Morphology Control of Transition Metal Oxides by Liquid-Phase Process and Their Material Development[†]

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Abstract

It is well known that the functionality of inorganic materials strongly depends on the chemical composition, morphology, particle size, crystal facet, etc., which are strongly influenced by the synthesis process. The precise control of the synthesis process is expected to lead to the discovery of new functionality and improvement of the functionality of materials. For example, in a high-temperature solid-phase reaction, it is difficult to control the morphology of nanocrystals. On the other hand, synthesizing functional materials using solution processes, such as hydrothermal and solvothermal reactions, makes it possible to control the morphology and particle size precisely. Usually, the solution process is strongly related to the dissolution reprecipitation mechanism. Therefore, the material composition can be strictly controlled and is suitable for forming fine particles with high crystallinity. In this review paper, the role of the solvent in the solution process, its effect on particle size and morphology of the transition metal oxide, and the related functional improvement will be focused. Furthermore, the direct formation of functional thin films by the solution process and the morphology control by non-oxide materials by the topotactic reaction will also be introduced.

Keywords: morphological control, liquid phase synthesis, transition metal oxides, thin films, IR light response

1. Introduction

It is known that the functionality of inorganic materials strongly depends on the chemical composition of the materials, particle morphology and size, specific surface area, crystal structure, crystal facet, etc. In order to realize functional control of inorganic materials, precise control of the synthesis process is important. Until now, while there are many materials synthesis processes, liquid phase reaction uses liquid solvent as a reaction medium and carries out the reaction in a sealed pressure reaction vessel (autoclave) is called a hydrothermal or solvothermal reaction. Not only the temperature but also the pressure control of the reaction system, together with the use of additives, the particle morphology and size of the product, crystal structure, crystal plane, crystallinity, etc. can be efficiently controlled. Therefore, it has been accepted that the hydrothermal or solvothermal processes show great potential for improving the functionality of various materials, and offer many applications such as non-toxic pigments, photocatalysts, ultraviolet rays, and infrared shielding materials etc. (Cao et al., 2022; Guo et al., 2010; Hermawan et al., 2021; Taufik et

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al., 2020; Xue and Yin, 2022; Yin, 2015; Yin and Asakura, 2019). The liquid phase reactions proceed under mild conditions compared to high-temperature methods such as solid-phase reactions, which are environmentally friendly. They are expected to be effective for the industrial synthesis of materials. Usually, electric furnace heating is used for traditional hydrothermal and solvothermal reactions. Using a microwave irradiation heating method becomes a complex chemical reaction field, resulting in a quickly synthesizing process for nano / micro functional materials, generating a metastable crystal phase, suppressing crystal growth, etc. (Liu et al., 2012). In addition, for oxide materials, elements replaced by cations and anions in the material will significantly change their physical and chemical properties, and it is expected that new functionality of the material will be discovered, and the functionality of materials will be dramatically improved (Cao et al., 2022; Kageyama et al., 2018; Zhao et al., 2017). It is possible to synthesize oxides and nitrides with different morphologies and sizes via a topotactic method, using the precursors with controllable morphology and particle size synthesized from the solution process. It is expected that some novel material functionality could be found because of their unique morphologies (Hermawan et al., 2018b; 2020; Yin et al., 2012). Furthermore, the liquid phase method could directly prepare powder materials and functional thin films (Yin and Sato, 2005). In this review paper, some examples



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will be introduced in detail from the viewpoint of particle morphology control and functionality control.

Composition, morphology, and functional control by a solution reaction process Hydrothermal and solvothermal reactions

A chemical reaction that occurs in the presence of hot water at a temperature above 100 °C and high pressure of more than 1 atm is called a hydrothermal reaction. It is said that it was initially developed by geology-related scientists in the former Soviet Union to study the mechanism of mineral formation, and to imitate the high-temperature, high-pressure reaction environment similar to that of underground magma. Since the 1980s, it has been used as a new method for synthesizing inorganic functional materials, and has made remarkable progress. Depending on the type of chemical reaction, the hydrothermal process is divided into five categories: hydrothermal oxidation, hydrothermal synthesis, hydrothermal precipitation, hydrothermal decomposition, and hydrothermal crystallization (Somiya, 1984). In recent years, hydrothermal reactions have come to be used not only for inorganic materials but also for organic synthesis. Instead of a water solvent, various organic solvents can be used as reaction solvents for the mentioned liquid-phase reactions. Among them, when liquid ammonia is used as a solvent, it is called amonothermal (Hertrampf et al., 2018). When using glycol or ionic liquid as a solvent, it was called glycothermal (Zhu et al., 2020) or ionothermal (Jaleel et al., 2022). A liquid phase reaction using various solvents containing water is universally referred to as a solvothermal reaction. Compared to high-temperature methods such as solid-phase reactions, many solvothermal reactions can synthesize materials in a relatively low-temperature range of around 200 °C and a low-pressure range with little energy consumption. In addition, some post-processing processes such as calcination or pulverization can be omitted after the solvothermal treatment. So, it is an environmentally friendly synthesis method and could be classified as a soft chemical process (Byrappa and Yoshimura, 2012).

Many solvents in solvothermal reactions have change-

able physical and chemical properties due to temperature and pressure changes, resulting in different reaction environments by simple condition changing (such as temperature, pressure, pH, additives, etc.). In general, solvothermal reactions produce particles by a dissolution-reprecipitation mechanism, in which the existence of water molecules significantly affects the crystalline growth of the products (Sato et al., 1998).

