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A surfactant free synthesis and formation mechanism of hollow Cu₂O nanocubes using Cl⁻ ions as the morphology regulator†

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Hollow nanomaterials have attracted intense attention due to their special structures and potential applications in many fields. In this paper, we report a surfactant free synthesis of hollow Cu₂O nanocubes by reducing Cu²⁺ precursors using Cl⁻ ions as the morphology regulator at room temperature. It is found that in the presence of Cl⁻ ions, hollow Cu₂O nanocubes can be easily synthesized by directly reducing Cu²⁺ precursors with ascorbic acid. Through well-designed experiments, we propose that, in this surfactant free synthetic route, the formation of hollow Cu₂O nanocubes results from a reaction activated Kirkendall diffusion process of cubic CuCl intermediates, which are formed in the reaction process and act as self-sacrificial templates. The amounts of Cl⁻ ions and NaOH are two key factors to determine whether hollow Cu₂O nanocubes are formed or not.

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1. Introduction

Crystalline nanomaterials with hollow interior have attracted intense attention these years, as they possess high surface area, low density and special geometric structure and are potentially applied in many fields including catalysis,^{1,2} lithium-ion batteries,^{3,4} biomedical delivery,⁵ gas sensors,^{6,7} and so forth. For crystalline materials, however, the formation of hollow structures is thermodynamically inhibited during the crystal growth process, due to high surface energy. It is therefore a challenging task to develop strategies for the controllable syntheses of crystalline nanomaterials with hollow interior. So far, the synthetic strategies for hollow nanomaterials are mainly based on the application of various templates, including hard templates, soft templates and self-sacrificial templates.^{8,9} Noticeably, the synthetic methods based on hard templates or soft templates face the problem of removing templates, which greatly limits their practical applications. In contrast, the self-sacrificial template based methods are more ideal to prepare hollow nanomaterials as the templates finally convert into the products. For the self-sacrificial template methods, the reaction activated Kirkendall diffusion process where the template material is diffused to the outer shell *via* a solid phase reaction is found to be a good way to achieve single crystalline hollow

nanostructures.^{10,11} However, a complicate two-step process is usually needed. As a result, it is desirable to explore more simple and efficient methods to synthesize single-crystalline hollow nanomaterials.

Cu₂O is a p-type semiconductor and widely applied in catalysis, sensing, water splitting, photo-catalysis, *etc.*^{6,12-19} The synthesis of hollow Cu₂O micro/nanoparticles has been intensely reported in past years and various formation mechanisms have been proposed and well discussed.^{6,20-26} In the previous reports, hollow Cu₂O nanostructures were mostly formed in the presence of surfactants, which play a soft template-like role in the formation of hollow structure. By using Cu₂O as example, in this paper, we try to demonstrate that single-crystalline hollow nanostructures could be likewise fabricated in the absence of foreign surfactants and hard templates. We propose that cubic CuCl, which is the reaction intermediate produced in the reaction process, plays a self-sacrificial template role in the formation of hollow Cu₂O nanocubes.

2. Experimental section

2.1 Chemicals

Copper chloride dihydrate (CuCl₂·2H₂O, 99.0%), copper sulfate pentahydrate (CuSO₄·5H₂O, 99.0%), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.0%) and L-ascorbic acid (AA, analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium chloride anhydrate (NaCl, 99.5%) and sodium hydroxide (NaOH, 96.0%) were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. All chemicals were used as received without further purification.

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† Electronic supplementary information (ESI) available: SEM images and XRD patterns of precursors, and SEM and TEM images of Cu₂O obtained with different amounts of NaCl and reaction times. See DOI: 10.1039/c5ra08988c

2.2 Synthesis of hollow Cu₂O nanocubes

In a typical synthesis, 5 mL of deionized water, 0.5 mmol CuCl₂·2H₂O and *X* mmol (*X* refers to 0, 3, 5 or 7) NaCl was successively added into a transparent glass vial to get 5 mL of 0.1 M CuCl₂ aqueous solution. Then 0.9 mL of 1 M NaOH solution was added into the vial with vigorous stirring for 5 minute to obtain a deep blue flocculent precursor solution. After that, 2.5 mL of 0.1 M AA aqueous solution was added under vigorous stirring at room temperature. The color of the resulting solution was gradually turned from deep blue to yellow with the reaction. After 10 min, the precipitate was separated from the solution by centrifugation at 8000 rpm, washed several times with ethanol, and finally dried under vacuum at ambient temperature.

