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Abstract

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Morphology tuning of inorganic nanomaterials grown by precipitation through control of electrolytic dissociation and supersaturation

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Abstract

The precise control of the morphology of inorganic materials during their synthesis is important yet challenging. Here, we report that the morphology of a wide range of inorganic materials, grown by rapid precipitation from a metal cation solution, can be tuned during their crystallization from one- to three-dimensional (1D–3D) structures, without the need for capping agent or templates. This control is achieved by adjusting the balance between the electrolytic dissociation (α) of reactants and the supersaturation (S) of solutions. Low- α weak electrolytes promoted the growth of anisotropic (1D and 2D) samples, with 1D materials favoured in particular at low S . In contrast, isotropic 3D polyhedral structures could only be prepared in the presence of strong electrolyte reactants ($\alpha \approx 1$) with low S . Using this strategy, a wide range of materials were prepared, including metal oxides, hydroxides, carbonates, molybdates, oxalates, phosphates, fluorides, and iodate with a variety of morphologies.

Materials with well-defined microscopic and nanoscopic morphologies hold great promise for various practical applications, for example in catalysis, batteries, semiconductors, supercapacitors,

hydrogen storage, and magnetic and optical devices¹⁻⁵. These can be tuned to some extent by traditional synthesis methods, such as the hydro- or solvothermal method, preformed-seed-mediated growth strategy, polyol approach, template method, and electrochemical synthesis, but those are not ideal for large-scale commercialization because they typically require complex equipment, the use of toxic solvents, and time-consuming high-temperature or high-pressure processes⁶⁻¹⁰.

A variety of inorganic materials can also be obtained through a straightforward precipitation process. This growth method is widely used and generally well-understood¹¹⁻¹², but the rapid reaction rates involved make it difficult to precisely control the morphologies of the resulting products. We carried out a systematic study to explore precipitation processes carried out in a variety of electrolytes with different degrees of dissociation, to better understand the chemical driving force of the precipitation process and in turn precisely regulate the concentration of the reactants in solution to promote the precipitation of the desired species. Tuning two factors, the supersaturation (S) of solutions and the electrolytic dissociation (α) of reactants, enabled the control of morphologies from 1D to 3D during the rapid, room-temperature crystal growth.

S is widely known to significantly influence the surface engineering of crystals¹³. Theoretically, for each specialized material, the concentration of the desired ions in the solution determines the S by the following equation:

$$S = \sqrt[2]{\frac{C_M \times (C_{DA})^\delta}{K_{sp}}} \quad (1)$$

where C_M and C_{DA} represent the concentration of metal cations and dissociated reactant anions, respectively, δ is the number of ions in the material's formula unit, and K_{sp} is the solubility product constant¹⁴⁻¹⁵. This means that regulating the concentration of ions is crucial in thermodynamic growth¹⁶. Meanwhile, it is believed that both thermodynamic and kinetic effects influence the processes of precipitation through steps such as pre-nucleation, nucleation, and growth¹⁷⁻¹⁹. Organic surfactants have been commonly used to obtain kinetic control over orientated nanocrystal growth by selective adhesion effects along the organic-inorganic interface²⁰. Nevertheless, without the aid of capping agents and templates, controlling the evolution of crystallization by precipitation is not well understood and extremely challenging.

Here, we show that the judicious choice of reactants enables the successful synthesis of a series of precipitates with elaborate morphologies. We describe in particular the growth of various materials with adjustable morphologies through a rapid room-temperature precipitation process, including 1D metal hydroxides ($M(OH)_2$, $M = (Co, Mg, Mn, Zn)$), $Cu_2(OH)_2SO_4$, metal carbonates (MCO_3 , $M = (Co, Ba, Sr)$), BaF_2 , CoC_2O_4 and $BaMoO_4$; 2D metal hydroxides ($M(OH)_2$, $M = (Co, Ni, Mg, Mn, Zn)$), $Cu_2(OH)_2SO_4$, $Co_2S(OH)_2$, $Ca_3(PO_4)_2$, $Cu_2(Fe(CN)_6)$, $CoCO_3$, $BaMoO_4$, $Ca(OH)_2$, and BaF_2 ; and 3D metal hydroxides ($M(OH)_2$, $M = (Cu, Co, Mn, Mg, Ca)$), $CaCO_3$, BaF_2 , CuC_2O_4 , $BaMoO_4$, and $Ca(IO_3)_2$. Based on our study of a variety of conditions, we propose that the use of strong electrolytes ($\alpha \approx 1$), such as $NaOH$, NaF , and Na_2MoO_4 , is imperative to achieve isotropic growth and produce various 3D precipitates. In contrast, when the precipitation was carried out using weak electrolytes ($\alpha \ll 1$), such as NH_4OH , NH_4HF_2 , and $CO(NH_2)_2$, the process could be tuned to form either 1D rod-like or 2D nanosheet structures. In this case, lower S favors the formation of 1D nanostructures, whereas higher S typically promoted 2D morphologies.