Fig. 1 shows the dependence of the dissolution reprecipitation mechanism in the liquid phase reaction and the particle size dependence of oxides material synthesized in water or organic solvents. The water solvent has a high dielectric constant of 78.3, resulting in an environment with a low supersaturation and the particles tend to grow larger. In contrast, in organic solvents such as ethanol (EtOH), the dielectric constant is low as 23.8, the dissolution ability of the solvent is limited, and the supersaturation degree is high. In this case, instead of particle growth, nuclei are easy to generate, and many fine particles tend to be produced simultaneously, leading to the formation of fine particles with less agglomeration. When water is used as a solvent, the particle size grows relatively large, and hard agglomeration can be observed because of hydrogen bonding in the solution. On the other hand, when the organic solvent methanol or ethanol is used, less agglomeration could be observed. As the proportion of water in the water-ethanol mixture solvent increases, a tendency can be observed that the particle size of the oxide to be produced tends to increase. This behavior is strongly related to the existence of water, which can be reasonably explained by the dissolution-reprecipitation mechanism (Sato et al., 1998).

2.2 Composition, crystal phase control, and functionality of titanium dioxide

Semiconductor titanium oxide photocatalytic materials can effectively utilize solar energy and realize environmental purification, self-cleaning, etc. Generally, oxide semiconductor photocatalysts have a large band gap and can only be excited by ultraviolet rays. Therefore, it is essential to provide a visible light response from the viewpoint of improving the efficiency of solar energy. In order to realize



Fig. 1 (A) Dissolution reprecipitation mechanism in liquid phase reaction system, (B) Water-methanol ratio and particle size dependence of produced oxide (inserted TEM photographs: oxides produced by (a) solvothermal reaction, and (b) hydrothermal reaction).





Fig. 2 (A) TEM images, (B) Raman spectra and (C) photocatalytic deNOx photocatalytic activity of $TiO_{2,x}N_y$ powders with different phase compositions selectively synthesized by solvothermal reaction at 190 °C for 2 h in (a) $TiCl_3$ -HMT aqueous solution at pH 1, (b) $TiCl_3$ -HMT aqueous solution at pH 9, (c) $TiCl_3$ -HMT methanol solution at pH 9; ((a) anatase (\square); (b) rutile (∇); (c) brookite (\bullet); (d) P-25, standard photocatalyst Degussa P-25)). [Part of the figure is reproduced from Ref. (Yin et al., 2005) with permission from the RSC]

the visible light activity of titanium oxide-based photocatalysts, anion-doping is an effective way (Asahi et al., 2001; Kageyama et al., 2018; Zhao et al., 2017), and so far, RF (high frequency) magnetron sputtering, ion implantation, partial oxidation of non-oxide titanium compounds are utilized as the methods for doping anions on titanium oxide. Usually, it requires high-temperature treatment, expensive precursors synthesized in a high-temperature atmosphere, large-scale equipment, etc., and it cannot necessarily be said that they are environmentally friendly. The synthesis of anion-doped oxides by solvothermal reactions can be realized in a solution around 200 °C. Various crystal phases can be selectively synthesized, and no post-treatment is required, and anion dopants or dopants such as nitrogen, sulfur, and fluorine can be realized in one step (Cao et al., 2022; Yin et al., 2005; Yin and Asakura, 2019). In a typical synthesis process, a titanium compound (TiCl₃) is introduced in urea or hexamethylenetetramine (HMT) aqueous solution, followed by hydrothermal/solvothermal treatment at 190 °C. By controlling the reaction temperature, solvent and pH, it is possible to selectively synthesize three representative nitrogen-doped polymorphs of titanium oxide, i.e., anatase, rutile, and brookite phases as a single phase. All the nitrogen-doped titanium oxides possessed excellent light absorption and excellent NO_x removal (deNO_x) photocatalytic activity under ultraviolet and visible light irradiation (see Fig. 2) (Yin et al., 2005).

In general, titanium oxide is widely used as a photocatalyst and white pigment. Adding various transition metal elements is usually utilized to improve the functionality of the photocatalyst and realize the coloring of inorganic white pigments. However, in many cases, crystalline defects are produced due to metal ion doping, hindering photocatalytic activity improvement. In addition, due to the toxicity of transition metal ions, safety risks are concerned when they are used as raw materials for cosmetics, etc. Applying mixed ions doping makes it possible to synthesize colorful titanium oxide without using transition metals except for titanium (Cao et al., 2022). It is known that titania possesses yellow color when nitrogen is doped at the oxygen site of the titania and shows gray color when the boron element is doped. When nitrogen and boron are co-doped, the band gap is further reduced, and absorption in visible light becomes remarkable. At that time, various colors can be realized by changing their crystal phase. The presence of slight differences in the levels of the original valence bands of anatase, rutile, and brookite results in the formation of the colorful titanium oxide, such as red, cyan, and yellow-green can be realized. This result indicates that titanium oxide can be used as a colorful inorganic pigment, which is non-toxic without any other transition metal addition (Cao et al., 2022).

2.3 Morphology and functional control of zinc oxide

Zinc oxide possesses a hexagonal structure and has piezoelectric properties. Z.L. Wang et al. reported the morphology control of zinc oxide by a high-temperature sublimation method and various unique morphologies such as nanowires, nano-plates, nano-combs, nano-rings,



nano-springs, etc. can be synthesized (Wang, 2005; Wang and Song, 2006). In particular, the concept of nanogenerators using piezoelectric ZnO nanowires significantly impacted the world. On the other hand, in the high-temperature sublimation method, since the generated morphology differs depending on the temperature of the substrate in the electric furnace, it is difficult to ensure complete uniformity of the morphology because the substrate temperature changes a little with their position in the furnace. Therefore, it is challenging to realize the scale-up of the products. On the other hand, the solution process can cover the disadvantages of the high-temperature sublimation method and is also suitable for product scale-up. When slowly crystallized in a low-concentration solution, zinc oxide tends to grow according to the *c*-axis direction. While, when the ion concentration increases, nucleus formation accelerates and tends to become fine particles. Therefore, it is usually challenging to synthesize spherical microparticles with low anisotropy. In the solution process, various factors such as solvent, precursor type and concentration, reaction temperature and time, and various additives significantly affect the zinc oxide crystal growth and particle morphology.

