Supplementary Materials

Shaping Particles by Chemical Diffusion and Reaction

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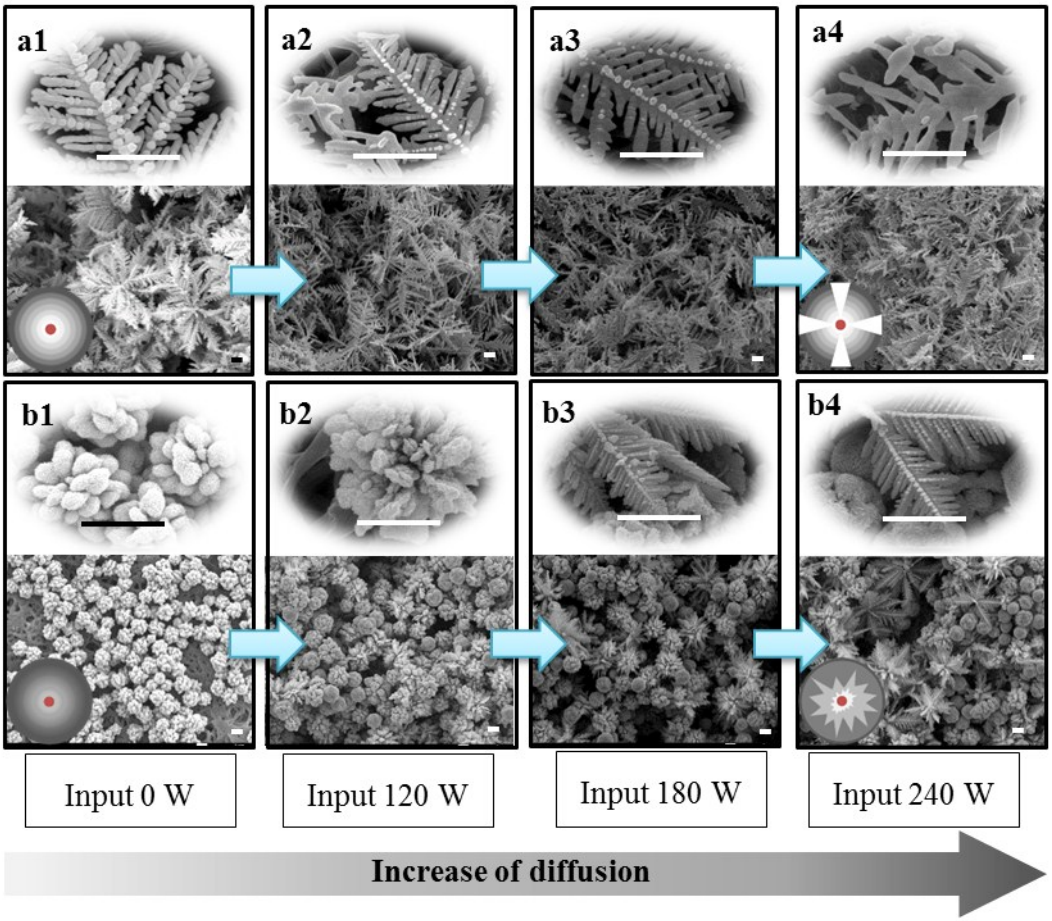

Figure S1. SEM images of silver products synthesized in 10mM hydroxylamine (a) and 200mM hydroxylamine (b) water solutions at various ultrasonic power. (a1-a4) show silver samples synthesized in ultrasonic power at 0W, 120W, 180W, 240W, respectively; the same to (b1-b4). The scale bar in all images is 1μm.

To further confirm the diffusion contribution on the proposed modes, we employ ultrasound to improve the diffusion of silver ions in the solution. Two reaction systems, namely the reaction at 10 mM hydroxylamine and the reaction at 200 mM

hydroxylamine, are chosen as examples to investigate the ultrasonic effects. Pure water acts as the solvent in both reaction systems. Without sonication, silver dendrites are formed at 10 mM hydroxylamine, while spherical aggregates are formed at 200 mM hydroxylamine, as shown in **Figure S1** a1 and b1, respectively. With the increase of ultrasonic power, the dendritic structures formed at 10 mM hydroxylamine deform slightly, as shown in Figure S1 a2-a4, which is attributed to the disturbance of the concentration distribution by sonication. The deformation becomes clear when the input of ultrasound is 240 W, as shown in the inset of Figure S1 a4. The employment of ultrasound also deforms the spherical aggregates. Radically symmetric aggregates are formed at low input of ultrasound, as shown in Figure S1 b2, while dendritic structures are formed at high inputs of ultrasound, as shown in Figure S1 b3 and b4, which is ascribed to the change of chemical distribution around the growth front. Due to the sonication, a concentration gradient around the growth front is partly established, leading to the formation of dendritic structures.

