxane-core PAMAM dendrons together with oleate-capping. The oleate-capped ZnO QDs were first synthesized by adding $\text{Zn}(\text{OAc})_2$ ethanol solution into oleic acid below 50°C . The oleate-capped ZnO QDs were then dispersed in toluene and treated with different generations of PAMAM at 85°C . The sizes of the ZnO QDs were around 9–10 nm.

Tin(IV) oxide nanoparticles were synthesized via the reaction of carbon dioxide with stannate ions immobilized by dendritic polymers [51]. In this study, two fourth generation dendritic architectures, PPI and PAMAM, were employed for the synthesis of SnO_2 nanoparticles. In a typical procedure, saturated aqueous or ethanol sodium stannate solution was well mixed with a polymeric host in a molar ratio of 1:4 and then bubbled with gaseous CO_2 to yield a light yellow solution. For the PAMAM and PPI dendrimer hosts, the resultant diameters of SnO_2 nanoparticle were 2.5–3 nm.

Surfactant-assisted synthesis of 0D nanostructures

The application of surfactants to synthesize size-controlled nanoparticles from size and shape defined reverse micelles or microemulsions is one of the most commonly used methods in nanomaterials fabrication [52]. Surfactants normally contain a hydrophilic head and a hydrophobic chain, and these amphiphilic molecules can self-assemble into a rich variety of organized structures in solution, such as normal and reverse micelles, microemulsions, vesicles, and lyotropic liquid crystals [53]. Specifically, reverse micelles are globular aggregates formed by the self-assembly of surfactants in apolar solvents, whereas normal micelles are globular aggregates formed by the self-assembly of surfactants in water [53,54]. The structure of reverse micelles is characterized by a polar core formed by the hydrophilic heads and an apolar shell constituted by the hydrophobic chains. Water can be readily solubilized in

the polar core to form water-in-oil (w/o) droplets, which are usually called reverse micelles at low water content and w/o microemulsions at high water content [54]. Fig. 2b shows a schematic illustration of a reverse micelle with a nanoparticle or precursor oligomers confined inside. This method has an advantage over other methods since it leads to homogeneous and monodispersed nanoparticles with a narrow size distribution. Compared to the dendrimer-encapsulated synthesis, the surfactant-assisted synthesis provides a relative simple and low-cost approach to separately control the sizes, shapes, and specific crystal facets of 0D nanocrystals and to further assemble into complex shapes and configurations [54]. Moreover, the surfactants used during the synthesis and attached to the surface of the nanocrystals can be exchanged against other ones, which allows not only chemical modification of the surface properties of the nanoparticles, but also the tailoring of the dispersibility behaviour in different solvents [52].

TiO_2 nanoparticles, aggregated from smaller anatase or rutile nanoparticles ranging in size from 20 to 50 nm, were synthesized by the precipitation of TiCl_4 with ammonium hydroxide by using nonionic water/Triton X-100/hexanol/cyclohexane microemulsions with a water fraction of 8% and subsequent calcination at different temperatures [55]. 0D TiO_2 nanoparticles in amorphous or crystalline form in controlled sizes were synthesized from hydrated reverse micelles [56–58]. TiO_2 nanoparticles with diameters varying from 10 to 20 nm were produced by the controlled hydrolysis of titanium tetraisopropoxide (TTIP) in the presence of reverse micelles formed in CO_2 with the surfactants ammonium carboxylate perfluoropolyether ($\text{PFPECOO}^-\text{NH}_4$) ($M_w = 587$) and poly(dimethyl amino ethyl methacrylate-*block*-1H, 1H, 2H, 2H-perfluorooctyl methacrylate) (PDMAEMA-*b*-PFOMA) [57]. Hernandez *et al.* [58] reported the synthesis of TiO_2 nanoparticles with a mean diameter of 3.5 ± 0.7 nm inside sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles with $w = 1$ ($w = [\text{H}_2\text{O}]/[\text{AOT}]$) suspended in *n*-heptane. It has been reported that shuttle-like crystalline TiO_2 nanoparticles were synthesized by hydrolysis of titanium tetrabutoxide in the presence of acids in polyethylene glycol (PEG) mono-4-nonylphenyl ether (NP-5 [Igepal CO-520])–cyclohexane reverse micelles at room temperature with a w value ($w \sim [\text{H}_2\text{O}]/[\text{NP-5}]$) of 8 and h ($h \sim [\text{H}_2\text{O}]/[\text{Ti}(\text{OC}_4\text{H}_9)_4]$) of 28 [59].

0D ZnO nanoparticles have been synthesized in reverse micelles or microemulsions, for instance, polystyrene-*b*-polyacrylic acid (PS(10912)-*b*-PAA(3638)) copolymer, PEG NP-5/cyclohexane, AOT, non-ionic Pluronic

F127, anionic surfactant sodium dodecyl sulfate (SDS), etc. [60,61]. For instances, Hirai *et al.* [60] reported that spherical ZnO nanoparticles with a mean particle size around 40 nm and a narrow size distribution were obtained by calcination of Zn(OH)₂ nanoparticles, which were prepared in a PEG NP-5/cyclohexane reverse micellar system and incorporated into polyurea (PUA) via an *in situ* polymerization of hexamethylene diisocyanate (HDI). Inoguchi *et al.* [61] successfully synthesized monodispersed and spherically shaped ZnO nanoparticles with particle sizes < 5 nm by the hydrolysis reaction of zinc diethoxide in the small water droplets in reverse micelles in a C₆H₁₂, nonylphenol ethoxylate (NP-10), CH₃(CH₂)₇OH, and NH₄OH solution at room temperature. The molar ratio of C₆H₁₂, NP-10, CH₃(CH₂)₇OH, and H₂O was adjusted to 171.3:1.3:6.5:1.0 and NP-10 and CH₃(CH₂)₇OH served as the surfactant and the cosurfactant, respectively.

Fine SnO₂ nanoparticles were also synthesized from reverse micelles for various functional applications, such as lithium batteries [62,63]. Ahmad *et al.* synthesized SnO₂ nanoparticles by using two microemulsions, i.e., microemulsion I and microemulsion II. Microemulsion I was composed of cetyl trimethylammonium bromide (CTAB) as the surfactant, 1-butanol as the cosurfactant, isooctane as the oil phase, and 0.1 mol L⁻¹ of SnCl₄·5H₂O solution as the aqueous phase. Microemulsion II had the same constituents as microemulsion I, except that the aqueous phase was (NH₄)₂C₂O₄·H₂O (0.1 mol L⁻¹) instead of SnCl₄·5H₂O. These two microemulsions were then mixed to form a precipitate by either the addition of 0.1 mol L⁻¹ NaOH solution or by stirring overnight. The white precipitate was then calcined at 60 and 500°C for 5 h to obtain crystallized SnO₂ nanoparticles of 70 and 150 nm in size, respectively [62]. PdO-SnO₂ nanocomposite was also prepared by precipitating Pd(OH)₂ and Sn(OH)₄ inside reverse micelles obtained by mixing cyclohexane (C₆H₁₂), a non-ionic surfactant (polyoxyethylene (6) nonylphenyl ether (NP-6)), and an aqueous solution containing [Sn(OH)₄]²⁻ (0.1 mol L⁻¹). The particle size of the resultant SnO₂ was ~10 nm, loaded with PdO nanoparticles ~4 nm in size [63].

