Regulating Silver Morphology via Electrochemical Reaction

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Abstract

Controllable synthesis of materials with designed structure is a long term dream of scientists and engineers. The challenge faced by dreamers is the complexity of material formation and the diversity of material structures. One way to discover this complexity is to simplify the reaction system. Electrochemical reduction is one of the simple reaction system in which an electron is used as the reductant to avoid the complexity of chemical effects. We design a two-cell electrochemical reactor. The cathode and anode are input in different cells connected by a salt bridge. The electron is introduced into the cell containing silver ions. By this approach, silver particles are synthesized on the cathode. The reduction rate of silver ions is regulated by varying the current density over two orders of magnitude. At various current densities, different morphologies of silver particles are synthesized. The dependence of silver morphology on current density is ascribed to the influence of current density on the nucleation and growth of silver particles, which is confirmed by later experiments. The results in this paper show that the electron is a simple and green reductant and the current density is an effective tool in regulating reaction rate to shape materials.

Keywords：Morphology control, Silver particles, Dendrites, Electrochemical Reaction, Nucleation

Introduction

Noble metal nanomaterials have attracted great attention owing to their unique properties in optics, electronics, magnetics and catalysis [1-3]. Among the precious metal materials, silver nanostructures have been investigated widely for their high abundance on the earth and low cost in comparison with others. Silver nanoparticles with diverse shapes, such as hexagon, triangle, cube, polyhedron, wire and hierarchical dendrites, have been successfully synthesized by different approaches [4-11].The silver dendritic structure is one of the interesting structures because of its complexity and the structure dependent properties. Various protocols have been developed to synthesize silver dendrites, including traditional solution-based chemical reduction, surface-deposition (direct replacement, electrolysis and galvanic replacement), and external-field-assisted preparation methods (magnetic and ultrasonic fields) [3，12-14]. Silver dendrites demonstrate some unique properties. For example, a sandwich-like dielectric medium containing silver dendritic cells displays properties of left-handed metamaterials [15], suggesting that these materials possess negative refractive index, negative dielectric permittivity and negative magnetic permeability, in which the silver dendrites have a dominant contribution [16, 17].

Although silver dendrites have been synthesized by different approaches, the formation mechanism of this complex structure still need to be discovered [13, 18-20]. It is commonly accepted, that dendritic patterns are not thermodynamically favored structures, but formed under conditions far from equilibrium [12, 21, 22]. Therefore they are the products of kinetics processes. Our previous studies have shown that the rates of chemical diffusion and reaction play a dominant role in shaping the morphology of particles. By regulating diffusion and reaction calcium carbonate particles with various morphologies have been prepared [23, 24]. The compromise between diffusion and reaction leaded to the formation of a snow-shaped particle which is a well-developed dendritic structure [24]. Later, we have extended the diffusion and reaction study to other material systems [25]. But accompanying these studies is the difficulty in distinguishing the role of diffusion and reaction in shaping

materials since in most cases these two processes are coupled.

In this paper, we aim to figure out the role of reaction kinetics in shaping structures of materials via simplifying the reaction system. Silver particles are synthesized in a designed two-cell electrochemical reactor. The electron is used as the reductant to reduce silver ions. By passing electrons to the cell containing only silver nitrate at broad current control, silver particles are synthesized on the surface of cathode. The silver products are collected and characterized by electron microscopy. The dependence of silver morphologies on the current density is investigated and the mechanism behind the dependence is discussed in the following.

Experimental Sections

Materials

Silver nitrate and potassium nitrate were purchased from Sigma-Aldrich. Al wire (>99.9%) was obtained from Beijing Jiaming Non-ferrous Metals Industry Co. Ltd. (Beijing, China). All chemicals were of analytical grade and were used without further purification. Deionized water with a resistivity higher than 18.2 MΩ generated by a Mili-Q system (Millipore, USA) was used throughout the experiments.

Synthesis of Silver Particles by Electrochemical Reaction

The silver particles were synthesized in a designed electrochemical reactor (as shown in Figure 1) which includes two cells connected by a salt bridge and an electric wire. A zinc rod and an aluminum rod were connected by a wire, the former serving as the anode placed in potassium nitrate solution, and the latter one as the cathode immersed in silver nitrate solution. A voltage-stabilized 12V power was linked in the middle of the wire. The current density was regulated by serial resistances. Electrons were passed into the nitrate silver solution via the cathode forming silver particles on the cathode. The electrodes are metal rods with a diameter of 1 mm. They were washed by ethanol and pure water to have a smooth and clean surface before immersing into the solution. The lengths of cathode and anode immersed in solution

are 3cm, 5cm, respectively.