A n-propanol is employed to regulate the viscosity of the solution, while the glycine is used to regulate the reaction rate [1]. From the bottom to the top in **Figure S2**, the diffusion of silver ions increases as a result of a change in volume ratio of n-propanol from 50% to 0% corresponding to a decrease of solution viscosity from 2.7 cP to 0.89 cP. From the left to the right in Figure S2, the reaction rate increases, as the concentration of glycine changes from 20 mM to 0 mM. Silver dendrites are largely formed, as shown in the right top of Figure S2 d4, which is attributed to the existence of a concentration gradient around the growth front of crystals. A decrease of diffusion from d4 to a4 in Figure S2 leads to the deformation of dendritic structures, which is ascribed to the change of the concentration gradient induced by diffusion regulation. A decrease of the reaction rate from d4 to d1 in Figure S2 leads to the switch of dendritic structures to spherical aggregates. In the corner down and left, compact silver particles are largely formed, which is attributed to the slow reaction. Owing to the much lower viscosity of n-propanol than that of glycine, here the diffusion effect is not as significant as the reaction effect. Therefore, the change of

morphologies from the top to the bottom is not as distinct as the change from the left to the right.

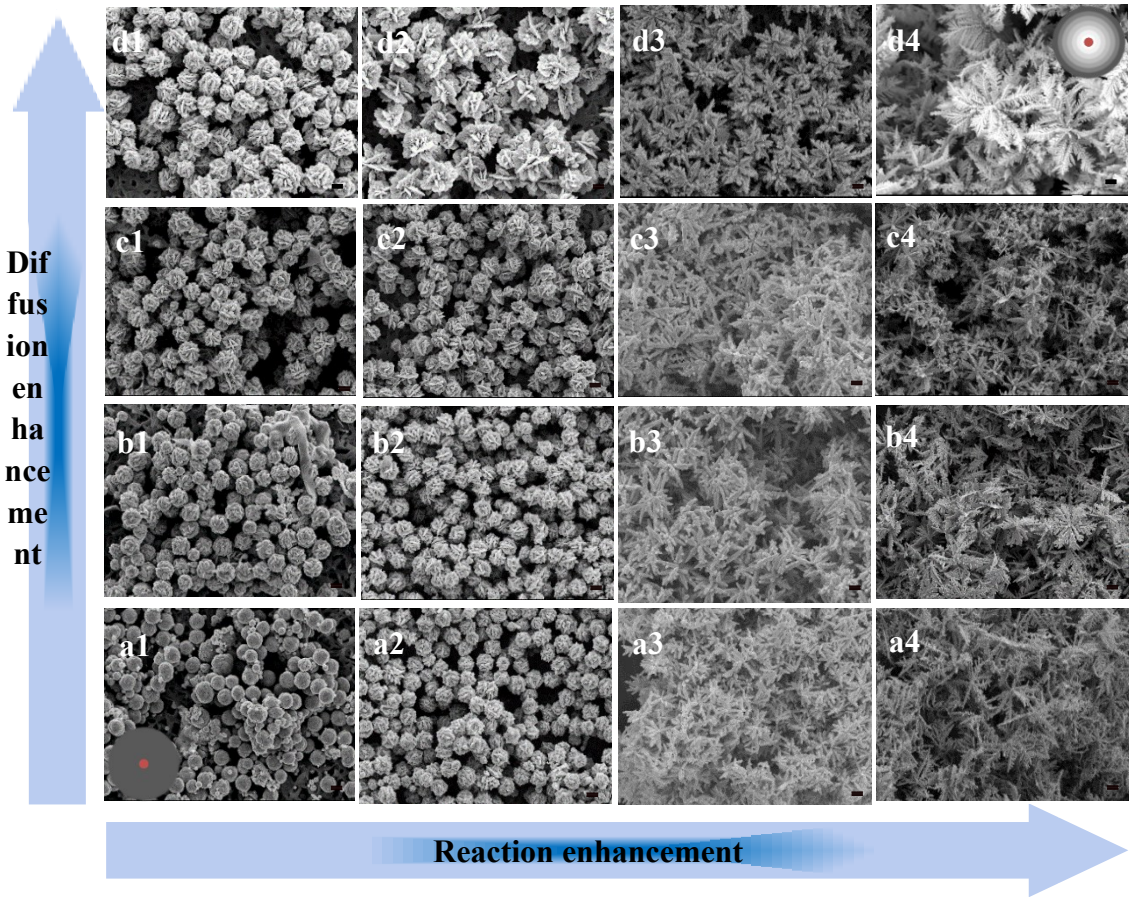

Figure S2. SEM images of the silver particles synthesized in a propanol and water solution at different diffusion and reaction conditions. The horizontal variable is the concentration of glycine, while the vertical variable is the volume ratio of propanol in water. Row a - row d show the silver products synthesized at 50%, 30%, 10%, 0% n-propanol ratio in solvents, respectively. Column 1-column 4 show the silver products formed at 20mM, 10mM, 0.1mM, 0mM glycine, respectively. The scale bar represents 1μm.