Results and discussion

Synthesis of tunable inorganic materials

In a typical synthesis, an aqueous solution containing metal cations (such as $Co(NO_3)_2 \cdot 6H_2O$) was first prepared. Another solution of an appropriate precipitant (such as NH_4OH) was then added at room temperature, under stirring at the rate of 300 rpm. The desired precipitation products (such as in this case $Co(OH)_2$ nanosheets) were immediately obtained. Reactants with different α were used; the dissociation equilibrium is shown in Equation (2),

$$\alpha = C_{DA}/C_R \quad (2)$$

where C_{DA} and C_R represent the concentration of dissociated anions and the concentration of reactant, respectively.

Typically, a strong electrolyte ($\alpha \approx 1$) could instantly release sufficient ions and lead to fast nucleation and a high growth rate for precipitation. For a weak electrolyte ($\alpha \ll 1$), the gradual release of target ions is expected to slow down the kinetics of nucleation and growth²¹. Thus, reactants with different α values can precisely regulate the concentration of desired ions and simultaneously manage to achieve appropriate S , which plays a critical role in obtaining various

products according to their solubility product constant (K_{sp}). Additionally, it is well known that the size of crystallites decreases with increasing S , which is mainly governed by the nucleation process.

For materials with high K_{sp} , precipitation occurs in a solution with low saturation, which indicates that 3D isotropic growth is very favorable. In the case of BaF_2 , when a strong electrolyte NaF/F^- (reactant/dissociated anions) ($\alpha \approx 1$) was used as precipitant, a supersaturated solution with $S = 70$ rapidly formed, which results in the formation of 3D polyhedra (Fig. 1aI). In contrast, the evolution of BaF_2 from isotropic to anisotropic, achieved by using NH_4HF_2 instead of NaF , indicates that the presence of the weak electrolyte is another factor (besides the control of supersaturation) that can provide a kinetic driving force to support an anisotropic growth as well. The use of weak electrolyte NH_4HF_2/F^- ($\alpha = 0.165$) leads to the formation of 1D rod-like structures from a solution with $S = 12.4$ and 2D nanoplate structures through a quick anisotropic growth process in a solution of $S = 40$ ($\alpha = 0.32$) (Fig. 1aII and III). It is notable that BaF_2 could further transform from 1D to 2D (Supplementary Table 1) on increasing the supersaturation S by using weak electrolytes with a relative high α . The manipulation from 3D to 1D for high- K_{sp} materials is simple, because it is relatively easy to tune a slightly supersaturated environment (Fig. 1a).

On the other hand, for low- K_{sp} materials such as metal hydroxides ($Co(OH)_2$, $MnOOH$) (Supplementary Table 1), the solution is saturated so quickly that a high number of nuclei of the precipitates are generated. The solution with a high supersaturation causes a high chemical potential, which is converted as surface energy of crystallites via the Thomson–Gibbs equation.¹³ The high surface energy is responsible for the extremely high nucleation rate during a short-time crystallization, leading to the formation of small, irregular particles, where the morphology is hard to control. In particular, when strong electrolytic $NaOH$ was selected as reactant, the corresponding metal hydroxides solution had extremely high S ($S_{Co(OH)_2} = 222,887$), leading to the formation of aggregated small irregular particles (Supplementary Fig. 1). In order to form 3D regular nanostructures, the solution should therefore exhibit low supersaturation to decrease the reaction rate on nucleation and thus achieve isotropic crystal growth into regular shape. An effective technique to resolve this problem is to decrease the concentration of metal cations, for example by using $CoCO_3$, MgF_2 , $MnCO_3$, and Cu_2O_4 as metal ion sources instead of $Co(NO_3)_2$, $Mg(NO_3)_2$, $MnSO_4$, and $CuSO_4$, respectively. This is because these salts ($CoCO_3$, MgF_2 , $MnCO_3$, and Cu_2O_4) are only slightly soluble, so that they can only provide very limited concentrations of