The electrochemical reaction was carried out in the designed reactor at room temperature (25℃). The electrochemical deposition was performed at various applied current densities and the cathode coated with silver product was gently taken out from the solution and cut into two pieces. One piece was dried in air for characterization by scanning electron microscopy. Another one was sonicated in pure water, and the silver samples were collected from the water for further characterizations.
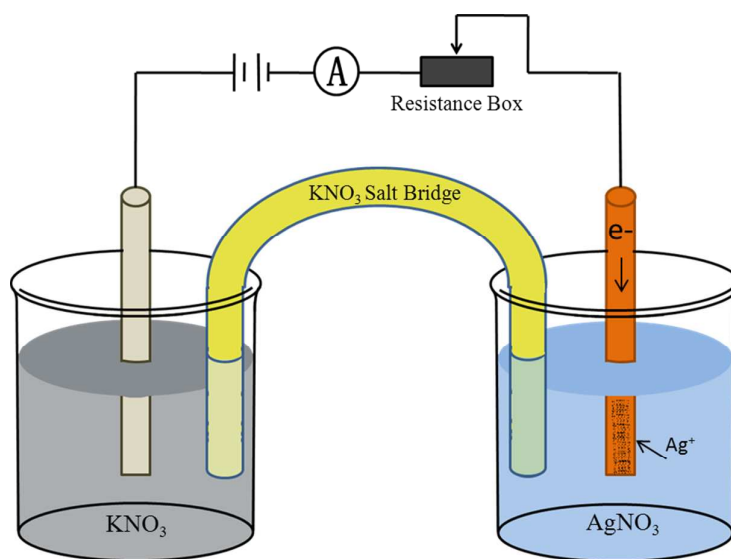

Figure 1 An illustration of the designed electrochemical reactor. Two vessels are connected by a salt bridge and an electronic wire. Silver ions are reduced by the electrons coming from an external power, forming silver particles on the surface of the cathode.

Characterization of Silver Products

The morphology of silver products was characterized by a field-emission scanning electron microscopy (JSM-7001F SEM) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) and a JEM-2100 (UHR) Transmission Electron Microscopy (JEOL, Japan) at an accelerating voltage of 200 kV. The phase and composition of the products were determined by X-ray Diffractometry (PANalytical B.V., Netherlands), using CuKα radiation, and the data were collected over the range of 2θ from 5° to 90° at a scanning step of 0.1°.
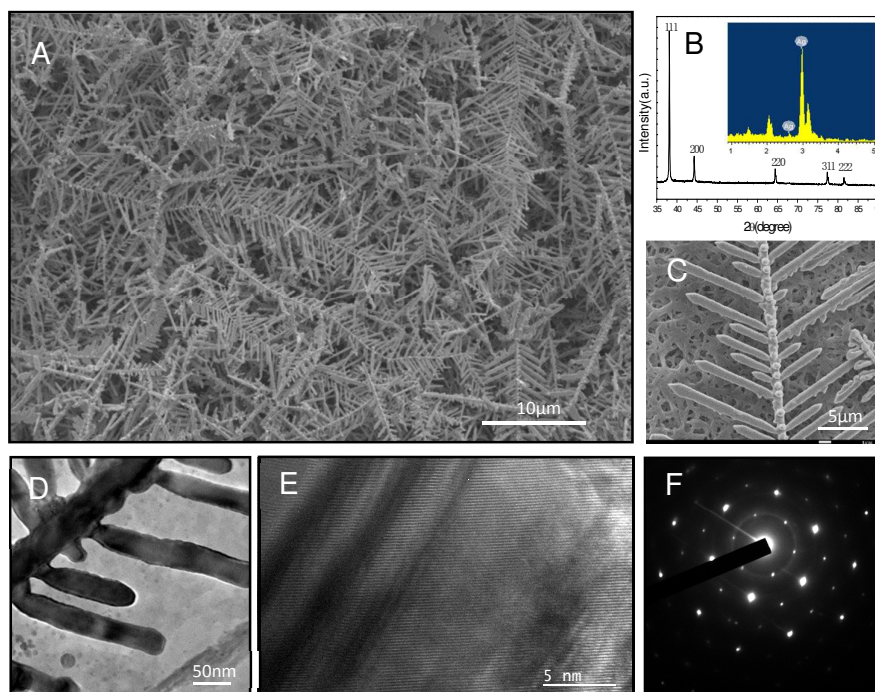
Results and Discussions

Figure 2 Morphologies of silver particles synthesized at a current density of 700μA for ten minutes reaction. A and C are scanning electron microscopic images at low and high resolution, respectively; D and E are transmission electron microscopic images at low and high resolution, respectively; B is the X-ray diffraction spectrum; F is electron diffraction pattern.