When various alcohol solvents were utilized, zinc oxide with different microstructures, such as symbiotic nanorods, radial symbiotic nano-screws, and incomplete crystals, was obtained. It seems to be because solvents with different dielectric constants have different solubilities on zinc ions, affecting the precipitation rate in the dissolutionreprecipitation process. **Fig. 3** shows the SEM photographs of various representative particle morphologies that successfully synthesized the solution process under different synthesis conditions. The ZnO tends to produce rod-like particles by growing in the c-axis direction (Fig. 3(a)(b)(f)(j) etc.) (Long et al., 2009a; Yin and Sato, 2005). When ethylene glycol was used, the morphology was significantly different from that obtained in ordinary alcohols. A mono dispersion rod-like structure with a low aspect ratio is successfully obtained. In all cases, the size of the particles was relatively uniform. By controlling the amount of ethylene glycol additive, it was possible to get the rod-like morphology with a precisely controlled aspect ratio. Furthermore, using different precursors makes it possible to realize a significant change in morphology. For example, when zinc chloride is used, plate-like zinc oxide can be synthesized (Fig. 3-(c)). It is because zinc oxide particles (Fig. 3-(c,d)) exhibiting plate-like or nutlike morphologies are generated through layered structure precursors such as simoncholeite, by taking in chloride ions and acetate ions into the products. The plate-like precursor can be decomposed by heat treatment while their morphology remains maintained, and converted to oxide with a similar morphology by the topotactic reaction (Long et al., 2009b). Spherical particles are ordinarily difficult to synthesize with high yields (Long et al., 2010a; 2010b). As an additive, the triethanolamine could be utilized to synthesize uniform spherical microparticles (Fig. 3(e)). Also, the as-prepared zinc oxide particles are further annealed in hexamethylenediamine (HMT) solution for more than 72 h. In that case, the microstructure of the particle surface is significantly changed by the dissolution reprecipitation reaction, resulting in the formation of developed unique surface morphologies, such as screw-shaped, hollow nut,



Fig. 3 SEM images of the zinc oxide particles with various morphologies synthesized by solution reaction process. (a) 0.01 M ZnNO_3 -HMT (95 °C, 3 h), (b) 0.05 M ZnNO_3 -50 %EG-HMT (95 °C, 12 h), (c) 0.05 M ZnCl_2 -50 %EG-HMT (95 °C, 12 h), (d) $0.05 \text{ M Zn(CH}_3\text{COO}_2$ -50 %EG-HMT (95 °C, 12 h), (e) 0.025 M ZnNO_3 -Diethanolamine-HMT (95 °C, 3 h), (f) post heat-treatment (a) in HMT solution for 72 h, (g) post heat-treatment of (d) in HMT solution for 72 h, (h) post heat-treatment of (e) in HMT solution for 72 h (i) 0.025 M ZnNO_3 -50 %EG-HMT (95 °C, 3 h), (j) 0.001 M ZnNO_3 -75 %EG-HMT (95 °C, 24 h), (k) 0.001 M ZnNO_3 -Urea (95 °C, 3 h), (l) microwave-hydrothermal reaction at 190 °C for 10 min, with mono-ethylamine additive. [Part of the figure is reproduced from Ref. (Long et al., 2010a) with permission from Springer Nature]





Fig. 4 Photoluminescence spectra of ZnO crystals with different morphologies.

rose-shaped, with a large specific surface area (Fig. 3(f-h)) (Long et al., 2010a; 2010b). In addition, when urea was used as a precipitating agent, the effect of CO₂ gas produced by hydrolysis reaction resulted in the formation of unique flower-shaped particles (Fig. 3(k)).

In the microwave-assisted hydrothermal and solvothermal process, instead of the electric furnace heating, irradiating a microwave with a frequency of 2.45 GHz equivalent to that of a microwave oven is utilized. The products can be obtained in a short period of heating. In the reaction field to which 2.45 GHz microwave irradiation is applied, a large amount of crystal nuclei are produced rapidly due to the fast temperature rise affecting the reaction product generation behavior. Also, it is possible to synthesize metastable crystal phase and unique morphologies of products that are difficult to be obtained by normal hydrothermal reaction (Liu et al., 2012). As shown in **Fig. 3(i)**, zinc oxide synthesized by microwave-assisted hydrothermal reaction has a petal-like morphology with uniform particle size.

The morphology and microstructure of zinc oxide particles change significantly in the solution. It depends on the solubility of zinc ions in the solvent, the rate of reprecipitation, and differences in ion adsorption ability on the surface of zinc oxide crystals. Therefore, some physicochemical properties related to their particle morphology are expected. For example, all the ZnO can be excited by 325 nm light irradiation, and a peak of near-ultraviolet emission of 390 nm can be observed. It was also observed that different particle morphology results in different luminescence properties with a clear morphological dependence (Long T. et al., 2010a; 2010b), and the emission intensity shows the sequence of bud-like > rod-like > flower-like > nut-like (see Fig. 4) (Long et al., 2010b).

