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Oriented aggregation of silver particles in gel solutions

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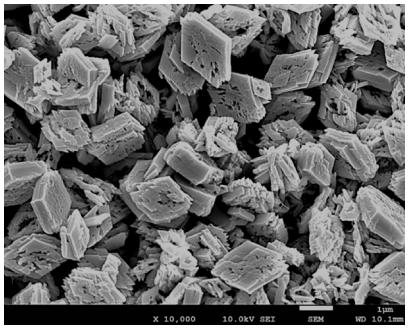
GRAPHICAL ABSTRACT

This paper reports an investigation on the mechanism of orderly aggregation of particles at a diffusion limitation.



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ABSTRACT

Here we report a mechanism investigation on the ordered aggregation of particles at a diffusion limitation. A gel solution is employed to create a diffusion limitation for the synthesis of silver particles. Diamond-shaped silver particles are largely generated in an agar gel solution. The time dependent characterization of samples indicates that the diamond-shaped silver particles are built up by the aggregation of primary nanocrystals. A molecular simulation is conducted to reveal this aggregation process. Under diffusion limitation these tiny crystals tend to aggregate by sharing the high energy facets of (100), while the low energy facets of (111) is largely exposed, which results in an oriented aggregation, forming diamond-shaped particles. This formation mechanism is confirmed by following experiments via conducting the synthesis in different gel systems at different gel addition. The results of this paper indicate that the diffusion of building blocks plays an important role in the structure development of aggregates, which was underestimated previously.

1. Introduction

Particles with hierarchical structures show enhanced performance in the fields of solar cells [1,2], catalysis [3,4] and surface enhanced Raman spectroscopy [5,6]. Great effort has been devoted to synthesize complex hierarchical structures of particles in laboratories [7–11]. Some approaches employ macromolecules or surfactants as structure directing agents [12–14] to synthesize hierarchical structures. Surfactants are supposed to adsorb selectively on the facets of crystals, leading to preferential growth of crystals on the facets with less surfactants. Scientists even synthesized many valuable multilayer capsules or core/shell nanocomposites by employing surfactants or macromolecule

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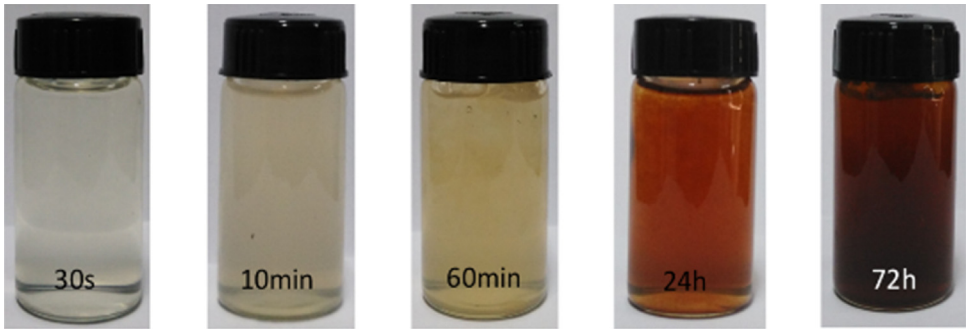

Fig. 1. Color change of the agar gel solution containing 46.3 mM silver ions as a function of the reaction time.