Besides the confined synthesis in reverse micelles, arrested precipitation of nanoparticles from a solution of long chain capping reagents is also a general approach to the synthesis of size-controlled 0D nanostructures, particularly QDs, for example, from the typical airless TOP-TOPO (tri-*n*-octylphosphine [TOP], tri-*n*-octylphosphine oxide [TOPO]) solutions [64]. Arrested precipitation in TOP-TOPO solutions has proven to be one of the most successful approaches for synthesizing nanocrystals in

the size range of 2–10 nm. This wet chemical synthetic method relies on organic ligands to passivate particle surfaces during growth to provide size control and colloid stabilization. Ultrafine TiO₂ nanoparticles with sizes below 10 nm were also synthesized via this arrested precipitation method in high boiling point solvents such as TOPO, benzophenone, and even aqueous-contained solutions [65–68]. One typical example is the synthesis of brookite TiO₂ nanocrystals via a surfactant-assisted nonaqueous strategy [67]. In a general procedure, 3 g of 1-octadecene (ODE), 13–52 mmol of oleyl amine (OLAM), and 0.5–2 mmol of oleic acid (OLAC) were loaded into a three-neck flask and degassed at 120°C for 30 min, after which the mixture was cooled down to 50°C under flowing N₂ gas. At this point, 0.5–2 mmol of TiCl₄ was added (such that the OLAC/TiCl₄ molar ratio was 1). The flask was then heated up to 290°C at a ramp rate of ~25°C min⁻¹ and held at that temperature for 30 min. The TiO₂ product was separated from its growth medium by acetone (or 2-propanol) addition and subsequent centrifugation (5000 rpm). Monodispersed ZnO nanoparticles have also been synthesized from TOPO [69]. A solid mixture of the molecular precursor, [EtZnOⁱPr] and 2 equivalents of TOPO were placed in a round-bottom flask and dissolved at 80°C, and the obtained clear solution mixture was stirred at 160°C for 5 h. Monodispersed spherical ZnO nanoparticles with an average size of 3.1 ± 0.3 nm were separated from the clear solution by centrifugation after a simple work up, in which the solid product was dissolved in a small amount of toluene and flocculated with the addition of an excess amount of methanol.

Hard-template assisted synthesis of 0D nanostructures

There is also an effective way to obtain nanocrystals from mesoporous hard templates, such as SBA-15, MCM-41, KIT-6, AMS-10, FDU-1 and FUD-12 (Fig. 2c) [70,71]. In the synthesis, the most important step is to effectively introduce inorganic ions into the pore channels of the mesoporous hard templates. The isomorphous substitution of surface silicon atoms by metals, however, could be likely leading to the localization of metals in the silicon framework, which leads to a major challenge on putting metals inside the mesoporous framework and formation of crystalline oxide nanoparticles homogeneously [71]. For obtaining 0D nanostructures from hard templates, we should etch away or remove the frameworks, which may result in high cost of the synthesis, time intensiveness of the approach, and even environmental issues [28].

It was reported that 0D TiO₂ nanoparticles were syn-

thesized from mesoporous silica hard templates such as SBA-15 and KIT-6 [72,73]. In the hard-template assisted synthesis of TiO_2 nanoparticles reported by Zhao *et al.* [72], 0.5 g dried SBA-15 powders was dispersed in a mixed solution containing 2 mL titanium tetrabutylorthotitanate (TTBT) and 5 mL ethanol. The mixture was stirred at room temperature for 8 h to allow natural evaporation of the solvent, and then the hybrid TiO_2 /SBA-15 products were dried in a vacuum at 80°C for 4 h and calcined in air at 550°C for 4 h at a heating rate of 5°C min^{-1} . Finally, the silica was dissolved in a 10 wt.% hydrogen fluoride (HF) solution and washed with sufficient distilled water to obtain template-free TiO_2 nanoparticles around 6 nm in diameter. The sizes of the well-controlled TiO_2 , SnO_2 , and ZnO nanoparticles that were synthesized from mesoporous hard templates exhibited obvious improvements, making them attractive for applications in photoluminescence, gas sensing, glycol conversion, etc. [72–74].

SYNTHETIC STRATEGIES FOR 1D METAL OXIDE NANOSTRUCTURES

1D nanostructures are specifically classified as nanomaterials with lateral dimensions that fall anywhere in the range from 1 to 100 nm and lengths ranging from several hundreds of nanometers to as high as a few centimeters, in forms including nanowires, nanorods, nanobelts, nanotubes, and nanoribbons [75]. 1D metal oxide nanostructures are the most widely studied nanostructures, as evidenced by the numerous excellent reviews on the synthesis and functional applications of 1D metal oxide nanomaterials that have been appearing almost every year recently [2,76–89]. In this review, we only intend to give some general information on the fabrication of 1D metal oxide nanostructures. 1D nanostructures are the result of anisotropic growth along only one dimension. Generally, as shown in Fig. 3, the synthesis methods for 1D metal oxide nanostructures can mainly be classified into the following four types: i) the vapour deposition method, including physical vapour deposition (PVD) and chemical vapour deposition (CVD), ii) chemical solution growth, including free growth, soft-template guided growth, hard-template guided growth, etc., from open or high-pressure chemical baths, iii) electrochemical anodization and electrodeposition, and iv) electrospinning. Some 1D nanopatterns or arrays on substrates can be fabricated via lithography or nanocarving. The later provides a relative simple approach to prepare oriented 1D TiO_2 nanoarrays by carving the titania crystals in a flowing 5% H_2 -95% N_2 gas at a high temperature [90].

Vapour deposition growth of 1D nanostructures

Among the above-mentioned methods, the vapour deposition method is one of the most widely used, owing to its simplicity and versatility when applied in many semiconductor systems, in which the growth of the 1D metal oxide crystals is realised via a vapour-solid or vapour-liquid-solid process. Fig. 3a illustrates the growth mechanism of 1D metal oxide nanostructures through the vapour deposition method. First, vapours are produced from metals, metal oxides, salts, or other precursors; second, by providing suitable temperature or vapour pressure fluctuation, the vapours become supersaturated and are deposited on the substrates, so that 1D crystal growth begins; finally, the 1D nanostructures grow on the substrates via continuing vapour diffusion. Depending on the sources of vapour generation, the vapour deposition method can be further divided into CVD, in which the vapour is produced by the evaporation and dissociation of chemical metal oxide precursors, and PVD, in which the vapour is produced by physical means, such as thermal evaporation, laser ablation, or evaporation by ion beam, electron beam, and molecular beam. The vapour deposition growth of 1D nanostructures, particularly PVD, is an extensively employed and inexpensive method for the growth of well-aligned 1D nanomaterial arrays with excellent crystallinity, which can provide outstanding but necessary electronic properties for the applications in nanogenerators, field emitters, and sensors, compared to other approaches. This method, however, is known to be very sensitive to parameters such as source type, substrate orientation, size of catalyst, temperature profile of the furnace, partial pressure and gas flow, and even the geometry of the tube furnace [82]. Via this approach, the length, diameter, and density of 1D nanomaterials can be precisely tailored by controlling the size and distribution of catalytic seeds. The direct fabrication of 1D nanostructures with extremely long length or in tube form via this method, however, still remains as a major challenge. The existence of residual catalysts as contaminations has also side impacts on the performance of 1D nanomaterials. Moreover, it is difficult to fabricate 1D nanostructures in horizontal geometries by the vapour deposition growth.

