The Synthesis of Hollow/Porous Cu$_2$O Nanoparticles by Ion-Pairing Behavior Control

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ABSTRACT: Owing to the properties of low density, large surface areas, excellent loading capacity, high permeability, and interstitial hollow spaces, hollow nanostructures have been widely applied in many important research fields, such as catalysis, drug-controlled release, confined synthesis, optics and electronics, and energy storage. This work provided a simple platform for hollow Cu$_2$O nanostructure synthesis based on the surfactant controlling methodology, which is under the supposed mechanism of ion-pairing behavior at the initial nucleation stage. Thus here, we explore our system in two different directions: (1) we get different types of hollow Cu$_2$O nanoparticles by controlling the surfactant concentration during the synthesis step in colloids, which is critical to the novel structure design and potential application in many different areas and (2) we explore the method to Cu$_2$O hollow particle synthesis to test the hypothesis of the ion-pairing behavior during the initial nucleation by tuning the solvent ratio, cation concentration (such as NH$_4$NO$_3$ addition amount difference in the synthetic step), and selective etching. By tuning the synthetic conditions as well as designing control experiments, we hope to provide a solid understanding of the crystal growth mechanism. Our improved understanding in similar systems (both Cu$_2$O and ZnO systems) will make it easier for interpreting nanostructure formation in new discoveries and, more importantly, in rationally designing various complex nanostructures based on a bottom-up strategy.

INTRODUCTION

Hollowing behavior is important to nanomaterial application because it could improve the surface area, porosity, and volume of nanomaterials. 1 People studied the hollowing behavior of nanomaterials for decades to control it better. Hollow nanostructures show great potential advantages in applications, such as catalysts, batteries, and solar cells, because of their large surface area and large volume. 2 Especially, the hollow oxide nanomaterials, such as silica, Ti$_2$O, Cu$_2$O, and ZnO, have been used in many different areas because of their unique physical and chemical properties. 3 More and more studies are focused on the hollowing behavior of oxide nanostructures in order to synthesize efficient materials for applications. For example, the electrode materials, depending on their structure, morphology, particle size, and guest ions, may display pseudocapacitive or battery-like behavior whose porosity and diffusion-controlled processes are critically important to the real application. 4

There are normally three main mechanisms for the oxide hollowing behavior: surface-selective etching under protection, 5 Ostwald ripening, 5 and surface redeposition. 6 For example, Yin’s group has reported that poly(vinylpyrrolidone) (PVP) can protect the outmost silica layer from etching while PVP is absorbed on the silica nanoparticle surface. 5 It cannot protect the inner layer because the PVP molecule size is larger than the silica pore size to diffuse inside. 5

In our previous work, we synthesized the sol–gel silica nanoparticles and analyzed the silica composition via elemental analysis and inductively coupled plasma mass spectroscopy, and we found that certain amounts of N and C are trapped within the silica nanoparticles, which shall be from the incorporation of ammonia cations and unhydrolyzed tetraethyl orthosilicate (TEOS) and solvent isopropanol. The ion-pairing mechanism was introduced to explain the phenomenon. NH$_3$ not only catalyzed the hydrolysis of TEOS but also functionalized as a deprotonating agent to facilitate the formation of ion pairs with silicate species, which has a great influence on the formation and dissolution of silica nanoparticles. The ion-paired silica species with a longer chain length will preferentially precipitate out in nonpolar solution (alcohol) and form aggregates. These silica aggregates can function as the seeds for further growth of silica species, which with a short chain length in the monomer addition mode. When they are transferred to an aqueous solution for etching, the inner part of silica can dissociate into soluble species, while the outer
Figure 1. TEM images showing the purified products of Cu$_2$O nanocubes synthesized at different surfactant PVP concentrations of (a) 2, (b) 4, (c) 6, (d) 8, (e) 10, and (f) 12 mg/mL. Heavier hollowing at higher PVP concentration is clear.