Silver samples synthesized in the designed electrochemical reactor at the current density of 700 μA for ten minutes reaction are characterized by electron microscopy and X-ray diffraction, as shown in Figure 2. Figure 2A shows that massive dendrites are formed on the surface of the cathode. These dendrites have long trunks and short branches, looking like a fishbone. The branches are parallel seated on the side of the trunk. An acute angle of approximately 60 degree is formed between the branch and the trunk, as shown in Figure 2C. The Energy Dispersive X-Ray Spectrum (EDS) in the inset of Figure 2B indicates that the dendrites are composed of silver. The XRD spectrum in Figure 2B confirms the results of EDS. The sharp peaks and specific absorptions indicates that the product crystallizes well with a structure in good agreement with the JCPDS 04-0783. The TEM image of Figure 2D shows that the

silver dendrite is not fully symmetrical. The trunk has protuberances on its surface, and the side branches have different lengths and intervals. The inhomogeneous density in the branches indicates that they have different thickness. The high resolution TEM image in Figure 2E shows that the crystal has the same lattice distance in the areas with high and low density, indicating single crystalline feature of the sample, which is confirmed by the electron diffraction pattern in Figure 2F. These results indicate that the formation of these silver dendrites follows the classical crystallization via an atom-based layer by layer growth process, which is different from the particle-based non-classic crystallization [26, 27].
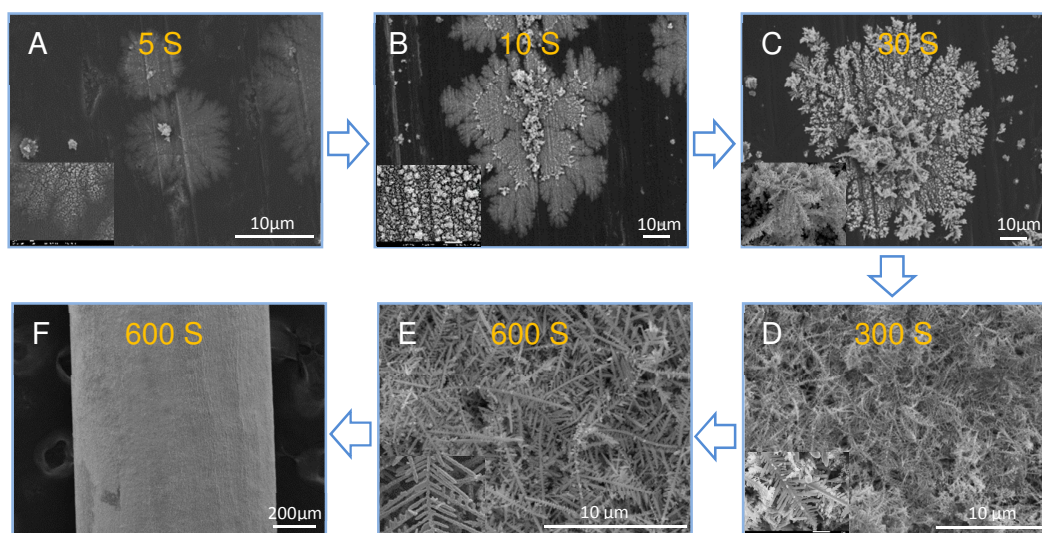

Figure 3 Evolution of silver dendrites as a function of reaction time at the current density of 700µm. Initially, the silver nucleates on the surface of the cathode. With the advance of reaction, the nuclei grow up, forming dendritic structures. The cathode is completely covered after the reaction time more than 300 seconds.