metal ions, leading to relatively low supersaturation and the formation of 3D polyhedra. As shown in Fig. 1(b-f)I, 3D polyhedral products (BaMoO_4 , $\text{Mg}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, MnOOH , $\text{Cu}(\text{OH})_2$) are successfully obtained. Similarly, suitable weak electrolytes can be used to produce 1D and 2D nanostructures for those low- K_{sp} samples. Lower supersaturation results in the formation of 1D BaMoO_4 , $\text{Mg}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, MnOOH , and $\text{Cu}_2(\text{OH})_2\text{SO}_4$, respectively (Fig. 1(b-f)II). Higher supersaturation is responsible for the corresponding 2D morphology (Fig. 1(b-f)III). For example, urea with low- α ($\alpha = 2.25 \times 10^{-6}$) leads to the growth of 1D $\text{Cu}_2(\text{OH})_2\text{SO}_4$ (Fig. 1fII), and in turn, NH_4OH with relatively high α ($\alpha = 2.68 \times 10^{-2}$) facilitates the formation of nanosheets of $\text{Cu}_2(\text{OH})_2\text{SO}_4$ (Fig. 1fIII).

These results indicate that the α of reactants and S of solutions play key roles in shape control. Specifically, only a strong electrolyte could lead to the formation of 3D anisotropic growth. In contrast, the weak electrolytes are favorable to achieve 1D or 2D isotropic growth, in which the evolution from 1D to 2D could be controlled by increasing S , which, in turn, is determined by selecting relatively high- α electrolytes. The values for α and S induced materials, including BaF_2 , BaMoO_4 , $\text{Mg}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, MnOOH , and $\text{Cu}_2(\text{OH})_2\text{SO}_4$, are summarized in Fig. 1(a-f)IV. For example, the value of $\log_{10}(\alpha)$ of 3D- BaF_2 tends to 0, which means that $\alpha \approx 1$, indicating that the strong electrolyte can release its F^- anions quickly, while 1D and 2D BaF_2 have much lower $\log_{10}(\alpha)$ values. This is the most common principle of evolution from anisotropic to isotropic structures, that is, strong electrolytes tend to promote the formation of 3D samples, while the weak electrolytes can be used for the synthesis of isotropic materials. This pattern can also be seen in these other materials, including BaMoO_4 , $\text{Mg}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, MnOOH , and $\text{Cu}_2(\text{OH})_2\text{SO}_4$. Moreover, we observe that increasing S promoted a change of morphology from 1D to 2D for all materials.

To further explore the generality of this issue, more 1D samples, including BaCO_3 , CoCO_3 , CoC_2O_4 , $\text{Zn}(\text{OH})_2$, and SrCO_3 (Fig. 2a-d, Supplementary Fig. 2), were successfully prepared by using various complexes with low α , such as $\text{CO}_2/\text{CO}_3^{2-}$ (considering that CO_2 gas can continuously provide soluble CO_3^{2-} , which is similar to a weak electrolyte), $\text{NaHC}_2\text{O}_4/\text{C}_2\text{O}_4^{2-}$, and $\text{Na}_2\text{SO}_4/\text{OH}^-$. Also, 2D nanosheets, such as from metal hydroxides ($\text{M}(\text{OH})_2$, $\text{M} = \text{Ni}$, Zn , metal sulfide hydroxides ($\text{Co}_2\text{S}(\text{OH})_2$), and metal phosphate ($\text{Ca}_3(\text{PO}_4)_2$), were synthesized in high S by using $\text{NH}_4\text{OH}/\text{OH}^-$, $\text{CH}_3\text{COONa}/\text{OH}^-$, and $\text{Na}_2\text{HPO}_4/\text{PO}_4^{3-}$ (Fig. 3e-h). The TEM images of representative 2D materials show rolled-up edges and wrinkled structures, indicating ultrathin

materials⁸. The thickness of typical materials, such as Ni(OH)₂ and MnOOH, is only ~ 10-14 Å, corresponding to approximately four-atomic layers, as shown by both HRTEM and atomic force microscopy (AFM) images (Supplementary Fig. 3). These 2D crystals with atomic thickness show enhanced intrinsic properties and expanded utilization beyond what is possible with the bulk materials²².