Figure 2. HRTEM images showing the purified products of Cu$_2$O nanocubes synthesized at a surfactant PVP concentration of 6 mg/mL. (a) TEM image of the nanocube. (b) HRTEM image showing the edge of the sample in panel a. (c) SAED image of the sample in panel a. (d) STEM image of the sample in panel a showing the porous property of the nanoparticle synthesized with PVP solution. (e) XRD spectrum of the sample in panel a. (f) EDX color maps of the Cu$_2$O hollow crystal shown in Figure 1f.
layer is cross-linked and not etchable, which eventually leads to the formation of hollow silica nanoparticles.  

Here, we report a method to synthesize hollow oxide nanostructures by using PVP as a surfactant/ligand. The porosity as well as the morphology of the nanostructures could be controlled by tuning the PVP concentration, solvent ratio, and growth solution environment. These parameters are critical to the synthetic control, which could give novel nanostructures showing unique physical properties, such as high porosity, large surface area, various morphologies, and so on.

## RESULTS AND DISCUSSION

First, Cu$_2$O nanoparticles were synthesized in colloids. Typically, DI water containing PVP (different concentrations of 0–12 mg/mL) aqueous solution was added to a 20 mL glass vial heated at 60 °C by using an oil bath to dissolve PVP to give a homogeneous clear solution. Then, CuCl$_2$ aqueous solution and NaOH aqueous solution were added in sequence under vigorous stirring to mix the solutions quickly. The NaOH solution was added to tune the pH of the solution. Finally, a hydrazine hydrate solution (reducing agent) was added by dropping (droplet addition) with vigorous stirring.

To study the hollowing mechanism in the ion-pairing hypothesis, different parameters were changed in the synthesis step, such as the ligand/surfactant concentration, salt concentration, and solvent ratio. All the nanocrystals have been characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and XRD to confirm the structure here.

For the Cu$_2$O nanocube synthesis, we find that the surfactant poly(vinylpyrrolidone) (PVP) concentration is critical to the final morphologies. A PVP concentration increase from 0 to 12 mg/mL could lead to surfactant micelles and different adsorption on the primary nucleation seed surface, which might be embedded inside the crystal. As shown in Figure 1, hollow Cu$_2$O nanocubes were collected at a high concentration of PVP solution during the synthesis. The Cu$_2$O nanocubes synthesized at a lower PVP concentration or without any PVP addition show a high density with a regular cubic shape. However, the nanoparticle morphology changed with PVP addition, especially the void that appeared in the center of the nanoparticles (Figure 1a–f). Also, the cubic shape changed from a cubic morphology to a not regular cubic one. Here, it is clear that the PVP and copper ions form a kind of cluster/template at the initial stage of the crystal nucleation, which is similar to the ionic polymer (polyelectrolyte) behavior. With knowledge of ionic polymers, the stability of the polymers in a solution is highly related with the concentration of counterions and solvent polarity in the growth solution. The counterionized polymers could be precipitated out under a nonpolar or lower polar environment and trap more organic molecules (or oligomers) to give hollow/porous nanostructures. Especially, when the surfactant concentration is very high (higher than 8 mg/mL), the nanocube would be heavily hollowed. The HRTEM data in Figure 2 show that it is a mesocrystal-like crystal. Here, this kind of control has never been reported for the Cu$_2$O nanocube synthesis. As it has been reported that PVP could be used as a template to synthesize some porous/hollow nanoparticles, systematically studying the PVP concentration effects on porous morphology has never been done (PVP–copper clusters showing polyelectrolyte-like properties). Also, this unique understanding demonstrates a series of control
experiments to test the ion-pairing hypothesis, such as the addition of counterions in the synthesis, change of the solvent polarity, and using different types of surfactants in the synthesis.

As shown in Figure 2a,b, the clear (111) and (110) lattice fringes of Cu$_2$O nanocrystals can be observed, and the XRD spectrum in Figure 2e also confirms the presentation of the nanocrystal phase. Interestingly, the EDX maps shown in Figure 2f (also, see the Supporting Information) clearly present the hollow morphology of the cube synthesized in the presence of PVP aqueous solution, identifying the successful synthetic control of hollow/porous metal nanocrystals in colloids. In order to clarify the porous nanoparticle formation, we conducted a EDX line scan to the final hollow nanoparticles, as shown in Figure S5 where Cu distribution shows the trajectory of the porous morphology, while carbon distribution is homogeneous in the whole area, which may be contributed by the carbon contamination as well as the TEM grid (carbon layer on the grid).