To disclose the formation process of silver dendrites, we collect samples at various reaction times and characterize these samples by scanning electron microscopy, as shown in Figure 3. In the beginning of the reaction (5s), silver nucleates on the surface of the cathode, forming a disconnected spherical-pattern coating. The inset of Figure 3A shows that the spherical pattern is composed of small crystals. With the progress of reaction, the spherical pattern become thick and small

particles start to grow on the surface of the pattern, as shown in the Figure 3B. These small particles tend to develop to dendritic structures after 30 seconds, as shown in the inset of 3C. After minutes, these particles grow up, forming silver dendrites [28], as shown in Figure 3D and its inset. These structure develop into clear dendrites in the later stage of the reaction. The dendrites loosely disperse on the surface of the cathode, forming a silver layer on the cathode, as shown in Figures 3E and 3F. Therefore the formation of silver dendrites experiences a nucleation on the surface of electrodes first, followed by the growth of silver particles.

Dendritic structures are often produced in electrochemical deposition, especially in fine powdery deposition [29, 30] occurring under the conditions of high over potential and relatively high concentration. Their formation was ascribed to the instability of the growth front in a diffusion limited field, which was extensively investigated by many researchers, such as Sekerka and Mullins [31]. It was proposed that the formation of dendritic structure is controlled by the chemical gradient on the growth front [32, 33]. Since the chemical gradient is determined by the supplement and the consumption of chemicals, the growth of dendritic structures is adjustable by changing chemical diffusion and reaction rates. In the electrochemical reaction, current density is related with reaction rate. Therefore, the current density should have an influence on the morphologies of silver products, which will be evaluated in the following.

The morphologies of silver products synthesized at various applied current densities are shown in Figure 4. At a low current density of 25 μA, polyhedral silver aggregates are formed, standing on the surface of the cathode. Around the aggregate, the surface of the cathode is largely uncovered. When the current density increases to 200 μA, long and thick silver rods are formed. On the surface of the rods there are a lot of protrusions which makes the rod look like the embryo of branches, as shown in Figure 4B. Increasing the current density to 300 μA let the protrusions grow up, forming thick dendritic structures, as shown in Figure 4C. When the current density increases to 500 μA, silver dendrites are largely synthesized, forming a coat on the surface of the cathode, as shown in Figure 4D. Further increasing the current density

to 700 µA makes the dendrites become thin and long, as shown in Figure 4E. When the current density increases to 1000µA, the silver dendrites are mixed with small cubic particles, as shown in Figure 4F. Further increasing the current density to 2000µA, the cubic particles turn into the main product, as shown in Figure 4G. Therefore, the morphology of silver products is largely dependent on the current density, which confirms our previous assumption that the current density is associated with the reaction rate and influences the structures of the silver products.
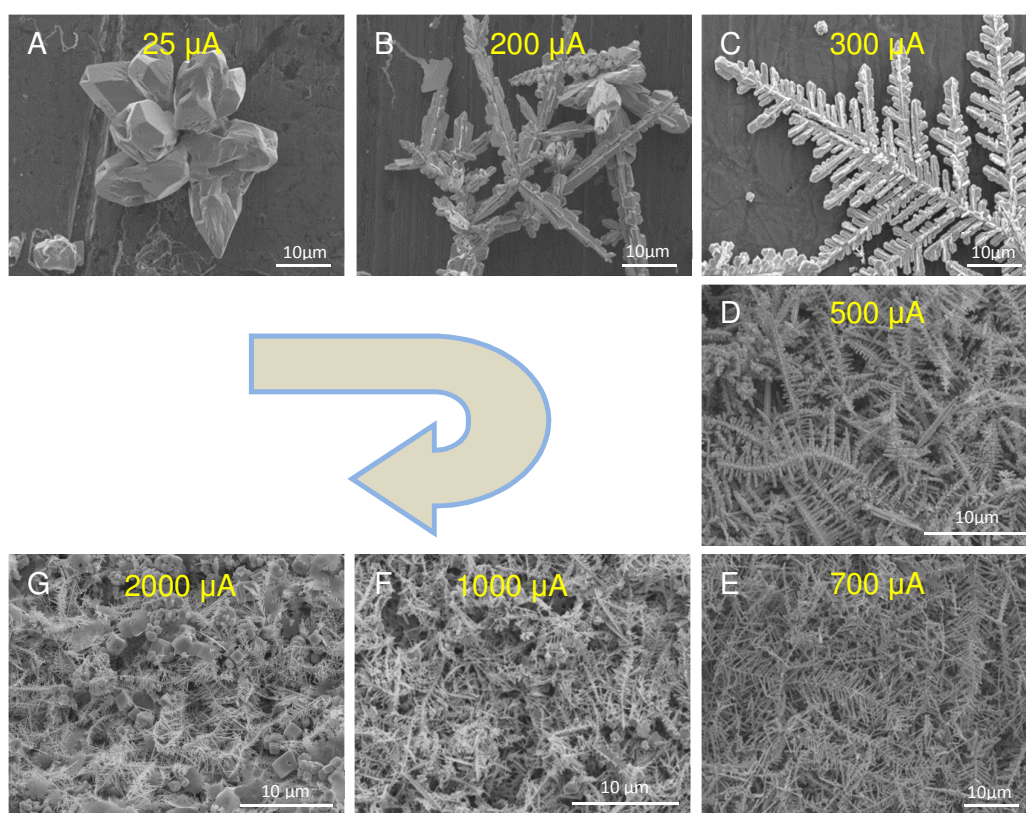

