Shape Controllable Synthesis of Silver Particles by Selecting the Crystallization Routes

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Abstract

Classic crystallization describes a burst nucleation followed by a layer-by-layer atom deposition. The non-classic crystallization refers to particle mediated crystallization process. Different crystallization routes lead to the formation of diverse structured materials. Here we report a rational synthesis of silver particles by selecting the crystallization routes. Silver particles were synthesized by a solution reduction approach. The crystallization routes were regulated by adding amino acids to stabilize silver ions which leads to the decrease of the reduction rate. Without amino acids, silver dendrites were largely formed. With the addition of amino acids, flower-like (low concentration of amino acids) and spherical silver (high concentration of amino acid) particles were synthesized. Three kinds of amino acids were tested and the similar results were obtained. The time-dependent characterization on the evolution of silver particles showed that silver dendrites were formed by the classic atom deposition while the other two morphologies were formed by the combination of classic and non-classic crystallization. The silver particles synthesized were evaluated for ethylene epoxidation and the dendritic particles demonstrated a high selectivity.

Keywords: crystallization, silver particles, shape control, reaction kinetics, catalytic selectivity

1. Introduction

Crystallization starts from nucleation followed by the growth of nuclei. It is a key process in materials formation and industrial production (Zeng J. et al., 2012). For many years, the crystallization has been described through burst nucleation followed by layer by layer growth or Ostwald ripening (Li Y. et al., 2018; Zeng J. et al., 2012). However, this traditional description faces challenges recently because more and more hierarchical structures synthesized in laboratories or found in nature, which could not be explained by the classic crystallization. For example, well-faceted porous calcium carbonate particles have been synthesized by the diffusion of CO₂ into the calcium chloride solution (Wang T.X. et al., 2005). These porous particles were built up by the perfectly 3D-aligned calcite nanocrystals superstructures. Based on these findings, the non-classic crystallization process is proposed, in which particles coalescence plays a major role on the growth of products (Colfen H. and Antonietti M., 2008; Runkana V. et al., 2005). Except this different conception on crystallization, Watzky and Finke (Watzky M.A. and Finke R.G., 1997) formulated a constant slow nucleation followed by autocatalytic growth, in which the nucleation lasts for a long time and competes with the growth of particles. The well-accepted Ostwald ripening also faces challenge by the Digestive ripening (Kalidindi S.B. and Jagirdar B.R., 2009). The former describes that big particles prefer to grow in solution on the cost of small particles while the later refers that small particles grow at the expense of large ones. Therefore, there are many debates in the field of crystallization, which leave the uncertainty but also the treasure to be discovered.

Although the traditional theory of crystallization faces challenges, scientists never stop their effort to synthesize crystals with controllable size and morphology. Different approaches have been developed to control the shape of crystals, which includes templating methods (Fuji M. et al., 2013), kinetic controlling methods (Xia Y.N. et al., 2015) and so on. Chemists have developed a fine shape-controlled method by adding surfactants or macro-molecules to interfere the growth of crystals (Ruditskiy A. and Xia Y.N., 2016). By this method, they have successfully synthesized various morphological metal particles,
including spheres (Han K.N. and Kim N.S., 2009), cubes (Zhang J. et al., 2010), tetrahedrons (Wiley B. et al., 2004), nanobars (Zhang Q. et al., 2012) and nanowires (Xiong W.W. et al., 2016). They ascribed the role of surfactants to their selective adsorption on the facets of crystals to block the growth of these facets. But different opinions also come up. David Wei and co-authors (Zhai Y.M. et al., 2016) proposed that the surfactant polyvinylpyrrolidone preferentially adsorbs along the perimeter and serves as a photochemical relay to direct the anisotropic growth.