For the Cu$_2$O nanocube coating another spherical layer of Cu$_2$O, we have tried to introduce the salt (NH$_4$NO$_3$) into the synthesis, which will help us to know whether the counterions can affect the oxide formation and hollowing, just like how it happens in the silica nanoparticle formation process. As the hypothesis shows above, the presence of ion pairs plays a very important role in pore formation and cube morphology, which is attributed to surface crystallization dynamic difference caused by polyelectrolyte-like cluster formation. Therefore, by changing the nature of ion pairs, we may further tune the solubility of cluster-like species in the primary nucleation stage. Intentionally, we added certain amounts of salts like NH$_4$NO$_3$ under the synthetic condition. Because the NH$_4^+$ ions can be counterionized with negatively charged PVP$^-$, copper polyelectrolyte-like clusters, they immediately aggregated to form oligomers. These are more likely to aggregate due to a lower solubility and fast deposition kinetics in different polar solvents, as shown in Figures 3 and 6a.

According to Figure 3, it is clear to see that the spherical Cu$_2$O shell morphologies are different at different salt (NH$_4$NO$_3$) concentrations. Typically, the core—shell nanoparticle was the final product without any NH$_4$NO$_3$ addition; it will be lightly hollowed at the interface of the nanocube core and the spherical shell when the salt (NH$_4$NO$_3$) concentration is 2 mM; the heavily hollowed shell would be observed when the salt (NH$_4$NO$_3$) concentration is increased to 8 mM or higher. The trend between the salt (NH$_4$NO$_3$) concentration and the spherical shell morphology is clearly seen there.$^{15,16}$ We think it is possible that ion doping caused by the ion concentration difference might affect the shell morphology.$^{17-19}$ Previously, van Blaaderen and Kentgens investigated the structure of the siloxane network in silica particles by nuclear magnetic resonance spectroscopy, which revealed the
existence of a small amount of clusters (oligomers) due to incomplete hydrolysis and condensation of TEOS. Similarly, PVP−Cu ion groups not only change the homogeneity in the internal structure of oxide particles but also affect the external morphology, as shown in this work.20,21

From a polyelectrolyte (or ionic polymer) point of view, the stability of the polymers/clusters in solution is highly related to the counterion concentration and solvent polarity. Based on its physical property, the solvent polarity can also have a great influence on the ion-pairing kinetics and also the surface nucleation. Since the solvent is a mixture of water and ethanol, different ratios between the two can give a different polarity, which shall lead to different deposition kinetics of Cu 2O nanoparticles.

The solvent ratio control experiments (Figure 4) of the nanostructure formation during the synthetic step show the trend clearly: at higher water content (EtOH/water = 1:4), the main product is the dense nanoparticles, as shown in Figure 4a. However, with an ethanol concentration increase in the solvent mixture, there would be heavier porous nanoparticle formation, as shown in Figure 4b,c. The trend of nanoparticle shell thickness (as well as size) change with the solvent ratio (ethanol/water volume ratio) change is shown in Figure 4d, which could tell the solvent polarity effect clearly. Theoretically, the higher the solvent polarity is, the easier the PVP−Cu ionic polymer to precipitate out. As for cluster species like monomers, dimers, or trimers, they will deposit on the precipitates in a manner that is quite different from the traditional crystallization (also called the polymer-trapped process, as shown in Figure 6a). This explains both the void/pore formation in the center of the nanoparticle and the cube-to-sphere overall nanoparticle morphology change.

