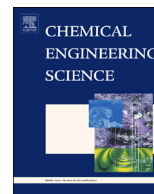




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Manipulating silver dendritic structures via diffusion and reaction

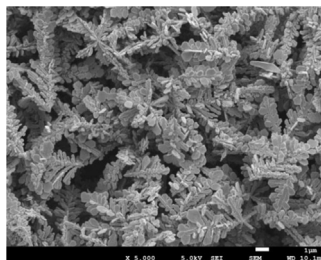
Tao Yang^{a,b}, Yongsheng Han^{a,*}, Jinghai Li^a^a State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China^b University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Dendritic structures are regulated by chemical diffusion and reaction.
- The decrease of reaction rate leads to the disappearance of side branches of dendrites.
- The reduction of diffusion rate shortens the main trunks of dendrites.

GRAPHICAL ABSTRACT

Silver dendrites were finely tuned by a chemical engineering approach via controlling chemical diffusion and reaction rates, which indicated that a regulation on diffusion and reaction rates is a promising way for controllable synthesis of dendritic structures and an effective approach to suppress the growth of dendrites in industries.



ARTICLE INFO

Article history:

Received 11 May 2015

Received in revised form

11 August 2015

Accepted 12 August 2015

Available online 20 August 2015

Keywords:

Shape control

Dendritic structure

Silver

Diffusion

Reaction

ABSTRACT

A dendrite is one of the most esthetically pleasing structures, with the best-known example being snowflakes. Although the formation of dendrites has been studied for centuries, the way to control their growth is limited. Here we report an attempt to manipulate the growth of dendritic structures via controlling chemical diffusion and reaction. The silver dendritic structures are synthesized by reducing silver ions in solution. The diffusion of chemical agents is regulated by changing the viscosity of the solution while the reaction is regulated by adding acids. The decrease of reaction rate leads to the disappearance of side branch of dendrites while the reduction of diffusion rate shortens the main trunk of dendrites. The silver dendrites are finely tuned by chemical diffusion and reaction. Following studies suggest that diffusion and reaction determines the chemical concentration around the growth fronts, which influences the growth of crystal structures, leading to the formation of diverse silver dendritic structures. The findings in this study indicate that chemical diffusion and reaction are two effective tools to regulate dendritic structures, promising a different way to promote or prevent the growth of dendritic structures in industries.

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1. Introduction

Dendritic structures are widely present in nature from the macroscopic olivine crystals in the mantle of Earth to the microscopic metallic dendrites in alloys (Warren, 2006; Huppert, 1986).

They are also typical structures of snowflakes and of other materials (Hoffman and Libbrecht, 2011; Maddox, 1983; Wisniewski et al., 2013; Harry et al., 2014), as well as a key element in the neural system of animals and human being (Wong and Ghosh, 2002; Scott and Luo, 2001). More than 10 billion metallic dendrites are produced in industry for every second during solidification (Rappaz and Kurz, 1995). The structure and interaction of metallic dendrites determine the properties of products. Therefore, controlling the formation of dendritic

* Corresponding author.

E-mail address: yshan@ipe.ac.cn (Y. Han).

structures is an important issue in solidification. On the other hand, dendritic structures are expected in the synthesis of nano-materials because they present distinctive properties (Rashid and Mandal, 2007; Gu and Zhang, 2008; Qin et al., 2012; Avizienis et al., 2013; Tang et al., 2014). For example, the sandwich-like structure containing silver dendrites exhibits multiple optical pass bands in the infrared region (Liu et al., 2008) while the silver dendritic array on a zinc oxide template shows a single transmission band (Liu et al., 2008).

Thanks to the development of theory and simulation over the past decades (Langer, 1980; Ben-Jacob et al., 1988; Cross and Hohenberg, 1993; Brune et al., 1994; Sander, 1986, 1987), our understanding of dendrite growth progressed remarkably. The steady-state dendrite growth model, which is based on the earlier diffusive transport theory of Ivantsov, is commonly accepted (Haxhimali et al., 2006). It is proposed that the complex morphology of dendrites reflects a competition between the order associated with the symmetries of the crystal structure and the morphological instabilities arising from the nonlinear transport process (Granasy et al., 2003). The growth of dendrites is a compromise of the interplay of transport of mass and surface energy (Rappaz and Kurz, 1995). On one hand, the surface energy tends to make the crystal as compact as possible (Ben-Jacob et al., 1988). On the other hand, the concentration gradient induces protrusions (Tiller, 1964).