Fig. 3e presents ZnO nanostructured arrays prepared via the vapour deposition method. In detail, the ZnO source material was put in the heating zone of the furnace at a temperature of $500\text{--}1150^\circ\text{C}$, and the 1D nanostructures grew on the substrates which were placed in the downstream cooling zone [91]. The shapes of the obtained 1D metal oxide nanostructures varied from nanowires and nanobelts to

Figure 3 Strategies for synthesizing 1D metal oxide nanostructures, including (a) chemical/physical vapour deposition, (b) chemical solution growth, (c) electrochemical anodization and electrodeposition, and (d) electrospinning. (e–h) Morphologies of the 1D nanostructures grown via (e) vapour deposition of ZnO nanowires (Reprinted with permission from Ref. [91], Copyright 2008, American Chemical Society), (f) chemical solution growth of TiO₂ nanorods and nanowires (Reprinted with permission from Ref. [117], Copyright 2010, Royal Society of Chemistry), (g) electrochemical anodization growth of TiO₂ nanotubes (Reprinted with permission from Ref. [135], Copyright 2010, Wiley; Ref. [136], Copyright 2012, Wiley; and Ref. [137], Copyright 2007, IOP Publishing Ltd.), and (h) electrospinning of TiO₂ nanofibers (Reprinted with permission from Ref. [144], Copyright 2013, American Chemical Society; Ref. [145], Copyright 2004, American Chemical Society; and Ref. [146], Copyright 2010, InTech), respectively.

hierarchical arrays, etc., depending on the synthesis temperature, with or without metal catalysis, and pre-treatment of the substrates [91–94].

1D SnO₂ nanostructures have also been reported to be synthesized via this method [95–98]. For example, large-scale SnO₂ nanowires were synthesized via laser ablation [95], and SnO₂ nanobelts were synthesized via thermal evaporation [96]. In the laser ablation synthesis of SnO₂ nanowires, the Sn vapour is ablated by a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser at 900°C and carried downstream by an oxygen-argon mixture. SnO₂ nanowires with a diameter of 20 nm were deposited on Au catalysis seeded Si-SiO₂ substrates [95]. Park *et al.* [96] reported the growth of SnO₂ via thermal evaporation from Au seeded Si substrates, in which the Sn

vapour was generated by heating the Sn powders at 900°C in a total gas pressure of 1 Torr.

Compared to 1D ZnO and SnO₂ nanostructures, the growth of high-quality 1D TiO₂ nanostructures via the vapour deposition method is much more difficult, due to the existence of multiple polymorphs and the thermodynamically unfavourable crystallography for anisotropic crystal growth, particularly with large aspect ratio [99]. Even though TiO₂ nanowires with morphology as perfect as those of ZnO and SnO₂ are difficult to achieve, we still can find some attempts to achieve the vapour growth of TiO₂ nanostructures [99–102]. Shi *et al.* [100] reported the growth of rutile TiO₂ nanowires by the pulsed CVD technique from Au seeded substrates at 650°C using TiCl₄ and H₂O as the precursors. The obtained aligned TiO₂

nanowire region typically consisted of a few rugged strips that were parallel to each other. The strips were composed of a group of nanowires with approximately the same orientation. The nanowires were a few micrometers long and the film exhibited a fairly uniform thickness of ~30 nm.

Besides the direct growth of 1D nanostructures via vapour deposition methods, the indirect synthesis via a combination of vapour deposition and hard templates is also an important method to fabricate oriented nanorod or nanowire arrays. For example, ZnO nanowires have been grown from an anodic alumina membrane (AAM) by combining with a vapour deposition process [103,104].

Chemical solution growth of 1D nanostructures

Chemical solution growth is another one of the most widely applied methods for fabricating 1D metal oxide nanostructures. 1D oxide nanostructures can be prepared more easily by solution based synthesis routes than by other approaches, which open up a rich variety of precursor chemistries, solvents, and organic additives such as surfactants to guide the crystal growth. Among various chemical solution growth methods, hydrothermal or solvothermal synthesis has shown great promise in the preparation of 1D oxide nanostructures [88]. In a standard procedure for chemical solution growth, such as with hydrothermal or solvothermal method, a solution containing metal ions and an oxidizing agent is heated with or without pressure to a desired high temperature. Depending on whether there is template addition, the chemical solution growth can be further divided into template-free growth, soft-template guided growth, hard-template guided growth, etc. [105]. The solution based synthesis routes in their simple form or the template-free growth referred here have several limitations with respect to the preparation of 1D oxide nanostructures, and it might be a challenge to grow most materials in 1D shapes without additional adjustments [88]. Only an oxide with a significantly anisotropic crystal structure, which facilitates the preferred crystal growth along a certain axis, can ordinarily grow into 1D nanostructures. For instance, 1D B-type TiO_2 and 1D ZnO nanowires and nanoribbons have been successfully synthesized from strong basic solutions [106,107]. Hence, a shape directing approach is normally necessary to grow 1D nanostructures if the crystal structure of the targeted oxide does not have an anisotropic crystal structure which easily grows in one crystallographic direction. In general, chemical solution growth is one of the most versatile and highly flexible techniques for nanomaterial synthesis. The growth of nanostructures from chemical solution is simple,

low cost, less hazardous, with low temperature, and thus capable of high volume production. In addition, there are a variety of parameters to effectively control the morphologies, sizes, and properties of the final products [108]. The main disadvantages of this method include the poor crystal quality, the abundant growth defects, and rough and contaminated surfaces of the resultant nanostructures, which result in low fracture toughness, low carrier mobility, short carrier lifetime, etc. of nanomaterials.

One of the most widespread methods of shape direction is the application of appropriate organic additives or surfactants to aid directed growth from chemical solutions [109]. As shown in Fig. 3b, the growth of 1D nanostructures is confined or guided in templates. The templates are divided into hard templates and soft templates. The commonly used hard templates usually include silica, anodic aluminium oxide (AAO), and mesoporous carbon [110]. For example, 1D TiO_2 nanowire or nanotube replicas have been obtained from AAO templates and ZnO nanorod array templates [111,112]; 1D SnO_2 nanotubes were synthesized by using silica mesostructures, 1D ZnO arrays, or other 1D nanomaterials as sacrificial templates [113,114], while 1D ZnO nanostructures were synthesized from AAO templates [115,116].

The soft templates have received more attention over the last decade for the generation of nanostructured materials, because they are more versatile and therefore more advantageous compared to hard templates. The soft templates are composed of soft compounds such as biomolecules, polymer gels, block-copolymers, fibers, and emulsions [110]. Considerable work has been done on the soft-template guided growth of 1D TiO_2 nanomaterials. Fig. 3f presents 1D TiO_2 nanostructures synthesized from solutions with a low concentration of the surfactant template CTAB, as reported by Sun *et al.* [117]. In this study, the 1D TiO_2 nanostructures with continuously adjustable morphologies ranged from coarse nanorods, to fine nanorods, and then to nanoribbons and finally fine nanowires, with the product controlled by adjusting the hydrolysis rate of the precursors. This was probably the first report on the successful synthesis of rutile TiO_2 nanoribbon arrays with well-defined shapes from chemical solution. In some cases, rutile TiO_2 nanorods or nanowires were grown on fluorine-doped tin oxide (FTO) substrates from the solutions, which lacked large surfactant molecules [118–121]. It is assumed that there may be (i) a thin layer of nano-sized seeds deposited or formed on the substrate in the initial hydrothermal stage or (ii) a high concentration of sodium or chloride ions to guide the growth of 1D TiO_2

nanostructures [118–121]. 1D ZnO nanowires have been synthesized with the addition of soft templates such as polyethylenimine (PEI) and ethylenediamine [122,123]. Law *et al.* [122] reported that arrays of ZnO nanowires were synthesized on F:SnO₂ conductive glass (FTO) substrates coated with a thin film of ZnO QDs with diameters of 3–4 nm. Nanowires were grown by immersing seeded substrates in aqueous solutions containing 25 mmol L⁻¹ zinc nitrate hydrate, 25 mmol L⁻¹ hexamethylenetetramine (C₆H₁₂N₄, HMTA), and 5–7 mmol L⁻¹ PEI at 92°C for 2.5 h and baked in air at 400°C for 30 min to remove any residual organics. 1D SnO₂ nanoribbons were also synthesized from a solution with CTAB surfactant [124]. Xi *et al.* [125] successfully synthesized rutile SnO₂ nanorods with a diameter of 2.0 ± 0.5 nm via a template- and surfactant-free solution phase method. It was assumed that the large quantity of urea added served as a slow-release basic reagent and helped in the controlled growth of SnO₂ nanorods from the solution.