Shape control of materials is a long-term interest of our group. We have developed a bubble templating method for one-step synthesis of hollow particles (Han Y.S. et al., 2007, 2009). Recently, we are focusing on the role of chemical diffusion and reaction kinetics in shaping particles. By regulating the diffusion and reaction rates of chemicals, we have synthesized diverse morphologies of metal particles and oxide particles (Wang H. et al., 2013; Yang T. and Han Y.S., 2016; Yang T. et al., 2015; Yang Y. et al., 2014). It was found that the diffusion of chemicals could switch the crystallization from classic to non-classic modes, which led to the formation of diverse morphology of platinum particles (Yang Y. et al., 2014). In this paper, we attempted to investigate how the reaction rate influences the crystallization process. Silver particles were synthesized by a solution-based reduction approach, in which hydroxylamine was used to reduce silver ions producing silver particles. The reduction rate was regulated by adding amino acid as complexation agents. With the addition of amino acid, the reduction rate was slowed down due to the complexation. In different reduction rates, the formation process of silver particles was monitored. Both the classic crystallization and non-classic crystallization were observed when the reduction rates changed, which led to the formation of diverse morphologies of silver particles.

2. Experimental sections

2.1 Materials

All chemicals used in this study are of analytical grade and used without further purification. They were purchased from Sigma-Aldrich. Deionized water with a resistivity higher than 18.2 MΩ used throughout the experiments was generated by a Mili-Q system (Millipore, USA).

2.2 Synthesis of silver particles with various morphologies

In a typical experiment, 2 ml silver nitrate (100 mM) and a defined amount of amino acid were dissolved in 40 ml deionized water, respectively, stirring for 10 minutes to form a stable complex. Then 2 ml hydroxylamine solution (200 mM) was added into the above mixture to initiate the reduction. To monitor the evolution of silver particles, the solution was taken out at different reaction time. The solution was immediately transferred to liquid nitrogen to terminate the reduction, and then the frozen samples were dried by freeze drier (Christ ALPHA 1-2 LD plus, Germany). The reactions were carried out in a thermostated water bath at 25 °C, and the concentration of amino acids varied from 0 to 40 mM.

2.3 Characterizations

The morphologies of silver products were characterized by a JSM-7001F Thermal Field Scanning Electron Microscope (JEOL, Japan) and a JEM-2100 (UHR) Transmission Electron Microscope (JEOL, Japan) at an accelerating voltage of 200 kV. Samples for SEM and TEM analysis were prepared by dipping solution on aluminum foils and carbon-coated copper grids, respectively.

2.4 Quantization of the reduction rates

When the silver ions are reduced by hydroxylamine, the hydrogen ions are the byproduct. The generation rate of Ag atoms is equal to the production rate of hydrogen ion, so the reduction rate can be quantified by measuring the increment of hydrogen ion, which corresponds to a drop of pH. The pH electrode (Mettler-Toledo S470 Seven Excellence pH/Conductivity meter) was placed in the solution to record the pH change during reaction.

2.5 Catalyst preparation and selectivity evaluation

The Ag/α-Al₂O₃ catalysts were prepared by an excessive impregnation method. Firstly, the silver slurry was prepared by dissolving cesium hydroxide (the mass fraction of Cs ion = 1000 ppm) and Ag₂C₂O₄ into an ethylenediamine (EDA) solution to form a diamine silver solution (the mole ratio of Ag₂C₂O₄:EDA = 5:12). When the silver particles were added into the ethylenediamine solution, the amount of Ag₂C₂O₄ was decreased to keep the same mole ratio of silver and EDA. Then the porous alumina supports were immersed in the slurry to load silver salt. The supports were heated by hot air at 300 °C for five minutes, generating the Ag/α-Al₂O₃ catalysts. The ethylene epoxidation was conducted in a stainless steel reactor with 4 mm inner diameter. The catalysts were broken and sieved to 0.9–1.4 mm, then 1 ml sample was loaded into the reactor. Quantitative analysis of inlet and outlet gas composition was performed on an online Prima dB mass spectrum produced by Thermo Scientific. The gas was ionized by the bombardment of electron current ion source. Stand Faraday detector was used to analyze the
3. Results and discussion

The main difference between the classic crystallization and the non-classic crystallization is the growth unit of crystals. In the classic crystallization, the growth units are atoms or ions or molecules which deposit on the surface of nuclei by a layer by layer mode. In the non-classic crystallization, the growth units are usually clusters or particle which aggregate to form products. We suppose that the reaction kinetics could change the crystallization routes. At a high reaction rate, quick reaction leads to a burst nucleation followed by a classic crystallization. At a low reaction rate, the nucleation lasts for a long time and the newly-born nuclei tend to aggregate to form particles, which leads to the non-classic crystallization, as shown in Fig. 1. In the following, the evaluation on this hypothesis will be conducted.