Figure 4 SEM images of the silver particles synthesized at various applied current densities for ten minutes reaction. With the increase of current density, polyhedral silver aggregates change to silver dendrites which are the main product at 300-1000 µA. Further increase of current density leads to the formation of cubic particles mixing with dendrites.

To understand the change of silver morphology with current density, we have to consider the nucleation and growth of silver particles at various current densities. At the low current density of 25 µA, the reduction of silver ions is slow, which leads to a limited nucleation on the surface of the cathode. Later growth of these nuclei is also

limited by slow reduction. Therefore, the growth of silver products is limited by the reaction rate, forming compact polyhedral aggregates, which is in good agreement with the reaction limited aggregation (RLA) model. When the current density increases to 500 μA, the reduction rate of silver ions is enhanced remarkably and the growth of silver products is dominated by the diffusion of silver ions, leading to the formation of dendritic structures, which accords well with the diffusion limited aggregation (DLA) model. Further increasing the current density to more than 1000 μA, secondary nucleation is accompanied by the growth of particles. The secondary nucleation slows down the growth of dendrites, leading to the formation of short and thin dendritic structures. The growth of the newly-born nuclei yields cubic particles which mix with silver dendrites. The dependence of silver morphology on current density is illustrated in Figure 5, which is expected to be helpful in understanding the results in Figure 4.
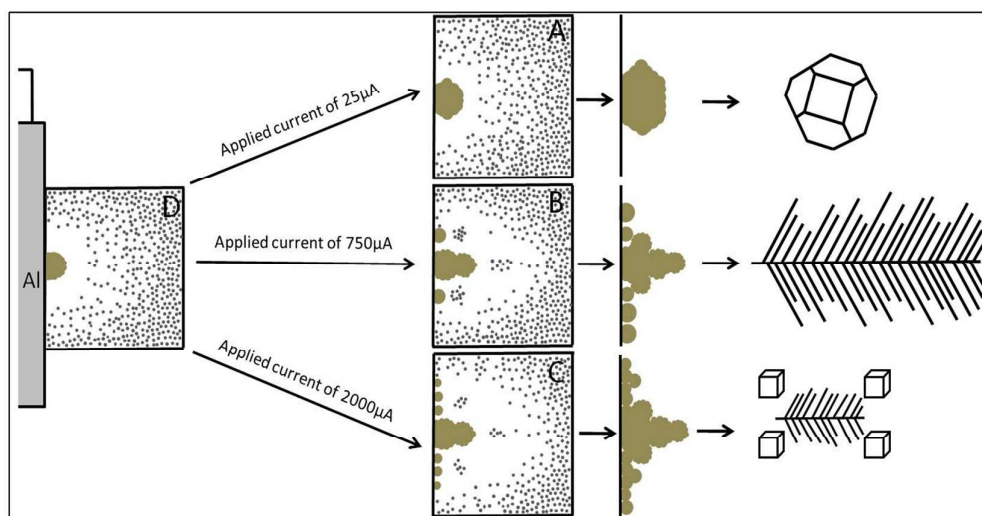

Figure 5 Schematic illustration on the change of silver morphology with applied current densities.