2.3 Characterization of samples

The composition and phase of as-prepared products were acquired from a Rigaku Ultima IV X-ray diffractometer operated at a voltage of 35 kV and a current of 15 mA with Cu-K α radiation. The morphologies of as-prepared products were observed by scanning electron microscopy (SEM, S4800). Transmission electron microscopy (TEM) images were taken by using a JEM-1400 microscope (JEOL, Tokyo, Japan) with an acceleration voltage of 100 kV and JEM-2100 high-resolution transmission electron microscope (JEOL, Tokyo, Japan) with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon-film-coated copper grid, followed by drying under infrared light.

3. Results and discussion

Fig. 1a shows a low-magnification SEM image of the products that were fabricated with CuCl₂ as source and AA as reducing reagent under standard conditions, *i.e.* with 0.9 mL 1 M NaOH and no extra NaCl added (*X* = 0). It can be seen that the products are cubic particles and their sizes are around 100 \pm 20 nm. It is noted that a small percentage of particles, which accounts for *ca.* 10%, have a hollow space in interior, as pointed with arrows in the low-magnification TEM image (Fig. 1b). The high magnification TEM image (Fig. 1c) of an individual hollow cubic nanoparticle clearly reveals that the hollow interior is regularly cubic, and the interior size is *ca.* 105.6 nm, smaller by 10.8 nm compared to the shell size. The corresponding selected area electron diffraction (SAED) pattern (inset of Fig. 1c) displays a group of well-arranged diffraction spots, which could be indexed as the [00-1] zone axis of Cu₂O of cubic crystal structure. This indicates that the hollow nanoparticles are single crystalline. The cubic Cu₂O phase of products is further confirmed in the XRD pattern (PDF no. 00-005-0667).

The presence of these single crystalline hollow Cu₂O nanocubes in the product is surprising, because there are no foreign soft templates and hard templates in the synthetic process. In addition, it has been demonstrated in previous studies that, in the template synthesis of single-crystalline regular hollow nanostructures, the shape of hollow interiors strongly depends on the shape of templates.^{4,27} However, the blue colloidal

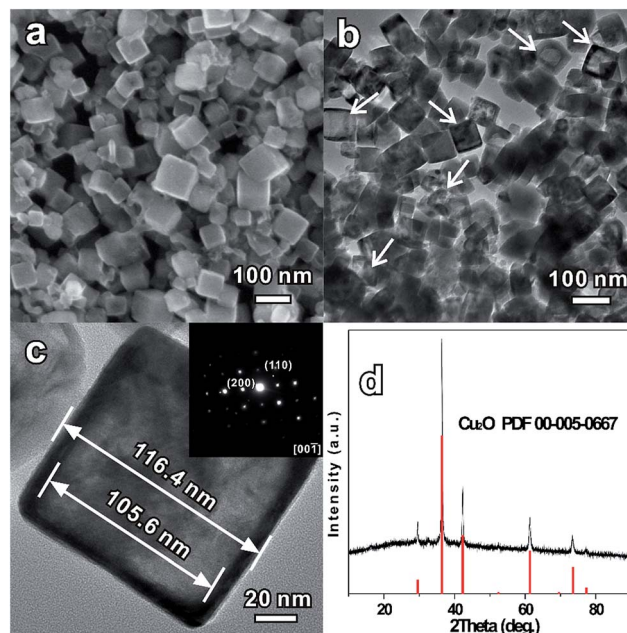


Fig. 1 Low-magnification (a) SEM and (b) TEM images of the products obtained with 0.9 mmol NaOH and without extra NaCl. (c) High magnification TEM image of an individual hollow Cu₂O nanocube. Inset is the corresponding SAED pattern. (d) XRD pattern of the products.