We synthesized silver particles by a solution-based reduction approach, in which hydroxylamine was used to reduce silver ions producing silver particles, as shown in the following:

$$2Ag^+ + 2NH_2OH \rightarrow 2Ag + 2H_2O + N_2 + 2H^+ \quad (1)$$

The reduction rate was regulated by adding glycine into the silver solution. With the addition of glycine, the reduction rate was slowed down due to the stabilization of silver ions by glycine. To quantify the reaction rates, the pH value of the solution was recorded during the reaction, which was used to calculate the reaction rates due to hydrogen ions are byproduct of the reduction, as shown in equation 1. Without glycine, the reaction rate is $1.166 \times 10^{-6}$ mol L$^{-1}$ s$^{-1}$, as shown in Fig. 2. With the addition of glycine, the reaction rates decrease to $0.335 \times 10^{-6}$ mol L$^{-1}$ s$^{-1}$ at 10 mM glycine and $0.147 \times 10^{-6}$ mol L$^{-1}$ s$^{-1}$ at 40 mM glycine, respectively, which confirms the complexation of silver ions by glycine. In the following, we attempt to synthesize silver particles at different reaction rates to evaluate the role of reaction kinetics in crystallization.

Silver dendrites were largely generated when the silver salts were mixed with hydroxylamine solution, as shown in Fig. 3. Fig. 3A shows the low-magnification image of silver products, indicating uniform and large scale of dendritic particles. Fig. 3B–3E show time-dependent evolution of silver dendrite, which was carried out by taking samples at different reaction times and immediately putting samples.
into the liquid nitrogen to stop the reaction. After the reaction of 1 second, the silver products already show dendritic characters with clear main trunk and side branches, as shown in Fig. 3B. When the reaction time is increased to 5 seconds, the dendrite prototype grows to three-dimensional complex structure. Small particles are formed on the surface of the trunk and the side branches become longer with the formation of next-level branches on their surface, as shown in Fig. 3C. Prolonging the reaction to 10 seconds, the dendrites become dense and compacted, as shown in Fig. 3D. Further prolonging the reaction time, small particles disappear and the dendritic structures become clear and complete, as shown in Fig. 3E. The time dependent characterization indicates that the formation of dendritic structures is pretty fast and the classic crystallization may dominate the growth of particles.

The silver dendrites were characterized by transmission electron microscopy (TEM), as shown in Fig. 4. Fig. 4A shows an overall dendritic structure of silver particles. The selected area electron diffraction (SAED) pattern of the growth front of silver dendrites marked by red circle is shown in Fig. 4B, which indicate that the silver dendrite is single-crystalline with the main growth direction of $<110>$, as shown in Fig. 4C. The single crystalline and boundary free characters of silver dendrites indicates that silver dendrites are formed by a classic crystallization process. Fig. 4D is the growth model of silver dendrites. In most cases of metal solidification and nano-synthesis, the formation of symmetric dendrites follows the classic crystallization in which atoms are the main building blocks for the growth of dendrites (Xing H. et al., 2016). If the silver dendrites are formed by a classic crystallization, a change on the reduction rate is expected to switch the classic crystallization to the non-classic mode, on the basis of the assumption in Fig. 1, which is the issues we want to evaluate in the following.