The above results and discussion suggest that the current density changes the morphologies of silver products via influencing the nucleation and growth of silver particles. In the following, we attempt to verify the influence of current density on the nucleation and growth of silver products, respectively. To disclose the nucleation

process, we have collected the silver samples after 10 seconds and 10 minutes of reaction, as shown in Figure 6. At the current density of 25 μA, a few nuclei are formed after 10 seconds and they grow into big polyhedral particles after 30 minutes. These particles loosely disperse on the surface of the cathode, as shown in Figure 6A2. The increase of the current density to 200 μA leads to the formation of dendritic crowns which are sparsely dispersed on the surface of the cathode in the initial 10 seconds. These crowns grow up after 10 minutes and disconnectedly attach on the surface of the cathode, as shown in Figure 6B2. When the current density is increased to 500 μA, the density of nuclei increases remarkably in the initial reaction and these nuclei grow up after 10 minutes, forming a silver layer on the surface of the cathode, as shown in Figure 6C2. Further increasing the current density to 700 μA, the density of nuclei is further enhanced in the beginning of the reaction, and a dense layer is formed after 10 minutes, as shown in Figure 6D2. When the current density is increased to 2000 μA, the surface of the cathode is fully covered by the nuclei after 10 seconds reaction. Irregular particles as well as dendrites are synthesized on the cathode in the beginning of the reaction. After 10 minutes, the cathode is covered by a thick silver layer as shown in Figure 6E2. Owing to the quick reaction at 2000μA, the layer is thicker than others and some uncovered parts are observed on the cathode at the same time. These results show that the increase of current density remarkably enhances the nucleation of silver products, which confirms our previous consideration that the current density influences the nucleation process.
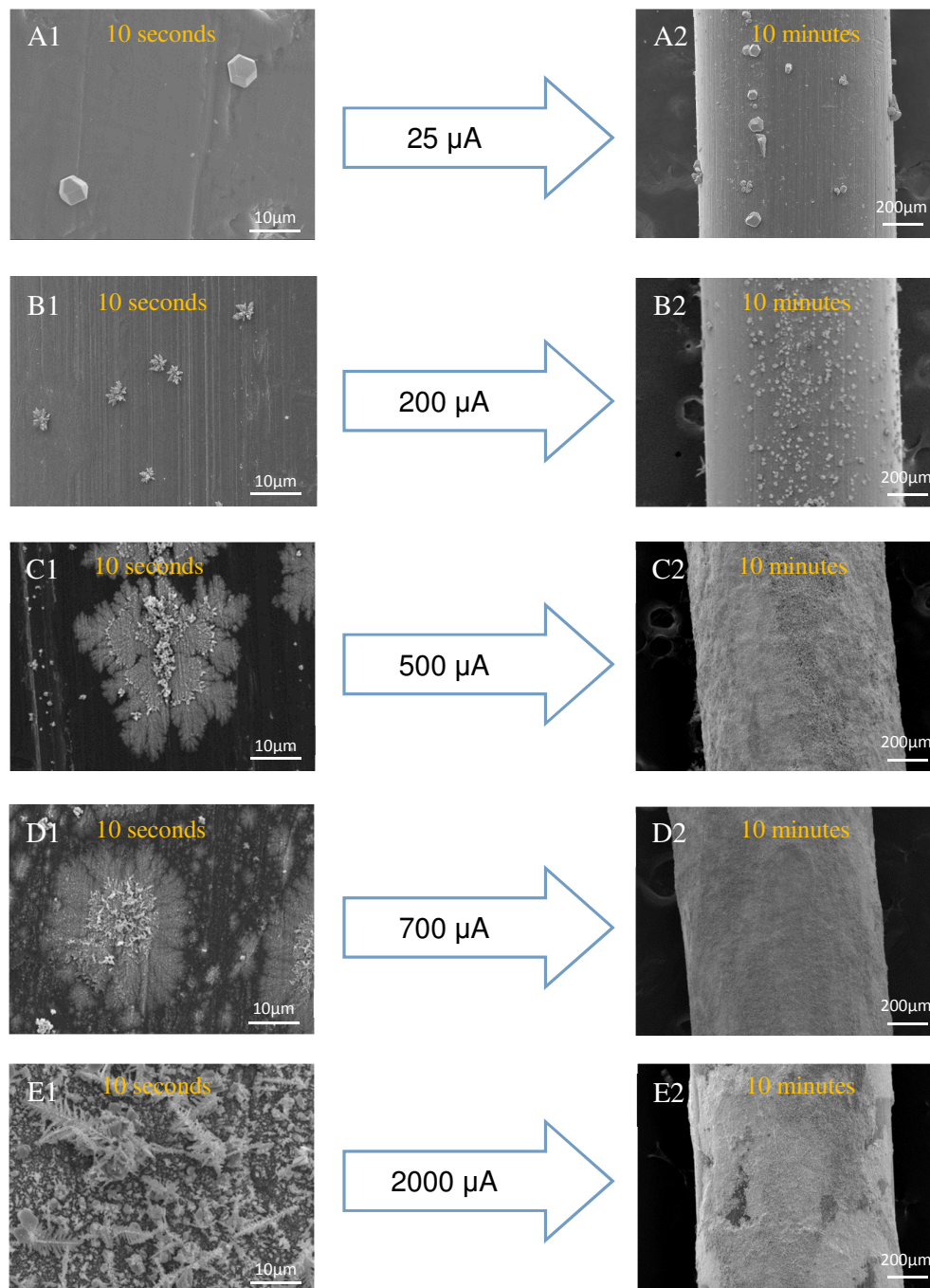
Figure 6 SEM images of silver products synthesized at various applied current densities in the reaction lasting for 10 seconds (left) and 10 minutes (right), respectively. Limited nucleation occurs at the low current density while extensive nucleation occurs at the high current density.

