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A Switch from Classic Crystallization to Non-classic Crystallization by Controlling the Diffusion of Chemicals

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Abstract: *Here we report a study on controlling the shape of particles via regulating the diffusion of chemicals. To change the diffusion rate of reactive ions, we use a designed three-cell reactor in which the reactive ions are separated by porous membrane. We take the reduction of hexachloroplatinate ions by sodium borohydride as an example. The experimental results show that the control on chemical diffusion leads to the platinum product changing from cubic particles to dendritic particles. Further analysis indicates that the cubic particle is formed by the classic crystallization process via layer wise deposition while the dendritic particle is formed by the non-classic crystallization process through clusters aggregation. The control on chemical diffusion prolongs the nucleation period and produces nuclei continuously, facilitating the aggregation of nuclei, which leads to the crystallization switching from classic model to non-classic model. The obtained results in this paper suggest that the control on chemical diffusion is a green and promising process to manipulate the structures of materials.*

It is a dream of chemists and materialists to fabricate materials as the children to stack building blocks with remarkable controllability. The difficulty is that the building units of materials is too small to handle and the building process is too fast to catch up. That is why the crystallization has been studied for more than 200 years but the understanding on the crystallization process is still rather restricted,[1] which is a limitation for the rational synthesis of materials.[2] Classically, crystallization refers to a layer-wise deposition of atoms/ions/molecules on the nucleus.[3] Nevertheless, this well-known model does not apply to many real crystallization processes.[4] For example, sea urchin spines, as a crystalline biomineral, have nothing in common with the conception of single crystal.[5] Their precise formation is a challenge for the classical crystallization.

With the advance of microscopy in the last 20 years, many particles-based crystals were observed in nature[6] and synthesized in laboratories[7]. These crystals are built up by particles, showing amazing hierarchical structures. Based on these crystals, a new crystallization model was proposed, namely non-classic crystallization in which particles/clusters/intermediates act as the building units to assembly the hierarchical structure.[8] Due to the difference of the basic building units, the physics governing the non-classic crystallization process should be different with that of the classic crystallization, which is the main scientific issue that interest us.

Platinum is a primary catalyst with various shapes including cube, octahedron, rod, plate and dendrite. Among the shapes of platinum particles, dendritic shapes with well-defined structures are highly desirable and technologically important since they provide high surface area at a reduced platinum consumption.[9] Dendritic platinum particles have been synthesized by different approaches. [10] Most of the approaches employs surfactants as structure-directing agents.[11] A few efforts went down to the kinetic regulation and found out that both the reaction[12] and diffusion[11a] of chemicals influenced the formation of dendritic platinum structures. But the reason and mechanism behind the kinetic effect are unclear so far.

In this paper, we choose diffusion as the study factor to investigate its influence on the formation of dendritic platinum particles in a surfactant-free condition, and to discover the mechanism behind the kinetic control on dendritic structures. To control the diffusion rate of chemicals, we use a three-cell reactor. The reactive ions are placed in the side cells while the middle cell is occupied by pure water. Among the cells, porous membranes are set in to separate the reactive ions and water. The reactive ions have to cross through the membranes and diffuse into the middle cell where the reactive ions meet and reactions occur, forming dendritic platinum particles.

Three types of experiments were carried out in this study, namely direct mixing experiments, free diffusion experiments and diffusion controlled experiments, which are described in the experimental section. The sample collected in the direct mixing experiment, consists of crystals with various shapes, as shown in Figure 1A. Elongating the reaction time leads to the formation of well-crystallized cubic particles, as shown in Figure 1B. The increase in size and the shape transformation of platinum particles are attributed to the ripening process, which was well studied.[13] Electron diffraction pattern of the crystal, as shown in Figure 1C, indicates that the products are single crystalline. The sample collected in the free diffusion experiment is composed of spherical particles, as shown in Figure 1D. Magnification on the spherical particle indicates that the particle is densely packed, as shown in Figure 1E. Further magnification shows that the spherical particle is built up by the closely packed nanocrystals with size of approximately 2 nm, as shown in Figure 1F. The electron diffraction pattern of the spherical particle shows that the particle has poly-crystalline feature, which indicates that the spherical particle is randomly assembled by nanocrystals. The sample collected in the diffusion controlled experiment comprises porous spherical particles, as shown in Figure 1G. The magnification on a porous particle shows clearly dendritic structure, as shown in Figure 1H. The electron diffraction pattern indicates that the dendritic particle also has poly-crystalline feature. Further magnification shows that the porous particle is made up by nanoparticles. But these nanoparticles aggregate more loosely and there are plenty space between the building particles. The porous particle demonstrates a branch like structure.