To regulate the reduction rate of silver ions, glycine was added into silver salt solution before the reduction. The glycine stabilizes silver ions by complexation, which leads to the decrease of reduction rate (Liu J.M. et al., 2015). Silver particles were synthesized at different amount of glycine. When the glycine concentration is 10 mM in the solution, flower like silver particles are formed, as shown in Fig. 5. These particles are composed of fan-shaped sheets which assemble together forming flower structures with the diameter of several micrometers. To track the formation process of silver flowers, we took samples at designed time and stop the reaction by putting the samples into liquid nitrogen. In the early stage of reaction, nanosized silver particles are formed, as shown in Fig. 5B. Prolonging the reaction to 10 seconds, nanosized particles grow and assembled together, forming the prototype of flowers, as shown in Fig. 5C. Further prolonging the reaction to 30 seconds, each particle in the flower grows to fan-shaped particle, as shown in Fig. 5D. On the surface of these particles, protuberances are observed, which is probably the result of later adsorption of small particles. When the reaction is increased to 30 minutes, the morphology of silver flowers does not change remarkably except the size, as shown in Fig. 5E. The time-dependent characterization indicates that silver flowers are formed by the aggregation of individual nanosized particles followed by the growth of each particle. The silver flower has been characterized by TEM, as shown in Fig. 6. The dark center in TEM image indicates that the flower has a dense core while the grey epilayer confirms the thin layer of each petal. The selected area electron diffraction pattern from the petal, as shown in the inset of Fig. 6, indicates that each petal is crystalline.

Flower structured particles have been synthesized in many materials. Different formation mechanisms have been proposed for these amazing structures. Among
them, self-assembly of individual particles is the most plausible (Sung H. and Choi M., 2013), in which the building block particles are formed firstly and then aggregate together following certain orientation. But this mechanism does not work well in our system because the initial particles are much smaller than the final petal and their morphology is also different, as shown in Fig. 5. Therefore, each individual particle should undergo a later growth process after the aggregation. Since the fan-shaped particle is formed in a short reaction time (30 seconds) with single crystalline feature, we suppose that atom deposition plays a key role in the later growth of individual particle. Therefore, it seems that the flower particles start from the aggregation of nuclei followed by the classic growth of nuclei. The formation of flower-like structures is a combination of the classic and non-classic crystallization. The involvement of non-classic crystallization is probably caused by the decrease of reduction.

Fig. 4 TEM image (A) of the silver dendrites synthesized. Selected area electron diffraction patterns (B, C) from the specific sites labeled in (A). D is the growth model of silver dendrites.

Fig. 5 SEM images of the silver products synthesized by the solution-based reduction approach in 10 mM glycine solution. A showing the low-magnification SEM image of silver flowers synthesized after 30 min, indicating uniform and high-yield of products. B showing nanosized silver particles synthesized after 5 s reaction; C showing the silver aggregates composed of flakes synthesized after 10 s reaction; D and E showing silver flower synthesized in 30 s and 30 min, respectively. The scale bars represent 1 μm.
rate of silver ions. At a slow reaction, the silver nuclei or small particles can not grow up quickly. They prefer to aggregate to reduce their surface energy under stirring and grow up later by atom feeding.

To further evaluate the role of reaction kinetics in crystallization process, we synthesized silver particles at 40 mM glycine solution. Spherical silver particles are largely synthesized in this condition, as shown in Fig. 7A. The time-dependent morphological evolutions of silver spheres are shown in Fig. 7B–7E. At the initial reaction time of 5 seconds, irregular particles are formed with the size of several hundred nanometers, as shown in Fig. 7B. Prolonging the reaction to 30 seconds, the flower aggregates are observed, as shown in Fig. 7C. When the reaction is increased to 5 minutes, spheres with rough surfaces are synthesized, as shown in Fig. 7D. Further prolonging the reaction time to 30 minutes, the size and morphology of silver spheres change, as shown in Fig. 7E. The time-dependent characterization indicates that the formation process of spheres is similar to that of the flower particles. They are the products of particles aggregation followed by classic crystallization. Owe to the decrease of reduction rate, the nucleation process is prolonged, which competes with the growth process to consume silver atoms. The newly formed nuclei adsorb on the surface of growing particles and become new sites for the growth, forming dense flower particles.

To exclude the role of chemical effect on the morphology of silver particles, we synthesized silver particles at two more amino acid solutions, namely arginine and phenylalanine solutions, as shown in Fig. 8. No matter which amino acid is added, the morphology of silver particles switches from dendrites to flower like particles then to spheres with the increase of amino acid concentration, which indicates that the change of silver morphologies is independent on the types of amino acid. Since the addition of amino acid slow down the reduction rate of silver salt, the reaction kinetics should play a key role on the change of silver morphology. It is normally accepted that the kinetics factors influence the growth rate of crystal facets, which leads to the formation of diverse shapes of crystals (Xia Y.N. et al., 2015). This interpretation works well for the anisotropic growth of single crystals. But it can not explain the formation of hierarchical polycrystalline crystals, such as the flower-shaped particles in which the petal originates from different nucleus. Therefore, we have to consider the aggregation of nuclei in the formation of hierarchical crystals.