products obtained before the addition of reductant AA are of nanowire morphology (Fig. S1, ESI[†]), which are not suitable templates for the hollow Cu₂O nanocubes. On the basis of above facts, we propose that cubic templates may be generated in the synthesis process, which act as self-sacrificial templates and finally vanish in the following growth process. In order to find out possible template for hollow Cu₂O nanocubes, we surveyed all the copper compounds possibly formed in our synthetic conditions. CuCl is found to be the only one with cubic structure, and thus it is a reasonable template for hollow Cu₂O nanocubes. To verify its template role, the volumes of shell and interior as well as the numbers of hollow Cu₂O product and solid CuCl template are roughly calculated according to their measured side lengths. We take the hollow Cu₂O nanocube shown in Fig. 1c as the representative example. According to our calculation (part I, ESI[†]), a solid CuCl cube of 105.6 nm in size, which consists of 2.97×10^7 CuCl molecules, practically transforms into the hollow Cu₂O nanocube with outer size of 116.4 nm and thickness of 10.8 nm, which consists of 1.03×10^7 Cu₂O molecules. This calculation result basically matches the theoretical one (1.48×10^7 Cu₂O), which indirectly confirms that it is reasonable that the hollow Cu₂O nanocubes should be transformed from CuCl in this case.

The solubility product constant (K_{sp}) of CuCl is 1.72×10^{-7} . According to calculation, the Cl⁻ ions from CuCl₂ in our synthetic process are enough for the formation of CuCl. However, only a small part of Cu₂O nanocubes are hollow in the standard synthetic process. We think that, in the standard synthetic condition, the Cl⁻ ions are relatively insufficient so that only a part of Cu²⁺ ions transform into CuCl, which acts as

self-sacrificial template for the subsequent transformation into hollow Cu_2O . To confirm this, the extra source of Cl^- ions, NaCl , was specifically added in the standard reaction condition. As we expected, the percentage of hollow Cu_2O nanocubes significantly arises after extra NaCl was added. As shown in Fig. 2, hollow nanocubes are overwhelming in the products obtained with extra 3 mmol NaCl , and the percentage of hollow nanocubes almost reaches 80%. Similar results were observed when 5 or 7 mmol NaCl was introduced (Fig. S2, ESI[†]). This suggests that the extra Cl^- ions added would be beneficial to form more cubic CuCl intermediates, thereby leading to better transformations into hollow Cu_2O nanocubes. It should be noted that, the yield of products would remarkably decrease when too much NaCl (>10 mmol) was added in the reaction solution, which is due to formation of soluble CuCl_4^{3-} in the solution. Similar phenomena were found in the case of high concentration Cl^- ions, where Cu_2O could be dissolved by the coordination with Cl^- ions.^{3,28}

Based on the analysis above, the formation of the reaction intermediate CuCl ought to be a key procedure in the fabrication of hollow Cu_2O nanocubes. Therefore, to better display the formation of CuCl and its role, CuSO_4 and $\text{Cu}(\text{NO}_3)_2$, instead of CuCl_2 , were used as copper source in the synthetic process. In the absence of Cl^- ions, only irregular balls that are composed of aggregated particles with smaller sizes are produced in both cases, as shown in Fig. 3a and d. Interestingly, hollow Cu_2O nanocubes were generated in both cases when extra 3 mmol NaCl was added into the solution of copper salts. As shown in Fig. 3b and e, a large amount of broken hollow nanocubes can be observed. According to TEM images (Fig. 3c and f), the percentage of hollow nanocubes are estimated to be 85% in the two cases.

The above results agree well with the prediction that CuCl acts as the self-sacrificial template for hollow Cu_2O nanocubes. In fact, there have been some other reports about the influence of chloride on the morphology of Cu_2O .^{21,29} For example, it has been demonstrated that hollow Cu_2O cubes could be formed directly from the transformation of CuCl by hydrolysis.²¹ To further verify this hypothesis, CuBr whose crystal structure and chemical nature is significantly similar with CuCl was employed as another intermediate. We found hollow Cu_2O nanocubes (Fig. S3, ESI[†]) could also be successfully fabricated when NaCl was replaced by NaBr in our experiment.