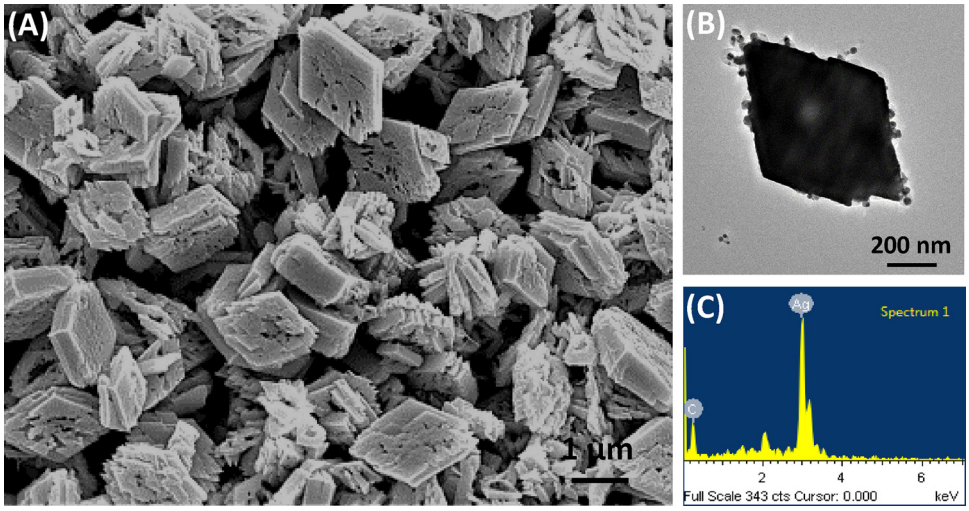

Fig. 2. Electron microscopic images of silver particles formed in an agar gel solution sealed for 1 day. SEM (A) and TEM (B) images show that the silver particles have diamond shape and the EDS pattern (C) indicates that the particles are mainly composed of silver.

polymers as "smart" or "intelligent" building blocks [15,16]. Although the synthesis of hierarchical structures undergoes a great process, the formation mechanism of different hierarchical structures does not have a consensus. There are lots of hierarchical structures formed in nature or synthesized in laboratories without the presence of surfactants [17,18], which cannot be interpreted by the selective adsorption. Therefore, the formation of hierarchical structures is still in a black box. There should be other mechanism(s) playing roles.

Diffusion and reaction processes are two common phenomena throughout the whole nature [19], which are routinely used to build and control structures on length scales from microscale (such as the deposition of minerals and crystals [20]) to mesoscale level (stripes on zebras [21]), even to the tremendous macroscale (the formation of a whole galaxy [22]). Many fascinating methods were developed to solve various problems in complicated chemical process systems [23–25]. Even though chemical diffusion and reaction are inevitably involved in the formation of materials, there are a few reports to investigate their role on the structure development of materials. Our recent study recognized that chemical diffusion and reaction influence both nucleation and growth of materials. Under diffusion limitation, hierarchical structures are usually generated [26–28]. For example, by changing the diffusion and reaction upon the precipitation of calcium carbonate, we synthesized highly ordered snow-shaped particles [29,30]. By changing the transport of chemicals, we synthesized dendritic platinum particles [31]. Both snow-shaped and dendritic particles are typically hierarchical structures, which direct our interest to discover the formation mechanism of hierarchical structures at diffusion limitation. Silver particles with diverse morphologies have been synthesized by regulating the chemical diffusion and reaction [32–34].

In this study, we employ gels as media to create a diffusion limitation, in which silver ions are reduced to form silver atoms followed by nucleation and growth of particles. Here we concern the diffusion of tiny silver particles and investigate its effect on the morphology development of products. The diffusion rate of silver particles is regulated by changing the viscosity of gels. Silver particles formed are characterized by electron microscopy. A molecular simulation is conducted to reveal the formation process of silver structures. A plausible formation mechanism of these ordered structures is proposed and evaluated in this paper.

2. Materials and methods

2.1. Materials

Silver oxalate ($Ag_2C_2O_4$, AR, Sinopec. Comp. LTD, Beijing, China), Ethanolamine ($H_2NCH_2CH_2OH$, for short MEA, AR, Xilong Chemical Comp., Shantou, China), Ethylenediamine ($H_2NCH_2CH_2NH_2$, for short EDA, AR, Xilong Chemical Comp., Shantou, China), Agarose G-10 (AR, GENE Compo. LTD, Spain), Agar Powder (CP, Beijing Anboxing BLO-Tech. Comp. LTD, China), Polyvinyl alcohol (PVA-124, AR, Sinopharm Chemical Reagent Comp. LTD, China) were purchased and used as received.

2.2. Synthesis of silver hierarchical structures

Firstly, a certain amount of EDA and MEA were dissolved in cold water below 20 °C. Then $Ag_2C_2O_4$ at designed amounts was slowly added into the EDA-MEA solution until $Ag_2C_2O_4$ completely dissolved,