2.4 Homogeneous particle morphology and functional control of cerium oxide

Similar to the plate-like zinc oxide synthesis process, pre-

cursors' topotactic morphological transcription techniques can be used to control the morphology of other inorganic compounds. For example, in the case of cerium oxide, spherical-like, rod-like, and plate-like cerium compound precursors can be successfully synthesized by applying a room-temperature aging process before a normal homogeneous precipitation reaction at 70 °C. Then, the precursors are decomposed to produce cerium oxide by heat treatment. As a result, the topotactic reaction can successfully synthesize a spherical, rod-like, plate-like cerium oxide. Under typical synthetic conditions, a 0.008 M aqueous solution of cerium (III) nitrate is mixed with a 0.5 M aqueous urea solution and aged at room temperature (25 °C) for 0 h, 72 h, 144 hours, followed by heating the aged solution at 70 °C for 2 hours. The cerium carbonate-based precursors with different morphology, spherical-like, rod-shaped, and plate-like, were obtained under different room temperature aging times. The size of the seed crystal generated at the initial stage changed depending on the room temperature aging time, thereby changing the shape of the grown crystal at the evaluated temperature process. Finally, similar morphologies of cerium oxides could be obtained by the following heat treatment at 400 °C (Yin et al., 2010).

It has also been found that cerium carbonate precursors having a larger plate-like size can be synthesized at room temperature by a simple solution process (Yin et al., 2012). In a typical thesis process, 5 mL of 1.0 M trivalent cerium nitrate solution was slowly added into a 45 mL 0.33 M-0.45 M sodium hydrogen carbonate/sodium carbonate mixed solution. Then, the precipitate slurry is kept in a constant temperature water bath of 25 °C for 24 hours, followed by filtration and washing, then drying at 60 °C overnight to obtain a single crystal of plate-like cerium carbonate octahydrate. After calcination at 400 °C for 1 h, the plate-like cerium oxide particles could be synthesized with similar plate-like morphology to that of the cerium carbonate single crystal. Fig. 5 shows the SEM, TEM images, crystal structure, and morphologies changing process of the plate-like cerium carbonate octahydrate precursor. Since cerium carbonate octahydrate precursor has a layered structure, plate-like morphology is easy to be formed. In the early stages of the reaction, nucleation is first carried out, then the crystal growth proceeds to create the plate-like morphology, and the plate-like particles gradually become larger. At about 30 min of reaction time, an apparent plate-like crystal is formed. As the time is further extended, tiny crystals coexisting dissolve progressively, and the cerium ions gather on the surface of the large crystals and gradually become larger, because of the Ostwald ripening mechanism. The spiral growth of crystals was also observed in some cases. The as-prepared plate-like cerium oxide particles possess high gloss derived from their large plate-like particle size and also show good slipperiness and suppressed oxidation catalytic activity, indicating its





Fig. 5 Typical (a) SEM and (b) TEM image (insert SED pattern) and (c) the layered structure of $Ce_2(CO_3)_3 \cdot 8H_2O$ projected on the a-b and a-c planes of the plate-like cerium carbonate hydrate single crystal synthesized in 0.1 M $Ce(NO_3)_3$ and 0.3 M NaHCO₃ mixed solution. (d) Mechanism of crystal-line formation and crystalline growth. [Reproduced from Ref. (Yin et al., 2012) with permission from the RSC]

potential applications as new functional cosmetics (Minamidate et al., 2010; Yin et al., 2012).

2.5 Novel water molecule control release solvothermal process (WCRSP) for the synthesis of uniform nanomaterials

Usually, a simple solvent such as water or alcohol is used in the conventional solvothermal reaction. In this case, particle growth and agglomeration are easy to occur. By controlling the dielectric constant of the solvent and introducing some additives, it is possible to control the number of crystal nuclei and the crystal growth rate of particle formation, which is effective for synthesizing fine particles with good dispersibility. Also, the particle morphology can be precisely controlled by using a surface surfactant as an additive. Since the slight amount of water in the solvent significantly affects crystal growth, further precise control of the synthesis process is required to synthesize monodispersed nano-sized uniform particles. Here, a novel solvothermal process, denoted "Water Controlled-Release Solvothermal Process (WCRSP)" is designed to synthesize the particle with homogeneous morphologies.

The WCRSP uses a mixture of alcohol and carboxylic acid as a reaction solvent and skillfully utilizes the water produced by the esterification reaction between alcohol and carboxylic acid at high temperatures. The released water molecules amount in the reaction solvent can be precisely controlled by changing the ratio of the starting alcohol and carboxylic acid solvents. The released water amount significantly affects the crystal growth of the products. In principle, changing the composition of solvents will result in different water amounts in the reaction system, finally affecting the particle size and morphology of the products. Therefore, the WCRSP process can be utilized for controlling particle size and morphology because the water molecular is slowly released, and the reaction environment can be kept in a constant state, resulting in the formation of homogeneous particles size and morphology (Guo et al., 2010; 2011d; 2013a).

Fig. 6 shows the principle and reaction mechanism of the WCRSP process. There are three key points in the WCRSP process. First, water is not the starting solvent in the reaction, but carboxylic acids and alcohols are used. At high temperatures, the esterification reactions proceed, and water molecules are produced and released in the reaction system; Second, the number of water molecules can be previously controlled by controlling the solvent composition; Third, the subsequent reaction should be a hydrolysis reaction. In some cases, the release of water molecules is also possible by etherification between various alcohol molecules. Still, in the case of esterification using carboxylic acids and alcohols, the control of water molecules is efficient. When the reaction temperature rises, the reaction between or among the liquid solvents such as ethanol (C₂H₅OH), n-butanol (C₄H₉OH), and acetic acid (CH₃COOH) is carried out. The self-dehydration of ethanol, n-butanol and the cross-dehydration between different organic molecules are carried out. Also, the reaction



with acetic acid produces ethyl acetate $(CH_3COOC_2H_5)$ or n-butyl acetate $(CH_3COOC_4H_9)$, at the same time releasing a certain amount of water molecular (Gao et al., 2019). Therefore, an increase in the reaction temperature benefits the formation of ether.