Furthermore, the low-magnification scanning electron microscope (SEM) images of various low-dimensional materials confirm that this facile approach could achieve high quality and excellent uniformity of anisotropic products (Supplementary Figs. 4 and 5). The elemental mapping analysis of representative 1D and 2D samples demonstrates that the expected elements are uniformly distributed within their corresponding morphologies (Supplementary Figs. 6 and 7). More specifically, the 1D materials formed in a solution with low S are found to grow into single crystalline form with a dominant direction, but polycrystalline samples are formed for 2D materials obtained in a high- S solution (Supplementary Fig. 8); thus, the electronic structure of precipitates could be tuned to realize variable crystalline structures and band gaps via selecting α in relation to S (Supplementary Figs. 9-11). Meanwhile, the X-ray diffraction patterns of these 1D, 2D, and 3D materials can be indexed to their corresponding crystalline phases (Supplementary Figs. 12-14), confirming the formation of diverse products. Similarly, with strong electrolytes, such as NaOH/OH⁻, Na₂MoO₄/MoO₄²⁻, and Na₂CO₃/CO₃²⁻, the resultant precipitates are prone to exhibit 3D isotropic polyhedral morphology, including Ca(OH)₂, CaCO₃, CuC₂O₄, and Ca(IO₃)₂ (Fig. 3i-l) in a slightly saturated solution. These 3D materials show different polyhedral morphologies, such as spheres, cuboctahedra, cubes, octahedra, and dodecahedra.

Balance between electrolytic dissociation and supersaturation

To further investigate the mechanism, the calculated values of $\log_{10}(S)$, $\log_{10}(\alpha)$, and $-\log_{10}(K_{sp})$ applied in selected materials with different dimensions are summarized in Fig. 3a (Supplementary Table 1). From the projected image of $\log_{10}(S)$ vs. $-\log_{10}(K_{sp})$, the supersaturation S of 1D materials is separated from that of the 2D materials by the critical threshold of supersaturation. Compared to 2D materials, the 1D materials are prone to grow in a solution at lower supersaturation, which is achieved upon the synchronous with low α , such K_{sp} (Fig. 4b). Also, according to the projected image of $\log_{10}(\alpha)$ vs. $-\log_{10}(K_{sp})$ (Fig. 3c), isotropic (3D) structured materials are located at the top

near to the $\log_{10}(\alpha)$ value 0, but anisotropic (1D and 2D) structured samples have relatively low $\log_{10}(\alpha)$, which indicates that low α determines the anisotropic growth. Moreover, as summarized in Fig. 3d and Supplementary Fig. 15, the S tuned by α is the most critical factor to determine the specific 3D morphology, in which $S_{\text{irregular particles}} > S_{\text{spheres}} > S_{\text{polyhedra}}$; for instance, CaCO_3 polyhedra (Fig. 2j) could be tuned into spheres by increasing S from 56 to 154 (Supplementary Fig. 15). More specifically, the evolution amongst multiple dimensions has been simulated in Supplementary Fig. 16a and b, which indicates the morphologies distribution of various materials (different K_{sp}) with 1-3D edges tuned by S and α , respectively. This process can be confirmed by preparing the mixture of 2D and 1D $\text{Cu}_2(\text{OH})_2\text{SO}_4$ through using relatively high- α aniline to replace urea (Supplementary Fig. 16 and Fig. 1fII).

Formation mechanisms

The formation processes of various morphologies are illustrated in Fig. 4a. For the weak electrolytes, once the precipitation reaction between reactant anions and metal cations occurs, the non-equilibrium environment of a weak electrolyte serves as a chemical driving force to trigger the release of new anions from the reactant and induce the outward-migration for continuous growth of precipitation. Also, the cycle of achieving re-equilibrium of a weak electrolyte based on α can provide a consistent kinetic driving force to support the orientated expansion of growth. Specifically, when a low- S solution is achieved, the material is favorable to be a slow epitaxial growth, leading to 1D morphology (The green reacting path). When a weak electrolyte is relatively strong and can release more anions during dissociation process, a high- S solution can be realized with a larger saturated region, which can support 2D growth rather than 1D growth. (The orange reacting path). In contrast, strong electrolyte-based reactants with $\alpha \approx 1$ can completely release the precipitant anions all at once, which results in the absence of a chemical driving force formed within the period of growth, so that the materials uniformly grow on each axis and are prone to form 3D isotropic morphologies. In particular, when the solution is controlled with a low S , the precipitates can have regular shapes with relatively slow growth rate rather than irregular small particles if in high- S condition. Thus, when selecting different weak electrolytes as anion-releasing solutions, the reaction solutions can be regulated to achieve different degrees of S , leading to 1D-crystal growth for a low- S solution and 2D structure in a high- S solution, respectively. By contrast,