To verify the influence of current density on the growth of silver particles, we synthesize silver particles at various concentrations of the silver salts. When other

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parameters are kept the same, the increase of salt concentration improves the supplement of silver ions to the surface of the cathode. At the current density of 700 μA, the morphology of silver particles changes from dendrites to polyhedral shape with the increase of salt concentration, as shown in Figure 7. At 1 mM of silver nitrate, the products are composed of silver dendrites which form a layer on the surface of the cathode, as shown in Figure 7A. Increasing the silver nitrate concentration to 6 mM does not lead to a remarkable change of silver morphology, as shown in Figure 7B. But when the concentration is increased to 20 mM, the silver dendrites disappear. Instead thick rods and polyhedral particles are formed. These particles loosely disperse on the surface of the cathode, as shown in Figure 7C. Further increasing salt concentration to 30 mM only polyhedral particles are formed and sparsely disperse on the cathode, as shown in Figure 7D, which is similar to the samples formed at 25 μA in Figure 4. Hence, the reaction and diffusion are two relative parameters regulating the silver morphology. A quick reaction could become the rate control step when the diffusion is greatly enhanced. This can be easily understood within the MS model, in which the dendritic structures are proposed to be determined by the concentration gradient of reactive ions on the growth front. The reaction rate determines the consumption of reactive ions while the diffusion rate determines the supplement of these ions. The relative proportions of diffusion and reaction determine whether the concentration gradient could be formed and stably present, which dominates the growth and development of dendritic structures.
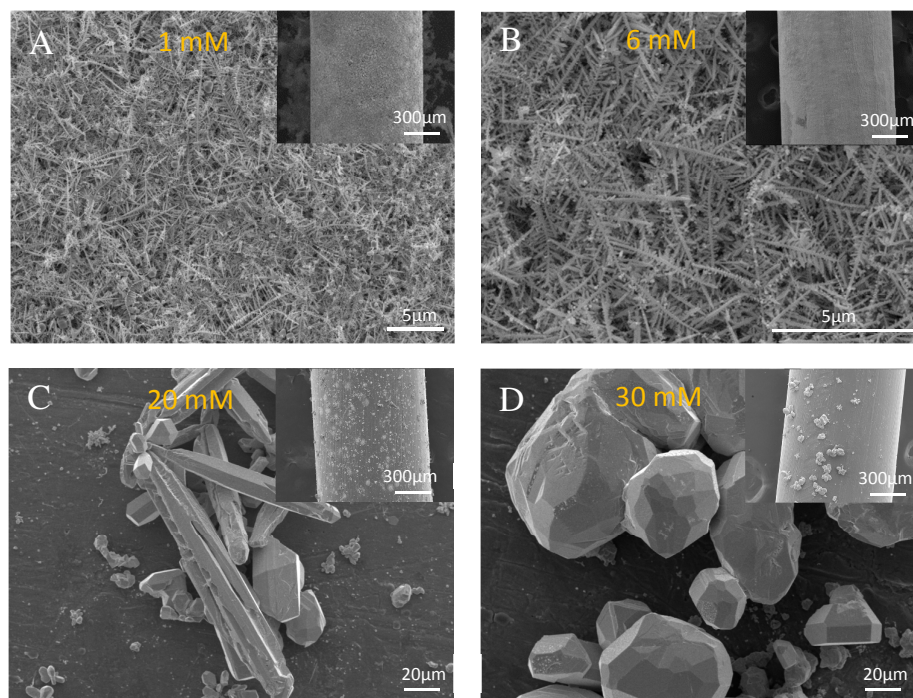
Figure 7 SEM images of silver products synthesized at different concentrations of silver nitrate under the current of 700μA. The increase of the concentration of silver salt results in the disappearance of dendritic structures and the formation of compact particles which are sparsely dispersed on the surface of the cathode.