In the case of titanium oxide formation, tetra-*n*butyl titanate $(Ti(OC_4H_9)_4)$ or titanium tetraisopropoxide $(Ti(OC_3H_7)_4)$ are utilized as a titanium source, acetic acid (CH_3COOH) and various alcohols are used as a solvent. The mixture is sealed in a 100 ml Teflon-lined stainless autoclave and reacted under a hydrothermal reaction at 200–240 °C for 24 h. The typical chemical reactions are shown in Eqns. (1) & (2):

$$R_1$$
-COOH + R_2 -OH $\rightarrow R_1$ -C-O- R_2 + H_2 O (1)

$$\mathrm{Ti}(\mathrm{OC}_{4}\mathrm{H}_{9})_{10} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{TiO}_{2} + 4\mathrm{C}_{4}\mathrm{H}_{9}\mathrm{OH}$$
(2)

$$Nb_2(OC_2H_5)_{10} + 5 H_2O \rightarrow Nb_2O_5 + 10C_2H_5OH$$
 (3)

The esterification reaction of carboxylic acids and alcohols produces esters and water molecules. The water

molecule produced by Eqn. (1) is utilized in the hydrolysis reaction with tetra-n-butyl titanate of Eqn. (2), and finally, titanium oxide is synthesized. The number of water molecules produced can be controlled by controlling the ratio of carboxylic acids and alcohols. Furthermore, using various alkoxides makes precise composition control of the products possible. For example, the Nb-doped titanium oxide (NTO) can be synthesized by introducing the desired amount of a niobium alkoxide (Nb₂(OC₂H₅)₁₀) into the titanium alkoxide to realize the composition control, as shown in the reaction of Eqn. (3) (Asakura et al., 2018).

Fig. 7 shows the TEM images of the 15 % Nb-doped TiO_2 particles (NTO) synthesized in the solvents with various ethanol: acetic acid (*x*:*y*) ratios. The produced and released water amount increases with the acetic acid amount increment in the solvent. As mentioned in **Fig. 1**, during the dissolution-reprecipitation process, water as a solvent with a large dielectric constant prefers to enhance crystalline growth, resulting in large particle size. As a result, less



Fig. 6 Principle and reaction mechanism of the WCRSP for TiO_2 formation in ethanol and acetic acid solution (TsOH (*p*-toluenesulfonic acid) is an acid catalyst that acts as a reaction-promoting catalyst, and the reaction can proceed without using it.) [Reproduced from Ref. (Gao et al., 2019) with permission from the IOP].



Fig. 7 TEM image of 15 % Nb-doped titanium oxide particles (NTO (*x:y*), *x*:ethanol (ml); *y*:acetic acid (ml)) synthesized by WCRSP in an acetic acid-ethanol mixed solvent. (a) NTO(60:0), (b) NTO(55:5), (c) NTO(50:10), (d) NTO(40:20), (e) NTO(35:25), (f) NTO(30:30). [Reproduced from Ref. (Asakura et al., 2018) with permission from the IOP]

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acetic acid in the WCRSP produces less water, leading to the formation of the tiniest particles, as shown in Fig. 7(a). When the ethanol: acetic acid ratio reaches 30:30 (i.e., 1:1), the most significant amount of water is produced, leading to the formation of the large particles, as shown in Fig. 7(f).

Another example is the mixed-valence state tungsten bronze structure $M_x WO_3$ (x = 0.33, M = Cs, Na, K, etc.), in which alkali metal ions are doped into the W site tungsten. The mixed-valence state tungsten base compound possesses high free electron density. It is expected to be applied to various new functional materials such as infrared shielding materials, transparent conductive materials, etc. Conventionally, M_xWO₃ is synthesized by solid-state reaction, and a high temperature of above 1000 °C is required. Usually, high reaction temperature results in a large product particle size. Also, morphological control is quite challenging. (Takeda and Adachi, 2007). Similar to that of Nb-TiO₂, the influence of the solvent is also obvious for the synthesis of $M_{0.33}WO_3$. Fig. 8 shows the SEM images of the M_rWO_3 (M = Cs, K, Na) obtained by the solution process. The Cs ion has a large ionic radius and is difficult to dope with high concentration. The maximum Cs doping amount is about 1/3, forming a tunnel structure with a hexagonal phase (x = 0.33). In a traditional hydrothermal synthesis process, a single phase of Cs_{0.33}WO₃ can be successfully produced; however, the particle growth is remarkable, and the particle size reaches large than 500 nm (Fig. 8-(a)) (Liu et al., 2010).

$WCl_6 + 3H_2O \rightarrow WO_3 + 6HCl$ WO ₃ + xCsOH + x/4 C ₂ H ₅ OH	(4)
$\rightarrow Cs_x WO_3 + x/4 CH_3 COOH$	(5)

On the other hand, by using the WCRSP process under the esterification reaction, the number of released water molecules can be precisely controlled. As a result, the single phase of M_xWO_3 with rod-like uniform morphology can be successfully obtained. Eqn. (4) shows that tungsten oxide is first generated, tungsten oxide further reacts with CsOH, the presence of alcohol also serves as a reducing agent. Finally, a part of tungsten is reduced, and the mixed-valence state Cs, WO₃ is generated (Eqn. (5)). Because of the continuously released small amount of water in the reaction system, the particle growth due to the dissolution reprecipitation is suppressed. As a result, the particle size can remain small, producing Cs_{0.33}WO₃ nanorods with a length of 90 nm and a diameter of 10 nm (Fig. 8(b)) (Guo et al., 2010; 2011d), which is about 1/5 or less of the size of that prepared by normal hydrothermal process (500 nm) (Liu et al., 2010). The tungsten bronze structure Cs, WO₃ has a hexagonal phase structure shown in Fig. 8(c). In the cases of smaller ions such as sodium and potassium being utilized instead of cesium, the nanowire morphology (Guo et al., 2010; 2011a; 2011c; 2011d) with long length and tetragonal structure will be produced (see Fig. 8(d-f)). The small particle size of the mixed-valence state possesses many benefits such as excellent IR shielding properties, less light scattering resulting in high transparency, and ease of being introduced in cells for bio-applications. The related results will be introduced in the following.