Brunauer–Emmett–Teller (BET) data shown in Figure 5 also support our hypothesis. For the Cu2O nanoparticles synthesized at a lower salt (NH4NO3) concentration, the BET data show that it has a smaller surface area (68.74 cc/g); for the Cu2O nanoparticles synthesized at a higher salt (NH4NO3) concentration, the BET data show that it has a large surface area (83.15 cc/g). The result means that at a higher salt concentration, the Cu2O nanoparticle porosity would be higher compared to that at the lower salt concentration. It can be explained under the ion doping mechanism, which means that a higher salt concentration might lead to a heavier ion doping inside the Cu2O nanoparticles by quick
precipitation, which would trap more counterions inside. Then, there would be more defects inside the Cu$_2$O nanoparticles leading to high porosity. However, the PVP–Cu clusters have more condensation time to grow into higher cross-linking clusters with higher crystallization, which in turn gives crystals with lower or no defect, showing a perfect cubic morphology and a dense solid domain without visible voids inside.

To understand the scenario of copper oxide morphology evolution at different stages, a key observable trend should be the shape transformation gallery, as shown in Figure 6a,b. As a common sense for polyelectrolytes, the solubility of the ion-paired polymer-like species should depend on the solvent polarity, positively charged ion concentration, and the primary cluster chain length, which are also variable at the different stages of Cu$_2$O nanocrystal formation. Considering the higher concentration of precursor at the initial stage, it is expected that a large size polymer chain would form. They would preferentially nucleate due to their low solubility, wrapping in with them a large number of counterions as well as PVP molecules. In contrast, the outer layer was built up from the subsequent addition of the leftover monomers and short-length polymers. These shorter polyelectrolytes retain less counterions and eventually give more cross-linked shells by crystallization. Hence, the dramatic difference between the two stages leads to an abrupt boundary of different deposition dynamics, which could give a hollow/porous structure after the addition of a high concentration PVP (cluster size is larger), higher positively charged ion concentration (concentrated ion-pairing formation), or higher ethanol/water ratio (lower polarity solvent leads to fast cluster precipitation with rich defects). We also characterize the intermediates of the crystal formation process, as shown in Figure 6b, by trapping the intermediates. It is clear to see that there are polymer-like species at the initial stage of nucleation (5 min after the reducing agent addition), which is an amorphous-like material (with the presence of the PVP). This trend supports our hypothesis of ion-paired polymer-like formation.

With the above knowledge, we could enrich the structure map of Cu$_2$O by adjusting the critical parameters, which could affect the ion-pairing behavior. Hence, in Figure 7, we summarized the hollow and porous nanoparticle formation, which is dependent on the experimental environments. With a higher PVP concentration, as shown in Figure 7a, more polymer-like amorphous material formation gives hollow-like particles. Similarly, a highly porous particle was the main product when a high cation concentration is present in the synthesis solution, as shown in Figure 7b, which could lead to more ion-pairing behavior at the initial stage of nucleation to trap more noncrystals within the nanoparticle domain. Finally, the water content (solvent volume ratio of ethanol/water) also plays an important role in the ion-pairing process, as shown in Figure 7c; a lower water concentration will lead to more amorphous polymer-like species formation at the initial stage of nucleation, which gives a porous-like nanoparticle rather than dense single- or polycrystalline nanoparticles. All these control experiments support our hypothesis of ion-pairing behavior during the Cu$_2$O formation in different solutions. Here, to explore this mechanism with other metal oxide synthesis, ZnO nanoparticle synthesis was chosen as another example.
model study. As shown in Figure S6, ZnO hollow nanoparticles were observed when PVP was introduced in the synthetic step under different concentrations or under different solvent ratios (Figure S7), which shows a similar trend with Cu$_2$O synthesis. As a comparison, we found that the ZnO nanoparticle hollowing behavior also depends on its ion-pairing behavior. We believe that it is helpful to the hollow mechanism study although it might be at a different level for different systems.