Electrochemical growth of 1D nanostructures

Among the various synthetic strategies, the electrochemical method is a relatively simple and effective way to prepare 1D semiconductor nanostructures by anodic oxidation or electrodeposition. Fig. 3c presents a standard procedure for fabricating 1D nanorod arrays via anodic oxidation, in which a metal substrate is immersed in an electrolyte solution and anodized to form oxide coatings with 1D oriented porous structures or oriented tubular oxide nanostructures. Various anodizing conditions have been tested to obtain the optimal products, including the voltage, current, duration, and kinds of electrolyte. It is notable that electrochemical anodization is recognized as the most suitable method for preparing 1D nanotubes. The electrochemical approaches also allow the direct synthesis of vertically aligned 1D nanostructures on the conductive electrode surface with a well-defined length. Furthermore, the 1D nanostructures are directly connected with the metallic substrates, which provides an excellent electrical conductivity. The main issues of this synthesis method are that (i) stress at the metal-oxide interface raised from volume expansion or electrostriction can result in crack and delamination of the nanostructured layer; (ii) harmful byproducts and difficult manipulation on length distribution. Electrochemical deposition is also a very attractive method for fabricating 1D nanomaterials because the process is simple and effective by using AAO as template. However, the size of nanostructures is strongly dependent on the pore diameter of the AAO templates, which is usually around tens to

few hundreds of nanometers.

A classic example of anodic oxidation was the preparation of highly ordered porous alumina by anodizing aluminium metal sheets in an acidic environment 60 years ago [126]. This method was then extended to the fabrication of TiO₂, SnO₂, and ZnO nanotubes and nanorods [127–134]. Fig. 3g shows some typical morphologies of TiO₂ synthesized via the anodic oxidation method [135–137]. By controlling the synthesis parameters, such as pH value and types of electrolyte, and the addition of active ions or salts, nanoporous TiO₂ layers with thickness to the order of several 10 μm and channel diameter from several nanometers to several tens of nanometers can be obtained. It was found that the anodization of Ti sheet in an ethylene glycol and HF containing electrolyte allows the preparation of nanotubes with inner diameters controlled in the range from 10 nm to more than 250 nm through changing the electrolyte temperature from -20 to 50°C [135]. Shin *et al.* [132] first prepared self-ordered porous SnO₂ using an anodic oxidation method. In their experiment, high-purity tin as the working electrode and a platinum wire as the counter electrode were immersed in 0.5 mol L⁻¹ oxalic acid electrolyte for anodization at an applied constant voltage (5–14 V). Highly ordered SnO₂ nanotube and nanowire arrays have also been fabricated using AAO as hard template [131].

Electrospinning of 1D nanostructures

Electrospinning seems to be the simplest and most versatile technique for generating 1D nanostructures, particularly nanofibers with length up to hundreds of meters [138–143]. Fig. 3d presents the basic configuration of a typical electrospinning apparatus, which consists of a spinneret (typically a hypodermic syringe needle) connected to a high-voltage (5–50 kV) direct current power supply, a syringe pump, and a grounded collector. During the process of electrospinning, the liquid drop elongates with increasing electric field. When the repulsive force induced by the charge distribution on the surface of the drop exceeds the surface tension of the liquid, a jet of liquid is ejected from the cone tip. By controlling the viscosity of the liquid with the addition of polymers, a solid and continuous fiber is generated through the electrostatic repulsion between the surface charges and the evaporation of solvent. There are some advantages of electrospinning of 1D nanostructure: (i) it produces nanowires or nanotubes with extremely large aspect ratios and controllable porosity with a diameter range from several tens of nanometers to a few micrometers; (ii) the nanotubes with multishells or multichannels can be formed by extension of the spinneret; (iii) it is easy for mass

production and applications. There are also some limitations to be overcome: the productivity of the complex structured fibers is limited; the poor mechanical property of the nanofibers is an issue; and the fabrication of single-crystalline nanofibers cannot be achieved by this approach, etc.

Fig. 3h shows some examples of electrospun TiO_2 nanofibers, ranging from solid fibers to single-channel and multiple-channel hollow nanofibers [144–146]. The solid fibers in Fig. 3h were fabricated by Kim *et al.* [144], by a method in which a yellowish precursor solution containing TTIP, acetic acid, and 4.5 wt.% polyvinylpyrrolidone (PVP) was put into the syringe placed at a 9-cm distance from the 15 kV charged collection substrate with a feeding rate of 0.5 mL h^{-1} . The diameter of the nanofibers was around 100–200 nm after heating at 450°C for 1 h. The single channel TiO_2 hollow nanofibers were prepared by simultaneous electrospinning of an ethanol solution containing PVP and TTIP, along with heavy mineral oil, from two coaxial capillaries. The feeding rate for the heavy oil was 0.1 mL h^{-1} , and the concentrations of the TTIP and PVP were 0.3 and 0.03 g mL^{-1} , respectively [145]. The collected fibers were calcined at 500°C in air. Multiple-channel TiO_2 nanofibers could be synthesized via either a multi-fluidic compound-jet electrospinning method or a microemulsion electrospinning approach [146]. In the former method, up to three inner nozzles are used for the formation of the multiple channels inside the nanofibers. The latter approach, however, has the advantage of avoiding the use of a complex spinneret through the formation of a water-in-oil emulsion inside the nanofibers.

SnO_2 nanofibers and nanotubes have been synthesized via electrospinning for application in dye-sensitized solar cells, gas sensors, batteries, etc. [147–149]. Krishnamoorthy *et al.* [147] developed a modified electrospinning set up with a multi-nozzle spinneret and a drum collector for the large-scale production of aligned SnO_2 nanofibers. The production efficiency is several times higher than with single-nozzle electrospinning. 1D ZnO nanostructures in the forms of nanofibers or hollow nanofibers could also be easily fabricated via the electrospinning approach [150,151]. Quasi-aligned hollow ZnO nanofibers were prepared by Choi *et al.* [150]. In contrast to the collector for preparing nonaligned nanofibers, two strips of aluminium wires were placed along the opposite edges of the substrate and connected to the ground terminal of the power supply, which imposed a directional distribution of electrical field flux lines between the nozzle and the aluminium wires, and facilitated the alignment of segments of the ZnO fibers across

the aluminium wires [150].

SYNTHETIC STRATEGIES FOR 2D METAL OXIDE NANOSTRUCTURES

Free-standing ultrathin 2D nanostructures are highly desirable for obtaining superior catalytic, photovoltaic, and electrochemical performances, due to their large surface-to-volume ratios and confined thickness on the atomic scale [152–162]. Strictly speaking, materials with few-layered atomic planes and 2D scalability should be called “2D crystals”, which can also be called as “ultrathin nanosheets” due to their appearance [163]. For example, the 2D carbon network—graphene—features extremely high carrier mobility, mechanical flexibility, optical transparency, and chemical stability, which provides a great opportunity for developing new electronic materials, novel sensors and metrology facilities, and superior energy conversion and storage devices [152–156]. Compared to the widely studied graphene and dichalcogenides, the ultrathin 2D transition metal oxide nanosheets have been relatively rarely studied, owing to the difficulties in the preparation of high quality 2D metal oxide nanomaterials.