Similarly, in the WCRSP process utilizing alcohols and carboxylic acids as solvents, it is possible to synthesize and control the morphology of various other oxide particles. **Fig. 9** shows various successful synthesized examples with unique particle morphologies. By using the WCRSP process, TiO₂ spherical particles with different sizes (Guo et al., 2013a), unique octahedron attached (Ta,N)-TiO₂ fibers, SnO spherical/hollow particles, plate-like, Moyatto ball-like, and tailed-shaped $W_{18}O_{49}$ particles, etc. are successfully synthesized by using different precursors (Guo et al., 2012a; 2012d; Yin et al., 2018). All the particles possess uniform and unique morphology. Therefore, the WCRSP method can be used as a general-purpose synthesis way. In



Fig. 8 (a) SEM photograph of $M_{0.33}WO_3$ by traditional solvothermal reaction, (b) TEM image of monodisperse $Cs_{0.33}WO_3$ nanorods synthesized by WCRSP process using ethanol and 10 % acetic acid as reaction solvents (90 nm in length, 5–10 nm in diameter); (c) Hexagonal crystal structure of $Cs_{0.33}WO_3$ (d) SEM image of Na_xWO_3 , (e) TEM image of K_xWO_3 nanowire; (f) crystal structure of tetragonal M_xWO_3 , (M = K, Na). [Reproduced from Ref. (Guo et al., 2011a; 2011d, Liu et al., 2010) with permission from the RSC, Elsevier, ACS]





Fig. 9 Uniform oxide particles with controllable morphology synthesized by WCRSP. (a) TiO_2 spherical particles, (b) Fibrous (Ta, N) $-\text{TiO}_2$ with the octahedral structure on the surface together with high specific surface area; (c) SnO spherical particles; (d) SnO hollow particles; (e) Plate-like WO₃ particles, (f) Moyatto ball-like W₁₈O₄₉ particles (using W(CO)₆ as a precursor), (g) W₁₈O₄₉ (using W(EtO)₆ as a precursor). (h) W₁₈O₄₉ (using WCl₆ as a precursor). [Part of photos are reproduced from Ref. (Guo C. et al., 2012a; 2012d; 2013a; Yin S. et al., 2018) with permission from the RSC, ACS]

addition to ethanol, a series of higher alcohols such as butanol, ethylene glycol, and higher carboxylic acids such as acetic acid, butanoic acid, hexanoic acid, and octanoic acid is available as a reaction solvent and expected to be applied for the synthesis of various kinds of uniform inorganic functional particles with unique morphologies.

Fig. 10 shows the schematic illustrations of the simulated experiment and temperature increment during the halogen lamp irradiation, together with the transmittance and reflectance spectra of Cs, WO3 nanorods and ITO glass. Again, the Cs, WO₃ film shows a better temperature depress effect than those of ITO. The mixed-valence state tungsten bronze compounds $M_{y}WO_{3}$ (M = Cs, Na, K, etc.) have high free electron density. The free electrons move back and forth between W⁵⁺ and W⁶⁺, resulting in an absorption of light corresponding to the vibration of electrons, leading to infrared light absorption. The tungsten bronze M_xWO₃ is comparable with tin-doped indium (ITO) transparent conductive oxide film. The MrWO3 can cover a more comprehensive infrared shielding range, realize excellent IR light-shielding properties over a broad infrared region than ITO conductive thin films, and show great potential as a smart window.

In order to improve visible light transparency and functionality of thin films, it is effective to reduce light scattering by using nanosize particles. The M_xWO_3 particles synthesized by the WCRSP show a tiny size of about 20 nm, and light scattering is suppressed when a thin film is formed, resulting in high transparency. Furthermore, the resistance of the pressed powder reached 0.03–0.96 ($\Omega \cdot cm$), suggesting its potential as a conductive material (Guo et al., 2012c). In addition, the nanowire morphology



Fig. 10 (a-c) Schematic illustrations of simulated experiment and (d) temperature increment during the halogen lamp irradiation for 1 h. Sealed boxes were covered by quartz glass, Cs_xWO_3 coated quartz glass, and ITO glass (10 Ω/sq .). (e) Transmittance and reflectance (R-a, R-b, R-c) spectra of Cs_xWO_3 nanorods and ITO glass (5 Ω/sq . and 10 Ω/sq .), The background shows the relative energy wavelength distribution of solar spectrum on the sea level. [Reproduced from Ref. (Guo et al., 2011b; 2011d) with permission from the RSC]



of M_xWO_3 (M = K, Na) shown in **Fig. 8(c,d)** possesses a low interparticle resistance so that it can realize better conductivity than nanoparticles (Guo et al., 2011c; 2012c). Some other tungsten bronze materials, such as (NH₄)_xWO₃ and W₁₈O₁₉ with a reduced tungsten valence state, also consist of mixed-valence state of W⁵⁺ and W⁶⁺. These compounds also contain free electrons and excellent infrared light-shielding properties (Guo et al., 2012b; 2012d; 2013b).

Fig. 11 shows the correlation between the particle size of $W_{18}O_{19}$ and the infrared shielding property. The $W_{18}O_{49}$ is also one of the mixed-valence state tungsten-based materials with a monoclinic crystal structure. As the particle size decreases, it can be confirmed that the infrared light-shielding property has been improved. It is thought to be due to the polaron effect on the surface of the $W_{18}O_{49}$ particles. In the $W_{18}O_{49}$, W^{5+} and W^{6+} are reversed due to the electrons' movement. It leads to the surface charge

revision of tungsten ions next to each other. As a result, free electrons cause plasmon oscillations on the surface of tungsten in the mixed-valence state, shielding light with energies lower than the infrared wavelength without passing through. The larger the surface of the particles, the stronger the polaron effect is considered to appear (Guo et al., 2012d). On the other hand, since WO₃ is not a mixed-valence state substance, it cannot cover the light in the infrared region and has no infrared shielding property.