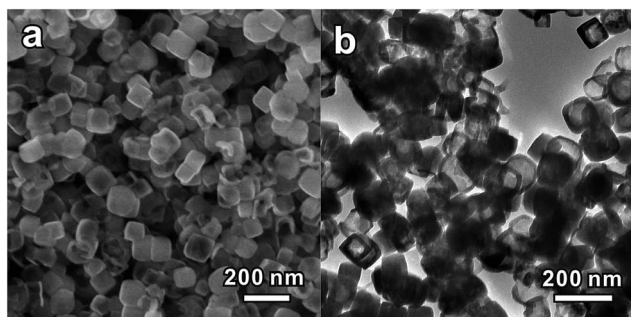


Fig. 2 (a) SEM and (b) TEM images of hollow Cu_2O nanocubes obtained with 0.9 mmol NaOH and 3 mmol NaCl .

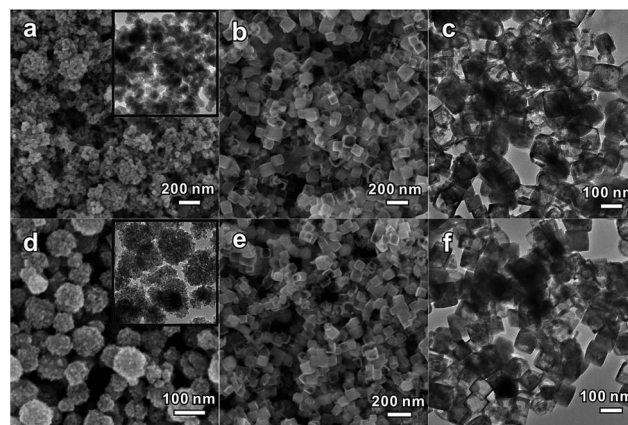


Fig. 3 SEM and TEM images (insets) of the as-prepared Cu_2O products with CuSO_4 as copper source with (a) 0 mmol NaCl or (b and c) 3 mmol added. SEM and TEM images (insets) of the as-prepared Cu_2O products with $\text{Cu}(\text{NO}_3)_2$ as copper source with (d) 0 mmol NaCl or (e and f) 3 mmol added.

The key role of CuCl in the formation of hollow Cu_2O nanocubes can be well understood through the above analysis on our experimental results. However, the total reaction processes and detailed formation mechanism of hollow Cu_2O nanocubes are still a mystery to us. Before the solution containing AA was added, blue colloidal nanowires were firstly formed in the solution containing copper salts, which was determined to be $\text{Cu}_2\text{Cl}(\text{OH})_3$ with a monoclinic structure through XRD analysis (Fig. S1, ESI[†]). However, in the standard reaction process, it is difficult to trace the existence of the CuCl intermediate in the transformation from the $\text{Cu}_2\text{Cl}(\text{OH})_3$ precursor to the Cu_2O product, due to too fast reaction rate. Hollow cubic interior had

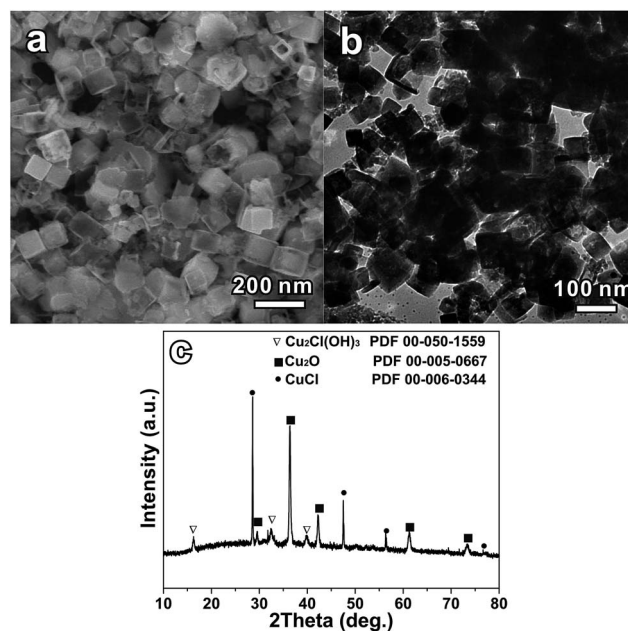


Fig. 4 (a) SEM image, (b) TEM image and (c) XRD pattern of the products obtained with 0.8 mmol NaOH and no extra NaCl .

been already formed in some Cu_2O nanocubes even after 1 min reaction (Fig. S4, ESI[†]). To slow down this transformation process, the amount of NaOH added was specifically reduced from 0.9 mmol to 0.8 mmol. As shown in Fig. 4a and b, the as-prepared product also displays a cubic shape, and a part of them are hollow. The corresponding XRD pattern (Fig. 4c) indicates that the products are a mixture of CuCl , $\text{Cu}_2\text{Cl}(\text{OH})_3$ and Cu_2O . This result indirectly proves the existence of the CuCl intermediate in the transformation from the $\text{Cu}_2\text{Cl}(\text{OH})_3$ precursor to the Cu_2O product.