These three types of experiments are carried out in the same condition with the same reagents. The only difference is the diffusion way of reactive ions. Therefore, the chemical diffusion is probably the key factor inducing the variation of particle morphologies. To verify the difference of chemical diffusion in these three experiments, we have measured the concentration of hexachloroplatinate ion in the middle cell during the diffusion process. We put only hexachloroplatinate and water in the reaction cell to prevent the reduction, which make the concentration of reactive ions only dependent on the diffusion. We picked up the solution at a fixed time from the central point of the middle cell and send it to the UV-Vis spectrophotometer. The results show that the maximal concentration of hexachloroplatinate ions reaches quickly in the direct mixing experiment while it takes nearly 1 minute in the free-diffusion experiment. In the diffusion controlled experiment, it takes nearly 3 minutes for the concentration reaching its maximum. These results confirm that the diffusion rates of chemical are remarkably different in these three types of experiments.

To figure out the reason why the chemical diffusion influences the morphology development of particles, we have to review the crystallization process. In the direct mixing experiments, reaction takes place instantly in the reactor, facilitating fast nucleation. The nucleation process consumes the atom leading to a quick decrease of the atom concentration. In the later stage, the left platinum atom grows on the surface of the nuclei following the classic crystallization process characterized by an atom-by-atom growth, as shown in Figure 2. Whereas in the free diffusion and diffusion controlled experiments, reactions mainly take place in the middle cell. The diffusion of reactive ions creates a concentration gradient in the reactor, which drives the diffusion of reactive ions from side cells to middle cell constantly, creating continuous supersaturation in the middle cell and making the nucleation lasting for a longer time. It is supposed that this nucleation process largely consumes the free atom in the middle cell, thus atom-by-atom growth on the nuclei is suppressed. Whereas, the nuclei tend to aggregate following the meso-crystallization process in which particles act as the building units to build up the hierarchical structures [14]. The aggregation of the nuclei follows two distinct ways based on the collision frequency. In the free diffusion experiment, the feeding of reactive ions into the middle cell is relatively faster than that of the diffusion controlled experiment. The density of nuclei is relatively high. In this case, the collision between nuclei is relatively sufficient, leading to the formation of compacted aggregate. On the other hand, in the diffusion controlled experiment, the feeding of reactive ions into the middle cell is relatively slow. The density of nuclei is relatively low, which leads to the lower collision frequency between nuclei. In such a case, the nuclei preferably attach on the outmost part of the particle, which leads to the growth of particles in radial direction, forming a dendritic structure, as shown in Figure 2. Therefore, the control on chemical diffusion prolongs the nucleation process, which results in the continuous production of nuclei. The collision triggers the aggregation of nuclei, leading to the formation of dendritic structure.

The catalytic activities of platinum particles are highly shape-dependent. [15] The electrocatalytic activities of the prepared particles were measured in the oxidation of methanol. The results are shown in Figure 3. The dendritic platinum particles demonstrate a high catalytic activity if they are compared with other particles. The peak current density of dendritic particles is approximately 50% higher than that of polyhedron particles. The improved catalytic activity of dendritic particles should be attributed to their porous structure which normally results in an increased surface area and enhanced edges and corners atoms.