At present, there are mainly three approaches to the fabrication of 2D metal oxide nanosheets, namely, liquid/chemical exfoliation of layered host materials, CVD growth, and wet-chemical self-assembly, as in the schematic illustration shown in Figs 4a–d [152–163]. Both the former two approaches start from bulk layered host materials to obtain low-dimensional nanomaterials; we usually call them forms of “top-down” synthesis. The latter two approaches start from molecules or atoms in solution or vapours, which are used to obtain low-dimensional nanomaterials and then high-dimensional nanomaterials, so we call these approaches examples of “bottom-up” synthesis.

Liquid exfoliation of layered materials

The exfoliation behaviour of layered compounds has been studied for more than 50 years, such as the mechanical exfoliation of smectite clay minerals in aqueous solution to obtain single layers of clay and the physical exfoliation of graphite into single layer graphene (Fig. 4a) [164,165]. The host materials, or the layered materials, which consist of 2D platelets weakly stacked to form 3D structures, such as graphite and MoO_3 , can be exfoliated into nanosheets in liquid, by oxidation, ion intercalation/exchange, or surface passivation by solvents. The biggest considerable advantage is that the liquid exfoliation allows the formation of nanosheets in a scalable way and may facilitate processing

Figure 4 Strategies for the synthesis of 2D metal oxide nanosheets: (a) mechanical exfoliation of layered host materials, (b) chemical intercalation induced exfoliation, (c) CVD growth, and (d) wet-chemical self-assembly; and the corresponding scanning electron microscopy (SEM) images of the 2D nanomaterials: (e) TiO₂ nanosheets synthesized via exfoliation (Reprinted with permission from Ref. [172], Copyright 2014, American Chemical Society), (f) VO₂ nanosheets synthesized via chemical intercalation (Reprinted with permission from Ref. [173], Copyright 2011, Wiley), (g) TiO₂ nanosheets synthesized via CVD growth (Reprinted with permission from Ref. [177], Copyright 2008, American Chemical Society), and (h) TiO₂ nanosheets synthesized via wet-chemical self-assembly (Reprinted with permission from Ref. [178], Copyright 2008, Nature Publishing Group).

by using standard technologies such as reel-to-reel manufacturing [160]. However, a number of substantial challenges remain. First, we cannot obtain nanosheets of the composites whose corresponding layered materials are absent. Second, the nanosheets obtained via this method usually have a huge deviation in thickness or stacking layers of monolayers. It is very difficult to control the quality of the products in a precise way.

Because the layered TiO₂ host materials have strong electrostatic interaction between the host layers, it is difficult to obtain single-layer TiO₂ nanosheets via direct physical exfoliation, unlike clay mineral, graphite, or dichalcogenides hosts. The synthesis of typical 2D TiO₂ nanosheets was first attempted by liquid exfoliation of the layered protonic titanate, H_xTi_{2-x}O₄·H₂O, by Sasaki *et al.* [166], in which the layered crystals were delaminated into single-layers by treating with tetrabutylammonium (TBA) solution. In detail, 0.025–1.0 g of H_xTi_{2-x}O₄·H₂O was

shaken at 150 rpm with 100 mL of TBA aqueous solution to form a stable colloidal suspensions, which was translucent or opalescent in appearance, depending on the titanate content. Thereafter, 2D TiO₂ nanosheets were synthesized by exfoliating different types of layered host materials such as Cs_{0.67}Ti_{1.83}O₄, H_{1.8}Bi_{0.2}CaNaNb₃O₁₀, Li_{0.5}TiO₂, K₂Ti₄O₉, and H₂Ti₄O₉ [167–171]. Fig. 4e presents the morphology of TiO₂ nanosheets exfoliated from a layered precursor: H_xTi_{2-x}□_{x/4}O₄·H₂O (□: vacancy, $x = 0.7$) [172].

The liquid exfoliation is usually a combination of intercalation of heteroatoms or molecules into the TiO₂ to form layered crystals, followed by subsequent swelling and delamination of the layered crystals into nanosheets. In particular, the intercalation of Li ions into layered materials to enlarge their interlayer spacing has been used for the preparation of atomic level 2D nanosheets, such as dichalcogenides and vanadium oxide (Fig. 4f) [173,174]. The direct synthesis of free-standing SnO/SnO₂

and ZnO ultrathin nanosheets via mechanical exfoliation or combined chemical intercalation and liquid exfoliation, however, has been rarely studied so far [175,176]. Machado *et al.* [175] synthesized bimodal ZnO nanostructures with ZnO nanosheet decoration by dodecylsulphate intercalation of zinc hydroxysalt, $\text{Zn}_5(\text{OH})_8(\text{DS})_2 \cdot m\text{H}_2\text{O}$.

The advantage of physical exfoliation or liquid exfoliation is that perfect crystalline single-layer nanosheets are easily obtained. Single-crystalline SnO nanosheets with exposed {001} facets have been prepared by ultrasonic aqueous synthesis combined with a liquid exfoliation process in the presence of PVP, which hinders the spontaneous formation of truncated bipyramidal SnO microcrystals. Instead, they are exfoliated into layer-by-layer hierarchical structures and then into separated SnO nanosheets [176]. The main drawbacks of these methods, as we have mentioned, are the low exfoliation efficiency, wide distribution of thicknesses, and non-homogeneous products.

Bottom-up growth of 2D nanosheets

Compared to the liquid exfoliation method, in which the lack of suitable layered host crystals has restricted the widespread fabrication of 2D metal oxide nanosheets, a generalized “bottom-up” strategy can provide a much more flexible way to synthesize ultrathin 2D nanosheets from vapours or liquid solutions. One typical bottom-up method for synthesizing 2D nanomaterials is the CVD, in which the volatile precursors are reacted and deposited layer-by-layer on substrates as 2D thin films. The CVD method allows the fabrication of high-quality 2D nanomaterials from compounds such as dichalcogenides and even carbides [154], although it seems unsuitable for fabricating perfect 2D nanosheets of metal oxides. Fig. 4g presents anatase TiO_2 nanosheets with exposed (001) facets fabricated via the CVD method by using TiCl_4 as the precursor and argon and oxygen as reaction gases [177]. The growth of TiO_2 nanosheets via this method, unfortunately, was not parallel to the substrate but in a vertical direction.

Quite recently, Sun *et al.* [178] developed a general approach to the molecular self-assembly or “bottom-up” growth of ultrathin 2D metal oxide nanosheets. As shown in Fig. 4c, metal oxide molecular precursors, amphiphilic block copolymers, and cosurfactants are mixed together. The hydrated inorganic oligomers are then confined inside the inverse lamellar micelles formed from the surfactants, leading to the formation of layered inorganic oligomer agglomerates. Hydrothermal or solvothermal treatment is then carried out to improve the organization and induce complete condensation and crystallization. Finally,

the well-crystallized ultrathin 2D transition metal oxide nanosheets are collected after the removal of the surfactant templates. In a typical synthesis protocol, Pluronic P123 ($\text{PEO}_{20}\text{PPO}_{70}\text{PEO}_{20}$, $M_w = 5800 \text{ g mol}^{-1}$) was dissolved in ethanol to form a transparent surfactant solution. To this solution, metal alkoxides or inorganic metal salts in the desired molar ratio were added under vigorous stirring. The resulting sol solution was then mixed with ethylene glycol (EG). Solvothermal treatment was then carried out on the as-prepared or the well-aged solutions to form crystallized metal oxide 2D nanosheets. Via this synthesis strategy, ultrathin 2D nanostructures of the typical transition metal oxides, such as TiO_2 , ZnO, Co_3O_4 , WO_3 , Fe_3O_4 , and MnO_2 , were successfully synthesized. Fig. 4h presents the typical morphologies of the ultrathin 2D TiO_2 nanosheets. An enhancement of the specific surface area of the obtained 2D nanosheets by 3–10 times higher than for the conventional nanoparticles was reported. This approach possesses the merits of homogeneous products (high quality), suitable for large-scale production (large quantity), and is appropriate for materials that do not have layered host crystals.