In addition, uniform $Cs_{0.33}WO_3$ nanoparticles can successfully be introduced into cancer cells by hydrophilic surface treatment using a PEG-silane coupling agent. The effect of the temperature rise under irradiation with a 980 nm infrared laser (0.07 Wcm⁻²) is confirmed, suggesting that $Cs_{0.33}WO_3$ nanoparticles may be utilized as a new hyperthermia treatment material for cancer cells (Guo et al., 2013b). Fig. 12 shows the temperature increment effect under IR light irradiation, with and without hydrophilic



Fig. 11 (A) SEM image of spherical $W_{18}O_{49}$ with different particle sizes; (B) Transmission spectrum (infrared shielding characteristics) of $W_{18}O_{49}$ samples; (C) Infrared light shielding mechanism of $W^{5+}W^{6+}$ mixed-valence state tungsten-based compounds. [Reproduced from Ref. (Guo et al., 2012d) with permission from the ACS]



Fig. 12 (a)Temperature increment thermographic images and (b)temperature distribution profile with/without $Cs_{0.33}WO_3$ nanorods ((c) TEM image) dispersed in simulated culture solution PBS, under infrared light irradiation for 2–12 min. (d) Efficient temperature increment by controlling the concentration of nanoparticles and irradiation time. [Reproduced from Ref. (Guo et al., 2013b) with permission from RSC]



 $Cs_{0.33}WO_3$ nanoparticles introduced in the pseudo-culture medium PBS. An efficient temperature increment effect can be observed by controlling the concentration of $Cs_{0.33}WO_3$ nanoparticles and the IR light irradiation time. The cancer cells take in excess nutrition, and blood vessels are often incomplete. It is difficult to transport decomposed products in blood; therefore, lactic acid accumulates and shows the property of being vulnerable to temperature. As a result, the cancer cells are more susceptible to heat than normal cells.

IR light possesses a deep reach distance in the human body and causes minor damage to normal cell tissues. By incorporating $Cs_{0.33}WO_3$ nanoparticles into cancer cells and exposing them to infrared light irradiation, it is possible to selectively kill cancer cells that can reach a temperature range above 42 °C under IR light irradiation. In order to efficiently introduce the nanoparticles that absorb infrared rays into the cancer cell, it is necessary to produce a uniform morphology and small particle size, so the WCRSP process shows its effectiveness and great potential for practice bio-applications.

2.6 Direct formation of functional thin films by solution reaction

Some vapor synthesis methods, such as vapor deposition, CVD, sputtering, etc., are usually used for thin-film formation. In the above cases, external energy such as high vacuum, high frequency, and a high electric field is required for these synthesis processes. On the other hand, as a method of forming a thin film starting from a powder material, pressure molding method, doctor blade method, spin coating method, or using the powders sintering body or powder casting body as a target for sputtering are widely utilized. Furthermore, as a novel thin-film synthesis method, the direct film formation of oxides is also possible using a solution process. Here, an example of the direct formation of a zinc oxide particle film is introduced.

In Section 2.3, it was introduced that the zinc oxide particles with various morphologies can be synthesized in the aqueous zinc nitrate solution with the addition of a specific concentration of hexamethylenetetramine (C₆H₁₂N₄, HMT). A glass substrate was introduced into the reaction system during the synthesis process. Not only the zinc oxide particles are produced in the solution, but a uniform thin film could also be precipitated on the surface of the glass substrate directly. The mentioned liquid-phase reaction can synthesize a relatively durable oxide particle film. Furthermore, the nanostructure of the zinc oxide particle film changed significantly by a long-term aging process treatment, similar to that of the formation process of rose-like particles. Fig. 13 shows the hydrophilicity evaluation results and surface morphology of particle films synthesized by the solution process. The contact angle of water drop on the surface of the zinc oxide single crystal (001) plane was 93°. However, the zinc oxide particle film with nanorod morphology shows a contact angle of 165°, indicating a super-water repellency of the surface. In contrast, the ZnO particle thin film with developed nano-screw morphology shows a complete opposite property. The water drop on the ZnO surface shows a contact angle of 0°, showing super hydrophilicity. Interestingly, the same material of ZnO with quite different morphologies can achieve the opposite super hydrophilicity and superhydrophobicity (Long et al., 2010b; Yin and Sato, 2005). The unique microstructure of zinc oxide thin films is thought to depend on the solubility



Fig. 13 (Upper) Top view CCD image of water drop on various surfaces. (a) ZnO single crystal (001) surface; (b) superhydrophobic surface of ZnO film with nanorod superstructure; (c) super hydrophilic surface of ZnO film with the nano-screw superstructure; (Middle) Side view CCD images (Evaluation of contact angle / hydrophilicity); (Bottom) SEM and TEM images of (b) nanorods and (c) nano-screws. [Reproduced from Ref. (Yin and Sato, 2005) with permission from the RSC]





Fig. 14 (Left) Formation process and SEM image of $TiO_{2,x}N_y/ZnO$ oriented tube structure composite thin film; (Right) Excellent transparency and conductivity of ZnO film consisting of hexagonal nanorods oriented on the substrate.

of zinc ions in the solvent, the dissolution-reprecipitation rate, differences in ion adsorption capacity at different zinc oxide crystal surfaces, etc.