In a summary, by changing the diffusion way of reactive ions, we successfully synthesized platinum particles with various morphologies including single-crystalline cubic particles and polycrystalline dendritic particles. The cubic particles were formed by the classic crystallization process while the dendritic particles were generated by the non-classic crystallization process. The control on diffusion prolonged the nucleation time and produced nuclei continuously in the solution, which facilitated the aggregation of nuclei and thus promoted the non-classic crystallization. The measurement on catalytic activities of the prepared particles showed that the dendritic platinum particles have a higher catalytic activity than that of other samples. Therefore, the control on the morphology of particles via chemical diffusion is a promising approach to synthesize functional materials with designed structures and enhanced performance.

Experimental Section

Hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot 6H_2O$, AR grade) and sodium borohydride ($NaBH_4$, AR grade) were purchased from Sigma (Beijing, China). The chemicals were used without further purification. Ultrapure water purified by Milli-Q plus system (Millipore Co.) with a resistivity more than 18mΩ was used in all aqueous solutions. The platinum was synthesized via the reduction of hexachloro-platinate ions by the solution of sodium borhydride,which can be represented by the following equation of chemical reaction.

$$2PtCl_6^{2-} + BH_4^- + 4H_2O \rightarrow 2Pt + B(OH)_4^- + 8H^+ + 12Cl^-$$

The aqueous solution of H_2PtCl_6 with a concentration of 2.25 mM and sodium borohydride solution with a concentration of 0.1M were prepared by dissolving the corresponding agents into the purified water. Equal volume of the above two aqueous solution was used in experiment. The experiments were carried out at 60℃ in a water bath. To control the diffusion of reactive ions, we used a designed reactor which is comprised of three cells separated by porous membrane and movable baffles, as shown in Figure 1. The reactor is 15 cm in length， 3 cm in width， and 8 cm in height. And it is divided into 3 equivalent cells along the long axis.

Three different types of experiments were carried out in this study, namely direct mixing experiments, free diffusion experiments and diffusion controlled experiments. For the direct mixing experiments, the sodium borohydride solution was directly injected into the cell containing H_2PtCl_6 solution. In the free diffusion experiment, the sodium borohydride solution and H_2PtCl_6 solution were placed in the side cells of the designed reactor while the pure water were put in the middle cell. The solutions were separated by movable baffles. When the baffles were drawn out, the reactive ions diffused from the side cell to the middle cell where they met and induced a reaction forming platinum particles. In the controlled diffusion experiment, the solutions and pure water were separated by movable baffles and polymer membranes. When the baffles were drawn out, the membranes were kept in the reactor. The reactive ions have to cross through the membrane to diffuse into the middle cell. Therefore, the introduction of membranes further slows down the diffusion rate of chemicals. Five minutes later after reaction started, the platinum particles were collected in the center of middle cell by a pipette. The sample solutions were dropped on the carbon-coated copper grids followed by a quick drying in air. The morphologies and electron diffraction patterns of the collected samples were characterized by a JEM-2100 transmission electron microscope (TEM) at an accelerating voltage of 200kV. Electrochemical measurements were carried out in a standard three electrode cell, which was connected to a PGSTAT 30 potentiostat. A leak-free Ag/AgCl (saturated with KCl) electrode was used as the reference. The counter electrode was a platinum mesh attached to a platinum wire. Methanol oxidation measurements were carried out in a solution of 0.5M H_2SO_4 containing 0.5M methanol at a scan rate of 50 mV/s [15a].

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Figure 1. Characterization on the particles synthesized in three different experiments which are distinct in the diffusion ways of reactive ions. A-C are the particles formed in the direct mixing experiment in which the chemicals are poured into the reactor and mixed by stirring. These particles are single crystalline and show cubic shape after ripening process. D-F are the particles formed in the free diffusion experiment in which the chemicals are put in the side cells and diffuse into the middle cell after the blocks are drawn out. The particles formed in the free diffusion are dense spherical particles which are built up by the random aggregation of nuclei. G-I are the particles formed in the diffusion controlled experiments in which the chemicals put in the side cells have to cross through porous membrane to enter into the middle cell. These particles show porous dendritic characters.