Besides the above graphene-analogous metal oxide nanosheets, some free-standing TiO_2 nanosheets with controlled exposed facets were synthesized based on an HF-assisted hydrothermal method. A typical example is the synthesis of TiO_2 nanocrystals with 47% exposed highly active {001} facets from hydrofluoric acid solution [179]. Thereafter, reports on research to maximize exposed high-energy facets of TiO_2 nanosheets increase dramatically [180–183].

The wet chemistry synthesis of SnO_2 nanosheets in the forms of either nearly free-standing nanosheets or agglomerates has been studied [184–187]. In a study by Sun *et al.* [188], SnO_2 nanosheets with five-atomic-layer thickness and (001) exposed facets were synthesized by the chemical reaction between $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and ethylenediamine at 180°C , and the specific surface area reached $173.4 \text{ m}^2 \text{ g}^{-1}$. Wang *et al.* [189] successfully synthesized ultrathin SnO_2 nanosheets with thicknesses of 1.5–3.0 nm from ethanol-water basic mixed solutions with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as the precursor after hydrothermal treatment at 120°C for 6 h. The specific surface area of the synthesized 2D SnO_2 nanosheets reached $180.3 \text{ m}^2 \text{ g}^{-1}$. It is also interesting that room-temperature ferromagnetism was observed in the as-synthesized SnO_2 nanosheets. Hierarchical 2D SnO_2 nanosheets were also grown on various substrates, such as nickel foams, Fe_2O_3 nanotubes, and carbon nanotubes (CNTs), via hydrothermal synthesis from SnCl_2 aqueous

solutions [190–193].

Square and rectangular ZnO nanosheets with thicknesses varying from 50 to 300 nm were prepared by a vapour-transport process, as reported by Chen *et al.* [194]. Zn metal grains were used as the source material. The Zn grains were etched by HF solution and washed, and then purged with N₂ in an air-tight tube. After heating at 600°C in pure O₂ for 2 h, white nanosheet powders were collected from the inside wall of the quartz tube.

SYNTHETIC STRATEGIES FOR ONE-STEP SELF-ASSEMBLY OF 3D METAL OXIDE NANOSTRUCTURES

3D nanomaterials represent spatial organizations of a group of 0D, 1D, 2D, or 3D nanomaterials [195]. Depending on the apparent morphologies, the free-standing 3D nanomaterials can appear in the forms of rods, cubes, spheres, hollow spheres, foams, hierarchical dendrites, spindles, etc. [196–198]. Compared to the bulk materials with similar overall size or the constituent nanostructures, the 3D nanomaterials usually have features that combine the merits of both materials, such as the quantum confinement effect brought by the constituent nanostructures and

the light scattering effect contributed by the larger overall size [196–198]. Wet-chemical synthesis is one of the most facile methods for the fabrication of 3D nanostructures, especially those with hierarchically-ordered subunits. The wet-chemical synthesis of 3D nanomaterials with complex configurations can be mainly divided into one-step self-assembly and two-step self-assembly. Fig. 5 shows the wet-chemical one-step self-assembly of 3D nanomaterials, which can be further classified as direct-growth and template-assisted growth [199].

Direct growth of 3D nanostructures

The direct growth of 3D nanomaterials refers to the synthesis of metal oxide aggregates with low-dimensional constituent nanostructures in well-defined shapes grown from the reaction solution in the absence of surfactants or templates, or grown by the vapour-liquid-solid (VLS) mechanism. The direct growth of 3D nanomaterials endorses the synthesis in a simplest way. The absence of surfactants and templates also avoids the contamination of samples. The arbitrary growth of nanomaterials, however, prevents the multi-scale tailoring of hierarchically-ordered nanostructures.

Figure 5 Wet-chemical one-step self-assembly of 3D nanomaterials, including (a) direct growth, (b) surfactant-assisted growth, (c) template-assisted growth, and (d) the corresponding SEM images of the fabricated 3D TiO₂ nanomaterials (Reprinted with permission from Ref. [199], Copyright 2016, Wiley).

Fig. 5a presents the schematic illustration of the direct growth of metal oxide in solution, in which the shapes of the nanostructures are governed by the anisotropic growth or the self-aggregation of the crystallites. As an example, TiO_2 microspheres composed of ordered single-crystalline TiO_2 nanorods were directly grown from a solution that only contained titanium alkoxide precursor, HCl or other acid reagents such as H_2SO_4 or acetic acid, and distilled water and/or ethanol via a hydrothermal reaction [200–202]. Fig. 5d (top) presents an SEM image of a TiO_2 dendritic structure with nanorod subunits fabricated via direct growth [199]. Mesoporous TiO_2 nanostructures including microspheres have also been directly hydrothermally/solvothermally synthesized from acetone/water mixed solutions [203]. TiO_2 microspheres or hollow microspheres with exposed mirror-like {001} facets were directly grown from F-containing solutions via hydrothermal synthesis [204,205].

The wet chemistry synthesis of 3D SnO_2 hierarchical nanostructures has been well documented in some quite recent review papers, in which the direct growth of SnO_2 nanostructures was summarized [206,207]. Zhang *et al.* [208] reported the direct growth of 3D SnO_2 dendrites with 1D nanorods as constituent nanostructures from a basic water-ethanol mixed solutions by using $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ as the precursor reagent. Hierarchical SnO_2 nanospheres were also synthesized from $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ aqueous solutions [209]. Vapour growth via a VLS mechanism is also an important approach to the fabrication of 3D hierarchical SnO_2 nanostructures. SnO_2 nanowire cross-linked networks were obtained by heating SnO powders at 700°C in flowing argon carrier gas and depositing the nanowires on sapphire substrates [210].

The direct growth of ZnO microspheres with nanorod or nanosheet constituents has been widely studied [211,212]. ZnO in the forms of nanoflowers, microdandelions, and microspheres with nanorod branches were synthesized via a template-free hydrothermal method, in which the morphology was controlled by adjusting the pH value of the reaction solutions [213]. Shi *et al.* [214] also synthesized hierarchical ZnO structures consisting of interconnected monocrystalline nanosheets using ultra-rapid sonochemical synthesis by directly adding 1 L $\text{Zn}(\text{NO}_3)_2$ solution into 1 L of NaOH under ultrasound irradiation, followed by mechanical stirring for 15 min. They also reported that ZnO microspheres with petal-like nanostructures were prepared by a surfactant-free approach for the first time from a mixed solution of heptanol and water with zinc acetate as the precursor reagent [215]. The addition of heptanol in this work,

however, should be as a kind of cosurfactant and it played the role of a structural agent. Hu *et al.* [216] also reported the synthesis of ZnO nanorod hollow microspheres without any structure-directing agents or templates, by adding $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ into 10 mL distilled water and 60 mL glycerol, followed by solvothermal treatment at 200°C for 12 h. Zhao *et al.* [217] synthesized ZnO microspheres composed of branches of nanorod from glycerol and isopropanol solvent. The role of glycerol in this glycerol-water system should also be as a cosurfactant and a kind of structure-directing agent. Zana [218] has reported that alcohols are the most commonly used cosurfactants, which are too weak to form stable micelles on their own, as well as some short-chain alcohols, such as propanol or 2-methyl-2-propanol, which behave in many respects like non-ionic surfactants. The alcohol-water mixed solutions, therefore, actually are similar to surfactant-water solutions to some degree.