In the past, CuCl_2 is often used as copper source for the preparation of Cu_2O . However, the exact formation mechanism of hollow or solid Cu_2O nanostructures behind the transformation from CuCl_2 to Cu_2O remains unclear due to the extremely fast reaction rate. On the basis of above results, we proposed that the formation of hollow Cu_2O nanocubes actually experienced three procedures from CuCl_2 to $\text{Cu}_2\text{Cl}(\text{OH})_3$,

then to CuCl , and finally to Cu_2O . In this reaction process, the concentration of hydroxyl ions (OH^-) is also a key factor, which influences the phase of initially formed colloidal precursors and determines whether the CuCl intermediates are formed in the reaction. If the concentration of NaOH is low, $\text{Cu}_2\text{Cl}(\text{OH})_3$ is the preferred product in the reaction of CuCl_2 and NaOH. When NaOH in the reaction solution is sufficient, the initially formed colloidal precursors would be $\text{Cu}(\text{OH})_2$, rather than $\text{Cu}_2\text{Cl}(\text{OH})_3$, because $\text{Cu}_2\text{Cl}(\text{OH})_3$ would quickly transform into $\text{Cu}(\text{OH})_2$ *via* a fast anion exchange.^{30,31}

Because K_{sp} of CuCl (1.72×10^{-7}) is relatively large (much larger than that of Cu_2O), $\text{Cu}(\text{OH})_2$ will not further transform into CuCl in the following reaction. In that case, hollow Cu_2O nanocubes will be not formed at last due to the lack of proper self-sacrificial templates. To verify this, the amount of NaOH was increased from 0.9 mmol to 5 mmol in the synthetic process, with keeping other conditions the same with the standard process. The XRD analysis demonstrates that the blue colloidal nanowires formed in the presence of 5 mmol NaOH are $\text{Cu}(\text{OH})_2$, rather than $\text{Cu}_2\text{Cl}(\text{OH})_3$ (Fig. S5, ESI[†]). Accordingly, the finally formed Cu_2O nanocubes after the subsequent reduction reaction with AA are solid, as shown in Fig. 5. This indicates that the forming pathway of solid Cu_2O nanocubes differs from that of hollow Cu_2O nanocubes.

On the basis of above results, we propose that the formation of Cu_2O with CuCl_2 as copper source actually experiences a series of chemical transformations, and the final product can grow into hollow or solid nanocubes, depending on the amount of NaCl and NaOH in the reaction. Scheme 1 illustrates two pathways to form hollow or solid Cu_2O nanocubes. As shown in the pathway (1) in Scheme 1, the formation process of hollow Cu_2O nanocubes is divided into three steps. Firstly, $\text{Cu}_2\text{Cl}(\text{OH})_3$ nanowires are generated when proper amount of NaOH is added into the CuCl_2 solution. Secondly, $\text{Cu}_2\text{Cl}(\text{OH})_3$ nanowires quickly transform into cubic CuCl *via* a dissolution-regrowth method when the reductant AA is introduced. Finally, hollow Cu_2O nanocubes are formed with the CuCl nanocubes as self-sacrificial templates *via* a hydrolysis reaction-induced Kirkendall process. The as-formed Cu_2O shell maintains a cubic shape, which is the same with that of CuCl , due to the same crystal nature.