Silver is an industrial catalyst of ethylene epoxidation to generate ethylene oxide (EO) which is the largest volume chemicals produced by chemical industry. The oxidation...
of ethylene in the presence of supported silver catalysts not only leads to the formation of ethylene oxide, but also induces the side reaction to form carbon dioxide. Therefore, the selectivity is the important issue of silver catalysts. Considerable effort has been devoted to understand the mechanism of silver-catalyzed ethylene epoxidation. There are two types of oxygen species playing the active centers for ethylene epoxidation on silver (Ren D.M. et al., 2017). One is the active oxygen in a nucleophilic attack of the C-H bond while the other is active in an electrophilic addition to the double C=C bond. The former facilitates the formation of carbon dioxide while the latter is in favor of the formation of ethylene oxide. It was reported that the electrophilic oxygen is dominant in the Ag (111) at the addition of cesium (Bukhtiyarov V.I. et al., 2003). Since the silver particles synthesized in this study have a major exposure of Ag (111), we added the synthesized silver particles to the silver slurry containing 1000 ppm Cs ions and loaded the slurry into the alumina supporter, to evaluate the effect of particles morphologies on the selectivity of catalysts. The total loading capacity of silver is 17 wt% which includes 20 % silver particles.

It is found that the addition of silver particles leads to the increase of the selectivity of ethylene epoxidation and the silver dendrites have the highest selectivity, as shown in Fig. 9. The dendritic silver particles grow along the <110> with the largely exposed facet of (111), as shown in Fig. 4, which leads to the highest selectivity of silver dendrites. The flower-like silver particles also demonstrate an anisotropic growth with the major surface of (111) while the silver spheres are polycrystalline having a reduced surface of (111). All these particles are well crystallized in solution, which benefits the desorption of oxygen to generate ethylene oxide. This study indicates that the facet control is an effective solution to develop high selectivity and efficient catalysts.

4. Conclusions

A rational synthesis of hierarchical silver structures was reported in this paper. Silver dendrites, silver flowers and silver spheres were largely synthesized by controlling the reduction rates which was regulated by adding ammonia acids to stabilize silver ions and slow down the reduction. With the decrease of reduction rate, silver dendrites changed to silver flower and then to silver spheres, which were observed in three kinds of ammonia acids.
Time-dependent characterizations on the evolution of particles showed that silver dendrites were formed by classic crystallization via atom deposition while the other two morphologies were formed by the combination of particles aggregation and atom deposition. At a high reaction rate, quick nucleation was followed by atomic layer growth on the surface of nuclei, forming silver dendrites. At a low reaction rate, the nucleation was prolonged. The later formed nuclei adsorbed on the growing particles and became new sites for the classic growth, which led to the formation of hierarchical polycrystals, such as silver flowers. This study confirmed the role of reaction kinetics in switching the crystallization routes, which is expected to improve our understanding on the growth of hierarchical structures and to enhance our ability for rational synthesis of material structures.

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Authors’ Short Biographies

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Jianmei Liu got her bachelor degree from Ocean University of China in 2013. As a highly distinctive graduate, she started her master at the same university, and as a joint student, she studied in Yongsheng Han’s group (Institute of Process Engineering, Chinese Academy of Sciences) for about three years until she got her master degree in 2016. Then in 2017, she started her PhD study in research school of chemistry, Australian National University, and works on functional materials, specially dielectric materials.

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Mr. Qiang Lin got his bachelor degree in 2002 and master degree in 2005 from Tsinghua University. After his graduation, he joined Beijing Research Institute of Chemical Industry, Yanshan Branch, SINOPEC and worked there on the research and development of catalysts for ethylene epoxidation. In 2012, he began to pursue his PhD at the Institute of Process Engineering, Chinese Academy of Sciences and passed the doctoral dissertation defense in July, 2018. Now, He focuses on the preparation and improvement of silver catalysts.
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