Template synthesis of 3D nanostructures

The synthesis of 3D nanostructures with complex configurations, for examples, 3D dendritic microspheres with fine constituent nanostructures, mesoporous structures, and hollow microspheres with controlled constituent nanostructures, is possible with the help of surfactants and hard templates [219–221].

Fig. 5b shows a concept for fabricating 3D dendritic microspheres with 1D nanostructured radial branches. Sun *et al.* [197–199] proposed a hydrothermal method for synthesizing 3D dendritic TiO_2 microspheres with morphology-controlled constituent nanostructures by controlling the hydrolysis rate of the TTIP precursor during the hydrothermal process with the help of a short-chain alcohol cosurfactant and a pH reagent. In detail, the TiO_2 nanostructures were synthesized using a simple one-pot hydrothermal method: firstly, an aqueous TTIP solution was prepared by mixing TTIP, HCl, and CTAB in distilled water. Then, the aqueous solution was removed to an autoclave with an appropriate amount of EG, and urea was added in some cases. The ratios of aqueous TTIP solution (TTIP_{aq}) to the EG ($\text{TTIP}_{\text{aq}}:\text{EG} = 1:0, 1:1, 1:2, 1:3$) were adjusted to control the hydrolysis rate of the precursors and the aggregation structure of the surfactant. Urea was added as a slow-release basic reagent to adjust the pH value of the reaction solution. Fig. 5d (middle) presents the resultant 3D TiO_2 dendritic microspheres with fine nanowire constituents synthesized from the solution with $\text{TTIP}:\text{EG} = 1:1$ and containing 5 mmol urea. Rutile TiO_2 microspheres with exposed nano-acicular single-crystals were synthesized by mixing TiCl_4 , HCl, and toluene, and heating

this mixture at 170°C for 2 h [222]. Quite recently, hollow TiO₂ microspheres were studied extensively due to their superior performance in sustainable energy applications, such as lithium ion batteries and photovoltaics, which were synthesized by using either surfactants [223–225] or hard templates [226–228]. One typical example of hard template-assisted synthesis is the fabrication of mesoporous TiO₂-B microspheres, which were prepared by using silica as the hard template [226]. In the synthesis, colloidal silica was added into titanium bis(ammonium lactato) dihydroxide solution under stirring. The mixed solution was nebulized into small droplets and carried through a tube furnace at 600°C. The collected powders were then refluxed in NaOH solution at 100°C to remove the silica template.

Highly-ordered mesoporous structures are also a family of typical 3D nanostructures, which can be obtained from the solution containing surfactant with a content higher than its critical micelle concentration (CMC) or those we called as lyotropic liquid crystals (Fig. 5c) [110,199,221]. Fig. 5d (bottom) presents the mesoporous TiO₂ nanospindles synthesized with the assistance of CTAB surfactants [199]. Sun *et al.* [221] fabricated mesoporous TiO₂ thin films by using either Pluronic P123 or Pluronic F127 surfactant (PEO₁₀₆PPO₇₀PEO₁₀₆, $M_w = 12,600 \text{ g mol}^{-1}$). The mesoporous thin films with channels 10–13 nm in diameter have been demonstrated to be helpful to improve the solar energy conversion efficiency. Liu *et al.* [229] also reported the synthesis of 3D-open radially oriented mesoporous TiO₂ microspheres with single-crystal-like anatase wall by an evaporation-driven oriented assembly (EDOA) approach in a mixed solution containing Pluronic F127 surfactant, which gives an energy conversion efficiency of 12.1% when this material is used as the photoanode of dye-sensitized solar cells.

3D SnO₂ nanostructures in the forms of hierarchical nanostructures, microspheres, hollow boxes, hollow microspheres, and some core-shell structures have been synthesized with the assistance of surfactants and hard templates [230–236]. Recently, Dong *et al.* [237] reported the fabrication of multiple-shelled SnO₂ hollow microspheres by a sacrificial template method by using carbonaceous microsphere templates. Lou *et al.* [238,239] successfully synthesized SnO₂ microspheres and hollow structures such as nanospheres, nano-cocoons, and nanoboxes by utilizing SiO₂ and Cu₂O nanoparticles as hard templates, such as in the case of SnO₂ cocoons with movable α -Fe₂O₃ cores that were synthesized from SiO₂ coated α -Fe₃O₄ nanospindle hard templates [239]. Liu *et*

al. [240] also synthesized SnO₂ hollow cubes by using NaCl crystals as templates.

The well-controlled growth of hierarchical ZnO 3D nanostructures with the help of surfactants, such as block copolymer and PEI, and hard templates such as PS microspheres, has attracted wide attention, owing to their promising applications in photovoltaics, sensing, field emission, etc. [241,242]. Hierarchical hollow-shelled ZnO structures made of bunched nanowire arrays through a wet-chemical route were reported by Jiang *et al.* [243]. In this process, ZnO nanowires were nucleated and subsequently grown into nanowires on the surfaces of metallic Zn microspheres in strong alkali solution in the presence of zincate (ZnO₂²⁻) ions. The metallic Zn microspheres added here played the roles of Zn-resource and hard template. With the consumption of Zn during the synthesis process, the metallic Zn template disappeared and left a spherical cavity inside. By adjusting the reaction sources and synthesis temperatures, the ZnO microspheres in different aggregations and surrounding nanowires with diameters varying from hundreds of nanometers to around 10 nanometers were obtained. Alenezi *et al.* [244] grew 3D hierarchical ZnO nanowires on ZnO seeded Si substrates from initial ZnO nanostructures that were prepared by sequential nucleation and growth following a hydrothermal process with PEI as capping agent. Hierarchical ZnO nanowires in the form of “nanoforests” were synthesized by repeated immersion of seeded FTO glass substrates in aqueous solutions containing 25 mmol L⁻¹ zinc nitrate hydrate [Zn(NO₃)₂·6H₂O], 25 mmol L⁻¹ HMTA, and 5–7 mmol L⁻¹ PEI [245]. Elias *et al.* [246] reported the fabrication of 3D urchin-like ZnO nanostructured thin films by electrochemical deposition. In detail, a monolayer of commercially available carboxylate-modified PS microspheres was deposited directly on transparent conductive oxide substrates by using a self-assembly technique. Then, the PS microsphere covered substrates were immersed in aqueous solutions containing ZnCl₂ and KCl to allow electrodeposition at a constant potential. After removing the PS by toluene, urchin-like hemispherical arrays ~220 nm in diameter with nanowire constituents were obtained on the substrates.

SYNTHETIC STRATEGIES FOR TWO-STEP SELF-ASSEMBLY OF 3D METAL OXIDE NANOSTRUCTURES

Even though significant achievements have been made in the synthesis of isolated 0D, 1D, 2D, and 3D nanostructures in the last decade, the well-controlled synthesis of complex

nanostructures having both appropriately designed constituent nanostructures and well-defined overall shapes still remains a challenge. Two-step self-assembly has been proved to be an effective way to design multi-scale metal oxide nanostructures, where the designed constituent oligomers or nanostructured subunits are first formed from structure-defined surfactant micelles, and then the desired architectural units are assembled into the final structures with the addition of a cosurfactant [247–249]. The term “two-step self-assembly” was first proposed in 1985 by Yurchenko *et al.* [250] for the self-assembly of laminin into large polymers, in which the overall laminin self-assembly can be divided into two steps: an initial temperature-dependent, divalent cation independent step, followed by a divalent cation-dependent step. Compared to the conventional one-step assembly, the two-step assembly approach allows the combination of multiple synthetic techniques and the realization of complex nanostructures with hierarchically-ordered multiscale structures. Moreover, this approach also allows the self-assembly of heterostructures or hybrid nanomaterials in a cost-effective way [247].