Despite the progress in theories and simulation, the practical technique to control the growth of dendrites remains limited. Since the dendritic structures are not thermodynamically favored but formed under conditions far from equilibrium, they are products of kinetic processes (Cross and Hohenberg, 1993; Ben-Jacob and Garik, 1990; Granasy et al., 2004). Consequently, kinetic factors should be considered with emphasis. Our previous studies (Wang et al., 2013; Yang et al., 2014) have shown that diffusion and reaction of chemicals are two important kinetic factors influencing the structure development of materials (Grzybowski et al., 2005). It is the aim of this paper to verify whether the chemical diffusion and reaction is effective in regulating dendritic structures. We synthesized silver dendrites by a conventional solution-based reduction approach with silver nitrate as the precursor and hydroxylamine as the reducer. The diffusion is regulated by the viscosity of the solvent and the reaction is regulated by adding nitric acid. A quantitative regulation of diffusion and reaction is conducted. The effect of diffusion and reaction on the structure of dendrites is investigated and the mechanism behind their effects is discussed in the following.

2. Materials and methods

Hydroxylamine aqueous solution was purchased from Sigma-Aldrich. Silver nitrate and ethylene glycol (EG) were obtained from Xilong Chemical Company. Ethanol and nitric acid were supplied by Beijing Chemical Company. All chemicals were of analytical grade and were used without further purification. Deionized water from a Millipore system has a resistivity of more than 18.2 MΩ cm.

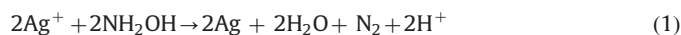
2.1. Preparation and characterization of silver dendritic structures

In the synthesis of silver dendrites, 46 mL deionized water in a round-bottom flask was kept at 30 °C by a water bath. Then 2 mL 50 mM NH₂OH solution was added followed by the addition of 2 mL 25 mM AgNO₃ solution under strong stirring. After the mixture was stirred for 5 min, the product was centrifuged and washed, and then the precipitate was collected and kept in an appropriate amount of ethanol. Subsequently, reaction temperature and AgNO₃ concentration were increased to 50 °C, 70 °C, 90 °C

and 10 mM, 50 mM, 100 mM, respectively, to study their effects on the evolution of silver dendrites, maintaining the mole ratio of AgNO₃ and NH₂OH at 1:2. In the reaction and diffusion controlled experiments, the reaction is regulated by adding 1 M HNO₃ (10 μL and 20 μL) to the system to slow down the reduction of silver ions. The diffusion is regulated by altering the solvent from deionized water to 50 vol% ethanol in water and pure ethylene glycol. Other procedures are similar to the standard process. The morphology of the products was characterized by a JSM-7001F field-emission scanning electron microscope (SEM), and a JEM-2100 transmission electron microscope (TEM) with an accelerating voltage of 200 kV.

2.2. Quantization of the diffusion and reaction of chemicals

According to the following reaction



the generation rate of Ag atoms is equal to the production rate of H⁺, so the reaction rate can be quantified by measuring the increment of H⁺, 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.

The diffusion was determined by chronocoulometry performed on a CHI600D electrochemical workstation (CH Instruments, Inc., China). In an electrochemical system, if the potential of the working electrode shifts from a nonreactive E_1 to a negative-enough reactive E_2 (which is sufficiently negative to enforce a diffusion-limited current), the charge Q passing to the working electrode is a function of time t (Anson, 1966)

$$Q = \frac{2nFAC_0D^{1/2}}{\pi^{1/2}} t^{1/2} + Q_{dl} + nF\Gamma_0 \quad (2)$$

where n , F , A , C_0 and D represent stoichiometric number of electrons, Faraday constant, area of working electrode, bulk concentration and diffusion coefficient of oxidized species, respectively; Q_{dl} represents the capacitive charge and $nF\Gamma_0$ quantifies the Faradaic component for the reduction of the surface excess (Γ_0) of adsorbed oxidized form. Both these two terms are independent of time. In different solvent systems, E_1 and E_2 were set as values more positive than the anodic peak potentials and more negative than the cathodic peak potentials, which were determined by cyclic voltammetry. The diffusion coefficient of Ag⁺ was calculated from the slope of the asymptote in the $Q-t^{1/2}$ curve.

3. Result and discussion

Silver dendritic structures are largely synthesized via a solution-based reduction approach without using any surfactants and templates. Each dendritic structure is composed of a trunk and numerous branches, as shown in Fig. 1a. The trunk has a diameter of approximately 200 nm and a length of several micrometers. The branches have different sizes with round heads. An interesting phenomenon is that most branches are perpendicular to the trunk. The transmission electron microscopic image in Fig. 1b shows, that there is no clear crystal boundary between the trunk and branches, indicating perfect single crystallinity, which is confirmed by the selected area electron diffraction (SAED) in Fig. 1c.

The formation mechanism of dendrites has been studied for decades. It is generally accepted that the dendrites are prone to form in a non-equilibrium condition in which the diffusion kinetics of chemical and growing dynamics of interface play a significant role in shaping dendrites. The Mullins-Sekerka (MS) instability model is one of the most plausible models for the growth of dendrites (Sander, 1986; Anson, 1966; Ferreira et al.,

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