■ CONCLUSIONS

In summary, we report a facile method to prepare hollow/porous copper oxide nanoparticles by controlling the ion-pairing behavior. By playing with the surfactant concentration, solvent ratio, and cation concentration, we achieved different types of hollow/porous nanoparticles, suggesting a new pathway in nanomaterial design. Our proof of concept is that the ion-pairing polymer-like behavior in the synthetic approach can create new morphologies of copper oxides (as well as ZnO), which is a clear demonstration for the porous/hollow nanoparticle design as well as its potential applications in catalysts, batteries, sensors, and so on.$^{22-27}$

■ EXPERIMENTAL SECTION

Materials. Copper chloride (CuCl$_2$, 98%, Aldrich), hydrazine hydrate (N$_2$H$_4$·H$_2$O, 99.8%, Alfa Aesar), ammonium nitrate (NH$_4$NO$_3$, Aldrich), poly(vinylpyrrolidone) (PVP, M$_w$ of 40,000, Aldrich), and sodium hydroxide (NaOH, 98%, Aldrich) were used as received without any further purification. All glassware for nanoparticle syntheses was treated with aqua regia (a mixture of HCl and HNO$_3$ with a volume ratio of 3:1), thoroughly rinsed with water, and dried under N$_2$ gas immediately before use. Nanopure water (18.2 MΩ·cm at 25 °C) purified using a Milli-Q Advantage A10 system was used for all washing and solution preparation.

Synthesis of Cu$_2$O Nanoparticles (Different PVP Concentrations). In order to test PVP concentration effects, the typical synthesis procedure was as the following that 9.0 mL of pure DI water and 7.7 mL of DI water containing PVP (with different concentration from 0 to 12 mg/mL) were sequentially added into a 20 mL glass vial. The mixture was heated at 60 °C by using an oil bath. Then, 0.1 mL of 0.15 M CuCl$_2$ aqueous solution and 0.1 mL of 0.1 M NaOH aqueous solution were added under vigorous stirring (600 rpm) in that order. The NaOH solution was added drop by drop under stirring. Finally, 0.15 mL of 0.25 M N$_2$H$_4$ solution (reducing agent) was added by dropping (droplet addition) with vigorous stirring. The final mixed solution was aged in an oil bath for another 1 h. The as-synthesized nanoparticles were purified by centrifugation at 8000 rpm for 8 min three times to remove the impurities.

Synthesis of Cu$_2$O Nanoparticles (Different Solvent Ratios). To the solvent ratio control experiments, 9.0 mL of ethanol/water mixed solvent (at different volume ratios) was added at the beginning, instead of using pure water. For the synthesis experiments under different solvent ratios, every step is the same as above except the usage of 9 mL of pure water, which was replaced by the mixture of water and ethanol.

Synthesis of Cu$_2$O Nanoparticles (Different Ion Concentrations). To test the positively charged ion effect on ion-pairing behavior, ammonium nitrate (NH$_4$NO$_3$) was added into the solution to give a solution with different cation molar concentrations (0, 2, 4, and 6 mM) at the beginning of the synthesis. Then, 0.1 mL of 0.10 M CuCl$_2$ aqueous solution and 0.1 mL of 0.1 M NaOH aqueous solution were added under vigorous stirring (600 rpm), whose following procedure is the same as above sections.

Characterization. TEM images were collected from a JEM-1400 (JEOL) transmission electron microscopy operated at 100 kV. High-resolution TEM (HRTEM) and energy-dispersive X-ray (EDX) images were taken from a JEOL 2100F field emission transmission electron microscope at 200 kV. X-ray diffraction (XRD) data were collected using a Bruker D8-Advance Soller 2θ–2θ diffractometer in reflectance Bragg–Brentano geometry employing Ni-filtered Cu Kα line focused radiation at 1600 W (40 kV, 40 mA) power and equipped with a Na(Tl) scintillation detector fitted with a 0.2 mm radiation entrance slit. All samples were ground to ensure monodispersity in the bulk and then mounted onto a zero-background sample holder by dropping powders from a wide-blade spatula, and the sample surface was then leveled with a razor blade. BET surface area and pore size measurements were conducted with N$_2$ adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 v3.04 H instrument.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03380.

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, figures of the control experiments, and photo of the reaction color change (PDF)

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Author Contributions

All authors contributed to the manuscript preparation and experimental design and discussion. The sample preparation was done by X.S., X.L., and W.X. TEM images were collected by X.S. and D.S. EDX line scan was collected by X.S., X.L., and J.T.
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Notes
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