the strong electrolytes enable the formation of 3D regular crystals in a low- S solution. This approach was successfully extended to the synthesis of different complexes with anisotropic structure, including 1D $\text{Cu}(\text{OH})_2$ and 2D $\text{Cu}_2(\text{Fe}(\text{CN})_6)$ (Supplementary Figs. 17-19). This precipitation strategy, based on adjusting S relatively to a , represents a universal way to tune 1D, 2D, and 3D morphologies for a wide range of materials.

More importantly, this approach is a flexible way to explore diverse unique nanostructures by virtue of various auxiliary conditions. The growth of $\text{Ca}(\text{OH})_2$ materials can be tuned to form either polyhedra (Fig. 2i) or nanoflakes by changing the sequence in which reactants are added. When adding $\text{Ca}(\text{CH}_3\text{COO})_2$ into NaOH , the dissociation equilibrium of $\text{Ca}(\text{CH}_3\text{COO})_2$ can be interrupted by OH^- and work as a weak electrolyte, continuously releasing Ca^{2+} as a kinetic driving force. Meanwhile, the mixed solution shows high S , generated very quickly at the interface of the growing material by the high concentration of OH^- . Like the reaction mechanism illustrated in Fig. 4b, the two factors jointly lead to favorable 2D growth into nanoflakes. (Supplementary Fig. 20).

We found that the mechanical driving force also influences the growth of the materials. For example, by increasing the stirring rate, the morphology of $\text{Co}(\text{OH})_2$ with NaOH as precipitant changes from aggregated irregular particles into small nanoplates, and CaCO_3 evolves from large layer-stacked secondary particles to small layer-stacked secondary particles (Supplementary Fig. 21). The increased stirring speed facilitates the reaction between metal cations and reactant anions, leading to increased S and abundant nucleation, which is conducive to structural evolution and smaller size. Furthermore, we found that the pH values due to reactant dissociation, or even deliberate pH adjustment, mostly induce slight structural variations, such as crystalline structures and nanosize, but the presupposed morphologies are maintained, especially for anisotropic materials (Supplementary Fig. 22). This innovative and facile technique is simply modified and realized several distinctive nanostructures for the first time with high specific surface areas, including hollow BaF_2 tubes and cubes, porous CaF_2 cubes, and holey $\text{Co}(\text{OH})_2$ sheets (Fig. 4b-e, Supplementary Figs. 23-26). These structures can hugely increase the specific surface area, which is in turn likely to increase performance in potential applications.

The precipitates obtained represent a wide variety of common materials, which generally hold promise for a broad scope of applications, such as in energy storage and conversion. As shown in Supplementary Fig. 27, 1D $\text{Co}(\text{OH})_2$ has an overpotential (η_{1D}) of 310 mV, which indicates better

oxygen evolution reaction (OER) performance than 2D and 3D Co(OH)_2 ($\eta_{2\text{D}} = 400 \text{ mV}$ and $\eta_{3\text{D}} = 400 \text{ mV}$). BaF_2 shows decent performance for the oxygen reduction reaction (ORR). Compared with 1D and 3D BaF_2 , the as-prepared 2D BaF_2 shows the highest half-potential $E_{1/2}$, suggesting its superior efficiency towards oxygen reduction. 2D Co(OH)_2 -derived CoO mesoporous nanosheets exhibit good electrochemical performance when applied as an anode in lithium-ion batteries (LIBs), delivering high reversible capacity ($\sim 850 \text{ mAh g}^{-1}$) at a current density of 2 A g^{-1} after 400 cycles, and the high rate capability of $\sim 700 \text{ mA h g}^{-1}$ at a current density of 5 A g^{-1} (Supplementary Fig. 28). The better performances of 2D Co(OH)_2 -derived CoO mesoporous nanosheets compared with the reported results on various CoO anodes (including nanocages²³, porous nanowire arrays²⁴, multilayer platelets²⁵, microspheres²⁶, mesoporous nanorods²⁷, mesoporous nanodiscs²⁸, microsheets²⁹, and nanowire clusters³⁰) stems from their nanoarchitecture. (Supplementary Figs. 29-31). Furthermore, the CoO nanosheets retained their mesoporous structure after 400 cycles (Supplementary Fig. 32). To illustrate the commercial potential of CoO mesoporous nanosheets, mass produced from the 2D Co(OH)_2 nanosheets and obtained here in high yield, we assembled a pouch-type full cell by pairing with a LiFePO_4 cathode (Supplementary Figs. 33 and 34).