The above results and discussions show that the current density determines the generation rate of silver atoms, which dominates the nucleation and growth rate of silver products. At a low current density, a nucleation is followed by the growth of the nuclei at a reaction limited condition. The growth of nuclei is dominated by thermodynamics, forming thermodynamically favored compact structures. With the increase of current density, both the nucleation and growth of products are enhanced. An extensive nucleation is followed by a quick growth. Therefore, the silver ions around the nuclei are quickly consumed. As the supplement of silver ions from the bulk solution is not improved, the quick consumption creates a concentration gradient around the growth front with a lower concentration near the front while a high concentration far from the front. This concentration gradient leads to an instability on the surface of crystals, triggering the formation of protrusions and later growing into dendritic structures [34]. At a high current density, the nucleation is prolonged and accompanied by the growth of products, which leads to a dynamic distribution of

silver ions. The heterogeneous chemical distribution causes the formation of silver particles with different morphologies. If the concentration of silver ions is highly increased, the supply of silver ions becomes sufficient even at a high current density. In such a condition, the silver particles with thermodynamically favored compact structure are formed. Therefore, the current density is a powerful tool to regulate the reaction kinetics which in turn influences the nucleation and growth of products forming diverse structures. The findings in this paper are expected to be helpful in discovering the phenomena and mechanism behind shape control via chemical diffusion and reaction.

Conclusions

The dependence of silver morphologies on current densities by variation over 2 orders of magnitude was investigated in this paper. Silver particles were synthesized in an electrochemical reaction at various current densities. At the low current density of 25 μA, polyhedral silver particles were formed and loosely dispersed on the surface of the cathode. If the current density increased to 300 μA, silver dendrites were largely produced and formed a coat on the cathode. If the current density increased to 1000 μA, both small silver cubes and dendrites coexisted. The silver cubes became the main products at the current density of 2000 μA. The change of silver morphology with current densities was ascribed to the current dependence of nucleation and growth of particles in an electrochemical reaction. At a low current density, nucleation was limited and the nuclei grew to thermodynamically favored shape. With the increase of current density, nucleation was enhanced and the growth of nuclei followed a diffusion controlled growth model, forming dendritic structures. At a high current density, continuous nucleation dominated the reaction and the newly-born nuclei formed cubic particles which mixed with dendritic structures. Therefore, the current density is an effective tool in regulating the reaction rate to shape materials. Further study in this direction is expected to improve our understanding on the shape control by diffusion and reaction, as well as to build up a new approach for rational

synthesis of materials.

Acknowledgements

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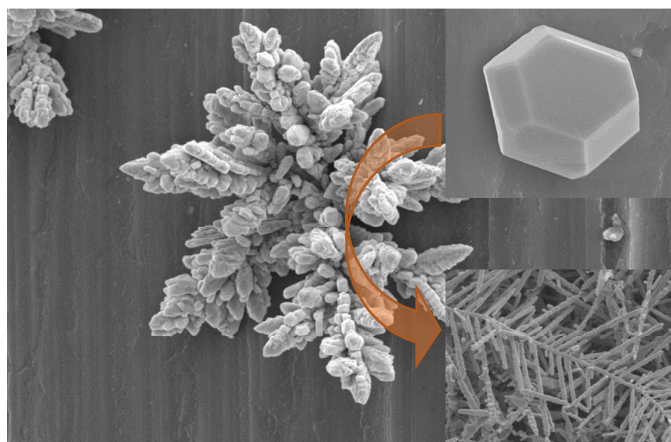
By regulating current densities over two orders of magnitude, silver morphologies changes from polyhedron to dendrites in an electrochemical synthesis.