In 2012, several structures of anatase TiO_2 , including nematic, spherulite, and lamellar phases, were obtained by a two-step assembly process to form different lyotropic liquid crystals in solution [251]. Primary self-assembly occurred in the synthesis process, and two structures were formed, with ribbon and honeycomb morphologies, respectively. Secondary assembly took place when the products were heated at lower temperature, where the final structures were obtained.

Very recently, Sun *et al.* [247–249] further developed the concept of two-step self-assembly of metal oxide complex nanostructures from one-pot solutions. Fig. 6a presents the concept of two-step self-assembly based on a good understanding of the phase diagram of a typical water-surfactant-cosurfactant system, i.e., the constituent nanostructured blocks are first synthesized from structure-defined surfactant micelles (the composition in area A), and then the desired architectural blocks are assembled into the final structures with the addition of oil that acts as a cosurfactant (composition B).

Figs 6b and c present examples of the fabrication of hollow ZnO microspheres with controlled constituent nanostructures with the forms of 1D nanowire networks, 2D nanosheets, and 3D mesoporous nanoballs [248,249]. The schematic illustrations in Fig. 6b show the difference between the traditional one-step self-assembly (first row), where the precursors are assembled into the final shape

Figure 6 Wet-chemical two-step self-assembly of metal oxide nanostructures. (a) Concept of two-step self-assembly based on a good understanding of the phase diagram of a typical water-surfactant-cosurfactant system, i.e., the constituent nanostructured blocks are first synthesized from structure-defined surfactant micelles (the composition in area A), and then the desired architectural blocks are assembled into the final structures with the addition of oil that acts as a cosurfactant (composition B) (Reprinted with permission from Ref. [247], Copyright 2013, Tsinghua University Press and Springer-Verlag Berlin Heidelberg). (b) Schematic illustrations and (c) the corresponding SEM images of the two-step self-assembly of hollow ZnO microspheres with controlled constituent nanostructures, varying from 1D nanowire networks, to 2D nanosheets and 3D mesoporous nanoballs (Reprinted with permission from Ref. [248], Copyright 2013, Royal Society of Chemistry).

directly, and the two-step self-assembly (second to fourth rows), in which the oligomers or the nanostructured building units are first assembled into the designed structures and then the constituent nanostructured units are self-organized into the final hollow spherical structures with the addition of a second cosurfactant. Fig. 6c shows the morphology of the hollow ZnO microspheres synthesized via either a one-step self-assembly method (first image) or the two-step self-assembly method (the second to fourth images). In the one-step self-assembly process, all the chemicals are put together according to the ratio of surfactant/water/alcohol in the micelle phase diagram to form inverse spherical micelles. The as-synthesized hollow

microspheres have very smooth surfaces with an overall diameter of $\sim 2.3 \mu\text{m}$. For the two-step self-assembled microspheres, the shells of the hollow microspheres consist of well-defined 1D nanowire networks, 2D nanosheets, and 3D mesoporous nanoballs. The introduction of well-defined sub-nanostructures in the 3D microspheres has been demonstrated to give the materials some unique properties, such as robust superhydrophobicity and enhanced visible light absorption, which opens up a new way to synthesize other novel metal oxide nanostructures and to improve the electrochemical performance of metal-oxide-based devices.

This concept was then used for the synthesis of fly-eye bio-inspired ZnO 3D nanomaterials, in which the three-zone structures were similar to the natural structure of biological compound eyes, including an outermost faceted microlens array, a middle rhabdom-like channel layer, and a central hollow zone [252]. In the synthesis, ZnAc_2 and Pluronic P123 were dissolved into the solvent to form primary lamellar micelles, and then EG was added into the solution to further assemble the primary structures into isolated spherical structures. During the crystallization process, lens-like nanostructures grew on the spherical surface to form fly-eye-like microspheres.

Jia *et al.* [253] reported the two-step self-assembly of 3D $\text{Fe}_3\text{O}_4/\alpha\text{-FeOOH}$ hollow microspheres with nanoneedle constituents. In a typical synthesis protocol, a certain amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in a mixture of deionized water and EG at room temperature. The concentration of the Fe^{2+} ions was 0.1 mol L^{-1} . After that, urea was added to the above solution at a concentration of 0.4 mol L^{-1} . After stirring for 10 min, the above solution was transferred into a conical flask with a stopper, heated at 100°C for 12 h, and then allowed to cool down to room temperature naturally. Liu *et al.* [254] also reported the synthesis of 3D CuO hierarchical microspheres with nanosheet subunits via a two-step self-assembly approach. The formation of CuO hierarchical microspheres involves two stages: tiny nanoplates are first attached side by side to form 2D nanosheets via an orientation attachment growth mode. Then, the as-formed sheets self-assemble in an orderly way, a radial alignment from the centre through a layer-by-layer growth style so as to form well-fined microspheres with a multilayered structure.

SUMMARY AND OUTLOOK

With the development of nanoscience and nanotechnology, nanomaterial morphologies have boosted the performance of various materials for applications in mi-

croelectronics, photoelectronics, catalysis, sustainable energy generation, transformation, conversion and storage, environmental technologies, etc. It is beyond question that the design of suitable nanostructures, which possess the necessary properties to suit particular functionalities, is still the most fundamental issue for the further advance of nanoscience and nanotechnology. This review article presents a comprehensive summary of the current status of the strategies for designing multi-scale metal oxide nanostructures, especially for the most studied wide-gap semiconductors, including TiO_2 , SnO_2 , and ZnO . The current approaches and technologies for fabricating the metal oxide nanostructures in different dimensions have been well documented and outlined to give an overall map to those who are interested in understanding nanomaterials.

The design of nanomaterials with the required properties, however, still faces a number of grand challenges. The emerging technologies have been increasing the demand for nanostructures with not only morphologies and sizes that are highly well-defined, but also controlled crystallinity, exposed surfaces, multiscale orderings, optimised coupling states, etc., which, in turn, require further substantial development of new synthetic strategies and theories. Therefore, the improvement of the existing synthesis methods and technologies, along with advancement of alternative fabrication processes, deserves substantial attention and investment in the near future.

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Conflict of interest The authors declare that they have no conflict of interest.

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金属氧化物纳米材料的设计与合成策略

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摘要 在过去十几年里, 纳米材料和纳米技术在新兴技术和新能源方面的应用获得了长足发展. 纳米材料由于其异于块体材料的独特性能完全改变了人们对材料性质的认识, 并且极大地提高了基于纳米材料的电子、催化、可持续能源转化与存储等元器件的性能. 纳米材料的性能随着材料形状、尺寸、以及维度的变化而改变, 因此, 纳米材料的合成与设计在合理使用与进一步提高现有纳米材料技术与功能材料性能上是至关重要的一步. 本综述总结概述了不同维度金属氧化物纳米材料, 尤其是以应用最为广泛的氧化钛、氧化锌和氧化锡为代表的纳米材料比较通行的合成方法与策略. 此外归纳了各类合成方法以及实验方案并分析了各方法中存在的优缺点. 通过对现行合成策略的纵览和理解, 我们期待能够进一步发展和优化出以性能为导向的纳米结构并进一步推动纳米科学和技术的发展与进步.