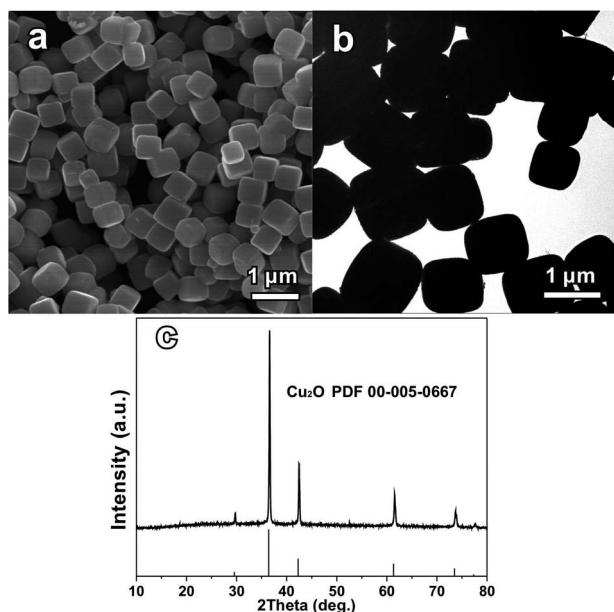
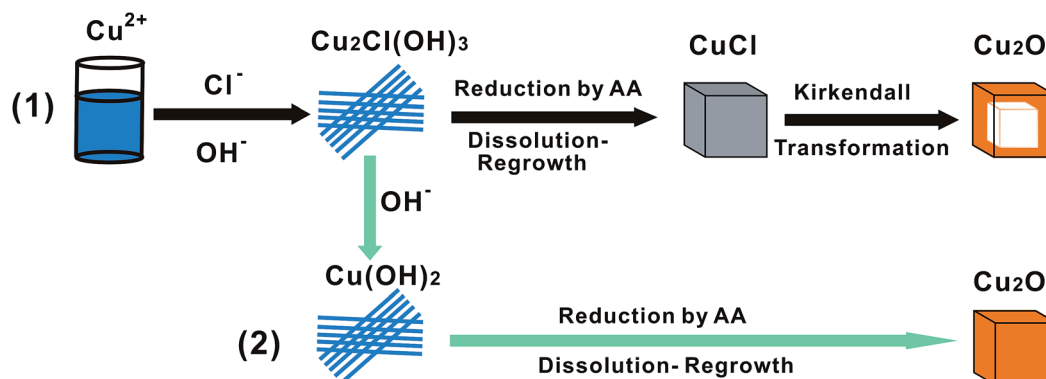


Fig. 5 (a) SEM image, (b) TEM image and (c) XRD pattern of the products obtained with 5 mmol NaOH and without NaCl.



Scheme 1 Schematic illustration of the synthesis of (1) hollow and (2) solid Cu_2O nanocubes.

In the transformation processes above, the amounts of NaOH and CuCl₂ are the two key factors that determine whether the self-sacrificial templates, CuCl nanocubes, are formed or not. The presence of Cl⁻ ions is the first condition. Increasing the concentration of Cl⁻ ions would be helpful for the formation of Cu₂Cl(OH)₃ and subsequent CuCl, thereby leading to the increase of the percentage of hollow Cu₂O nanocubes. On the other hand, the pathway discussed above is influenced by the amount of NaOH. High concentration NaOH (like 5 mmol) will promote the transformation from Cu₂Cl(OH)₃ to Cu(OH)₂.^{30,31} When AA was subsequently introduced, Cu(OH)₂ reacted with it and dissolved,³² then nucleated from the solution to form solid Cu₂O nanocubes, as shown in the pathway (2) in Scheme 1.

Conclusions

In summary, a great progress has been made on the study of growth mechanism of hollow nanomaterials, but it is still an enormous challenge in the case of the fast reaction system. In this study, single crystalline hollow Cu₂O nanocubes were successfully prepared with CuCl₂ as raw reactant *via* a surfactant free solution route. This is a very fast reaction process, and thus the detail reaction procedures are often ignored in the past years. On the basis of in-depth analysis on the effect of Cl⁻ ions and NaOH with a series of well-designed experiments, we found the formation of the hollow Cu₂O nanocubes results from the Kirkendall transformation mediated by CuCl that is the intermediate formed in the reaction in the presence of Cl⁻ ions in basic condition.

It is well known that crystalline crystals tend to generate solid particles rather than hollow ones in the crystal growth. However, the present work reveals that only precisely controlling reaction conditions and employing suitable template could regular hollow nanostructures be prepared. Therefore, this work inspires us to explore the potential of employing reaction intermediates as self-sacrificial templates in fabricating other single-crystalline hollow nanomaterials.

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