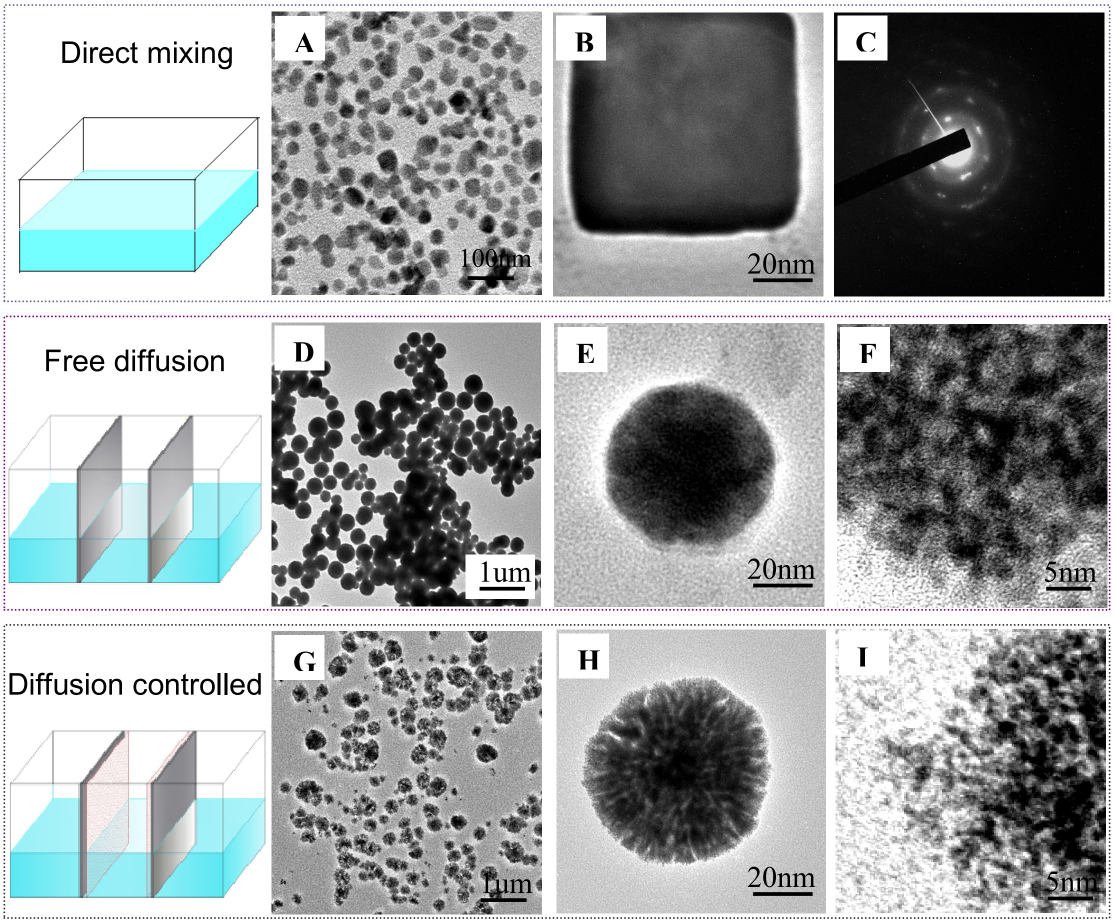


Figure 2. An illustration on classic crystallization and non-classic crystallization. The classic crystallization refers to an atom-by-atom deposition while the non-classic crystallization refers to the assembly of clusters. The switch between these two crystallizations can be realized by controlling the diffusion of reactive ions.