In summary, we successfully fabricated a wide variety of materials by virtue of our rapid chemical precipitation strategy. Reactants as precipitants with different α values can precisely regulate the concentration of desired ions and simultaneously manage to achieve appropriate S , which plays a critical role in obtaining various products according to their solubility product constant (K_{sp}). The synergetic control between α of reactants and S of precipitates, therefore, can tune the morphology from 1D to 3D through quick precipitation. The formation of 1D and 2D materials relies on the low dissociation capability of weak electrolytes. The selection of a strong electrolyte ($\alpha \approx 1$) is conducive to the growth of isotropic 3D structures. Moreover, lower supersaturation is critical for the formation of 1D and 3D polyhedral structures, whereas 2D materials require a high supersaturation condition. We hope that these insights will help the facile synthesis, and morphology control, of a variety of materials.

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Data availability statement

All data supporting the findings of this study are included in the Article and its Supplementary Information, and are also available from the authors upon reasonable request.

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Competing interests

The authors declare no competing interests.

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Supplementary information

Materials and Methods, Supplementary Figures 1-34, and Supplementary Tables 1-4 are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints.

Figure captions

Fig. 1: Morphological evolution of typical materials with 3D, 1D, and 2D nanostructures. a-f, Typical scanning electron microscope (SEM) (a-fI) and typical transmission electron microscope (TEM) images (a-fII, a-fIII) of several materials in various morphologies; BaF₂ (a) BaMoO₄ (b) Mg(OH)₂ (c) Co(OH)₂ (d) MnOOH (e) Cu(OH)₂ (f,i) and Cu₂(OH)₂SO₄ (f,ii,iii). In each case, panel (i), (ii), (iii)_show 1D, 2D and 3D morphologies, respectively, and (iv) shows the α and S conditions that promoted the growth of these structures.

Fig. 2: TEM and SEM images of various materials produced by the versatile precipitation. a-d, TEM images of 1D materials, including BaCO₃ nanoneedles (a), CoCO₃ nanoneedles (b), Zn(OH)₂ nanorods (c), and CoC₂O₄ nanorods (d). e-h, TEM images of various 2D materials, including nanosheet-like Ni(OH)₂ (e), CoSOH (f), Ca₃(PO₄)₂ (g), and CoCO₃ (h). i-l SEM images of diverse 3D polyhedral materials, including Ca(OH)₂ (i), CaCO₃ (j), CuC₂O₄ (k), and Ca(IO₃)₂ (l).

Fig. 3: Summary of the synergy between α and S for materials with different morphologies. a, Dispersion of K_{sp} of various materials depending on α and S (Note: the small coloured dots represent the projection of the data points on each corresponding 2D graphs in b and c). b, Projected image of S and K_{sp} of 1D and 2D materials; the regions shaded in pink and blue highlight the 2D structure and 1D structures, respectively. c, Projected image of α and K_{sp} : both of the 1D and 2D materials are anisotropic materials, while the 3D structures are considered isotropic; they are highlighted by brown and dark-blue shading, respectively. d, The average values of S (S_a) of 3D polyhedra (green bar), spheres (blue bar), and irregular particles (cyan bar). Data represents the means value; Error bars represent standard deviation, $n = 3$ independent experiments.

Fig. 4: The mechanism of the formation of 1D, 2D, and 3D morphologies. a, Schematic illustrations of the formation of 1D, 2D, and 3D structures with regular shapes. Color code: Green arrow: 1D reacting path; Orange arrow: 2D reacting path; Blue arrow: 3D reacting path; Purple arrow: the value of α ; Red arrow: the value of S . b-e, TEM images of a BaF₂ tube (b), a hollow BaF₂ cube (c), a porous CaF₂ cube (d), and a holey Co(OH)₂ sheet (e).