This zinc oxide morpho-regulatory method can also be used to realize new functionality by combining it with other functional materials. Combining high photocatalytic active nitrogen-doped titanium oxide with developed nanostructured zinc oxide particle thin film is an exciting combination. The thin film of $TiO_{2-x}N_{y}$ on a glass substrate is prepared by a spin coating method at first, and then the film is set in a Zn(NO₃)₂-HMT solution to precipitate a ZnO complex film at 95 °C. In another case, orientated ZnO nanorods are grown on the TiO2. Ny surface, then leached by alkali solution to produce a complex tubular ZnO structure (Fig. 14 (left)). The complex structure of ZnO or tubular ZnO possesses excellent adsorption properties, which can accelerate the photocatalytic reaction on TiO₂, N₁, The complex structures of the ZnO / tubular ZnO thin films also have a fantastic light-limiting effect. The irradiated light can be reflected inside the complex structure or tubular structure to achieve multiple irradiations on the TiO₂, N₂, photocatalytic surface (Huang et al., 2012; Yin et al., 2008).

In addition, in order to get a high-quality and dense ZnO thin film, another seed crystalline method is utilized. At first, ZnO nanoparticles less than 10 nm are prepared and coated in advance on the surface of a glass substrate by a spin coating method. Then, the as-prepared thin film is introduced in a Zn(NO₃)₂-HMT solution to precipitate a ZnO complex film at 95 °C. The nano-sized crystals on the substrate act as seeds during the following precipitation process. It is found that zinc oxide-oriented dense film that grew uniformly in the *c*-axis direction can be synthesized perfectly (Fig. 14 (right)). The hexagonal columnar rods are arranged in the same direction, making it possible to be a dense ZnO thin film in which only the {002} surface of zinc oxide is exposed. Because of the highly orientated crystal growth with high density and less porosity, such high transparency of 81.2 % and excellent conductivity of 9.68×10⁻² Ω ·cm are successfully realized, indicating its potential applications on transparent oxide conductive thin film.

2.7 Morphological control and functional improvement of non-oxide by topotactic reaction

Transition metal nitrides and oxynitrides have been focused on their novel functionality, and their importance has been recognized. By replacing the oxygen site of oxides with an anion having a different electronegativity, the material's electronic structure will be significantly changed, and the discovery of some novel physical and chemical properties is expected (Kageyama et al., 2018). Usually, the synthesis of transition metal nitride and oxynitride requires a high temperature, and its morphology control is difficult. As mentioned above, the solution process has the merits of particle size and morphological controllability so that the oxide could be utilized for the synthesis of the morphology controllable nitrides and oxynitrides. At first, hydrothermal or solvothermal reactions synthesize morphologically controlled metal oxides or hydroxide precursors. Then, these precursors are utilized to synthesize the non-oxide materials with similar particle morphologies and sizes by topotactic reactions under relatively low and mild reaction conditions. This method provides a possibility to synthesize nitrides and oxynitrides with controllable morphologies. For example, under hydrothermal conditions, aluminum hydroxide y-AlOOH (boehmite) with a nest-like or plate shape morphologies can be synthesized by controlling the reaction temperature, pH, and adding a surfactant. By using these aluminum hydroxides as the precursor, it is possible to synthesize aluminum nitride with different morphologies such as plates, fibers, nanosize, etc., by treating the mentioned precursors in ammonia gas. However, if the nitridation temperature is too high, the morphologies of the oxide precursor may collapse. During the nitridation treatment, a small amount of hydrazine addition can accelerate the nitridation reaction and reduce the nitridation temperature and time (Hermawan et al., 2020).

Fig. 15 shows the SEM photographs of boehmite and





Fig. 15 (a) Topotactic morphology conversion from AlOOH (left column) to AlN (right column); (b) sintering behavior of AlN particles with different morphology; (c) Hydrogen gas response properties of morphologically controlled AlN. [Reproduced from Ref. (Hermawan et al., 2018b; 2020) with permission from the Springer & Taylor]

nitrides with various morphologies. The sintering performance and hydrogen gas sensing properties of nitrides with various morphologies are also characterized. It is suggested that such topotactic reaction could realize the morphology control of non-oxides materials. Furthermore, the morphological dependence of functionality of the nitrides is observed. As shown in Fig. 15(b), the sintering properties of nitrides with different particle morphologies are significantly changed. However, the plate-like particles are easily arranged in the same direction and could be sintered at relatively low temperatures. Furthermore, aluminum nitride having a plate-like morphology, showed a superior hydrogen gas sensing functionality compared to aluminum nitride with other morphologies (Hermawan et al., 2018b). Also, in the case of α-GaOOH precursor, the same topotactic reaction enables the synthesis of nitrides (GaN) with the same morphology of oxides (β -Ga₂O₂). Therefore, it is found that the GaN possesses better hydrogen gas sensing sensitivity than that of β -Ga₂O₃ with the same morphology (Hermawan et al., 2018a).

3. Future outlook

The morphology control of various transition metal oxide materials and their functionality development are reviewed. This paper focuses on the synthesis process and the relationship between morphologies and their functionalities. Hydrothermal and solvothermal processes are environmentally friendly processes that provide the possibility for morphologies and particle size control. Water molecules are essential in promoting the dissolution-reprecipitation process and significantly affect the particle morphologies and size. The utilization of esterification reactions between various alcohols and carboxylic acids (WCRSP process) allows uniform morphologies and controllable particle size. Furthermore, the effectiveness of morphological control using the topotactic reaction is confirmed. The oxides and non-oxides with unique morphologies show many applications, such as photocatalysts, ultraviolet/heat ray shielding, cancer cell hyperthermia treatment, hydrophilic/ hydrophobic thin films, and gas sensor, etc. Different novel functionality can be realized by morphological control, material design, and the optimization of their synthesis processes, and further research and progress are expected in the future.

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