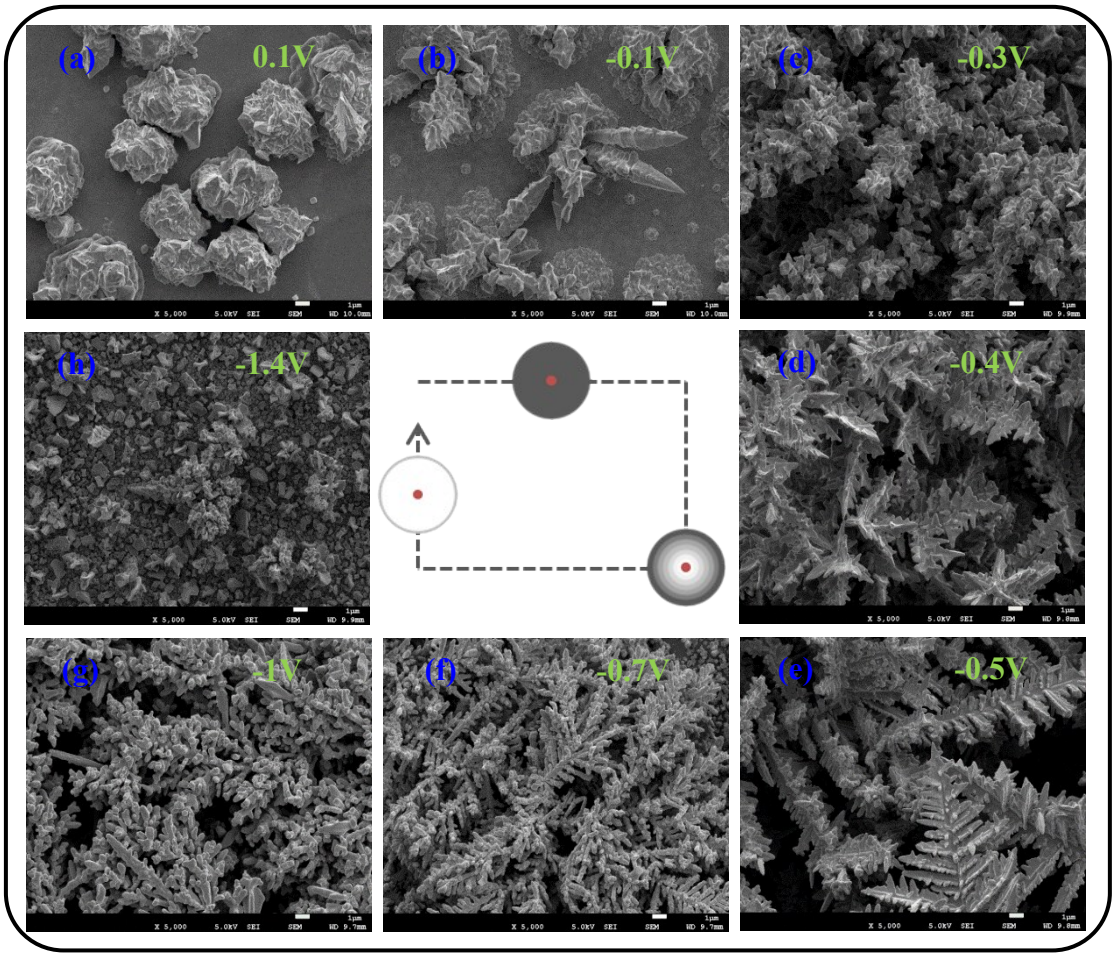

Figure S3. The structures of Au particles under different growth modes induced by different potentials in water. Dendrites are formed by degrees and disappear finally, which is the same as those happen to Ag and Cu.

Gold particles are also synthesized by the electrochemical deposition method in the potential range of 0.1V to -1.4V. Irregular polyhedrons are formed at the relatively positive potential 0.1V, as shown in **Figure S3**a. When the potential is moved towards the negative direction step by step, particles become long and sharp first, then muricate-like, finally typically dendritic shape at -0.5V. The leaf-like gold dendrites have hierarchical structures, and some tertiary branches are observed on the edge of leaves. In succession, dendrites undergo coral thicket-like shapes and disappear gradually, and tiny particles replace dendrites on the substrate at -1.4V. The change of gold morphology with reaction rates is similar to that of silver and copper, which confirm the general role of diffusion and reaction in shaping particles.

References

1 J. M. Liu, T. Yang, C. X. Li, J. H. Dai and Y. S. Han, Reversibly switching silver hierarchical structures via reaction kinetics. *Sci. Rep.,* 2015, *5*, 14942.