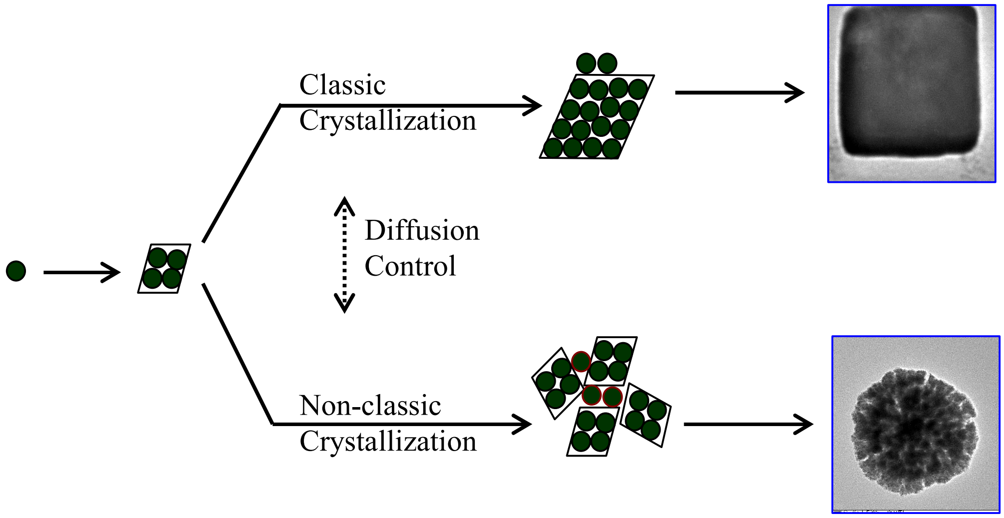
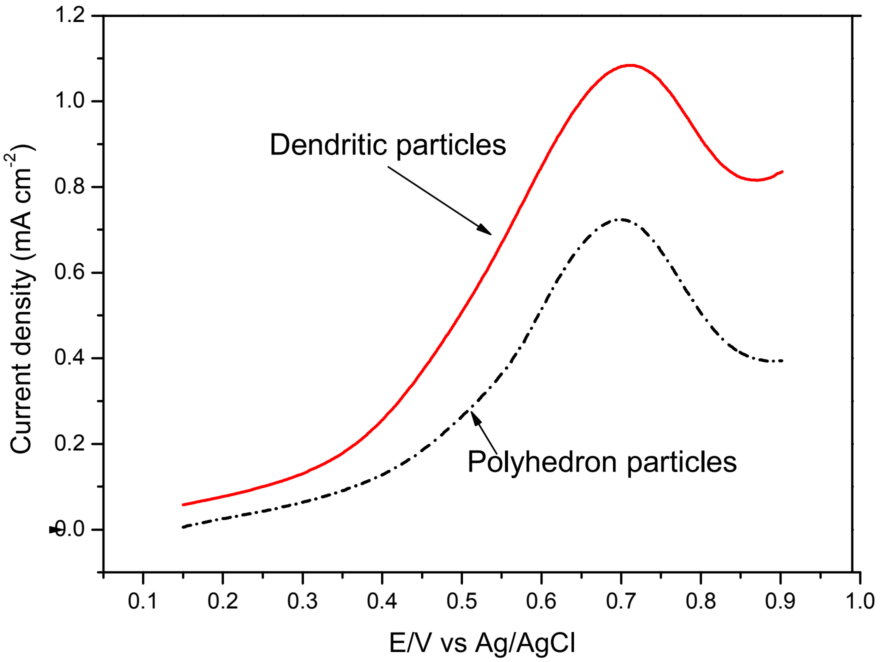


Figure 3. Comparisons of methanol oxidation activity on dendritic particles and polyhedron particles.



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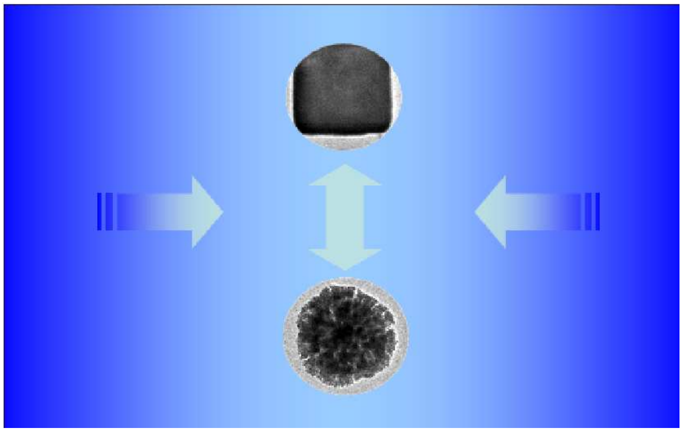

Here we report a study on controlling the shape of particles via regulating the diffusion of chemicals.