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Electrochemical synthesis of lamellar structured ZnO films via electrochemical interfacial surfactant templating

Kyoung-Shin Choi *, Ellen M.P. Steinmiller

Purdue University, Department of Chemistry, West Lafayette, IN 47907, United States

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Abstract

Interest in creating tunable, ordered mesoporous materials based on surfactant supramolecular templating has been increasing over the last decade. For the production of film-type mesoporous materials, the most common method currently used is sol–gel based dip-coating method, which utilizes evaporation induced self-assembly (EISA) of surfactants. A more recently developed method, electrochemical interfacial surfactant templating, exploits the interfacial surfactant assembly formed on the working electrode to electrodeposit inorganic mesoporous films. This method offers mechanisms for inorganic wall construction and amphiphilic assemblies that are quite different from those of the sol–gel dip-coating method. As a result, it offers new possibilities to produce mesoporous films that cannot be produced by other means. This paper reviews the recent advances in producing and tuning lamellar structured mesoporous zinc oxide films via electrochemical interfacial surfactant templating. The general principles of this method will be explained in comparison with other methods used for producing mesoporous films. This will be followed by discussions of the key synthesis conditions that govern the repeat unit, quality, and orientation of lamellar structures constructed during electrodeposition. This review will provide a useful foundation to further develop electrochemical interfacial surfactant templating as a versatile method to produce a broader range of mesoporous films.

Keywords: Zinc oxide; Electrodeposition; Mesoporous film; Surfactant assembly; Lamellar structure

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1. Introduction

Supramolecular assemblies of amphiphilic molecules have been extensively studied for the production of materials containing ordered mesoporous structures for the past 15 years [1–4]. The presence of ordered mesoporous structures in inorganic materials not only increases surface area per unit volume, but also offers opportunities to study the effect of specific details of porous structure (pore size, pore wall thickness, pore shapes, and pore connectivity) on chemical and physical properties of the electrodes. Typical mesoporous structures that can be templated by surfactant supramolecular assemblies include lamellar structures, two-dimensional hexagonal structures, and micellar and gyroid cubic structures.

To date, the supramolecular surfactant templating method has been primarily achieved through sol–gel based synthesis [1–4]. This method can be coupled with a dip-coating method when film-type mesoporous materials are desired [5]. The film-type morphology allows for easy integration of mesoporous materials into electrochemical and photoelectrochemical devices.

In film morphology, the orientation of the pore relative to the substrate as well as the type of pore structure becomes an important issue to determine the accessibility of the pores when the mesoporous structure is anisotropic (e.g. lamellar structure and 2D hexagonal structure) [5]. Unfortunately, the sol–gel dip-coating method is based on evaporation induced self-assembly (EISA) of surfactants, which does not offer the freedom to control pore orientations. Lamellar structures and 2D hexagonal structures prepared by EISA contain layers and pore channels always parallel to the substrate [5,6]. Another limitation of sol–gel synthesis is the limited compatibility of the method for generating semiconducting and metallic materials [1–11]. Thus, development of a synthetic method that can provide new mechanisms to incorporate various mesoporous materials in a broad range of inorganic films is highly desirable.

The purpose of this paper is to describe our recent efforts on establishing an electrochemical interfacial surfactant templating method that can complement the sol–gel dip-coating method

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* Corresponding author. Tel.: +1 765 494 0049; fax: +1 765 494 0239.
E-mail address: kchoi1@purdue.edu (K.-S. Choi).

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for the production of mesoporous films [12–18]. The general principles and unique features of the electrochemical interfacial surfactant templating method will be explained and compared with the sol–gel dip-coating method and other electrochemical methods. While this method can be used to template various mesoporous structures in many inorganic films, this paper will specifically focus on reviewing experimental conditions developed to incorporate and modify lamellar mesoporous structures in ZnO films [13–15]. The key synthesis conditions that govern the repeat unit, quality, and orientation of lamellar structures constructed during electrodeposition will be discussed in detail.

2. Surfactant assembly at the solid–liquid interface

Amphiphilic molecules in solution spontaneously aggregate at solid–liquid interfaces due to surface forces (i.e. electrostatic interaction between the surfactant head group and a surface charge) [19]. These surface micelles can be formed at concentrations well below their critical micelle concentration (cmc) due to the surface excess of surfactant molecules generated by the surface forces [20–23]. The formation of surface micelles can be further favored over formation of bulk micelles because the surfactants adsorbed on the solid substrate possess reduced conformational and transitional freedom compared to those in bulk solution. The reported surface cmc of charged surfactants (e.g. sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB)) is in the range of 1/2–1/3 of the cmc [20]. Fig. 1 shows schematic representations for a few known surface assemblies of surfactants.

It has been also emphasized that surface micelle structures are frequently different from those in bulk solutions because the substrate plays a dominant role in determining the surface aggregate structure [19–23]. For the same reason, it is also possible to stabilize various surface amphiphilic structures by changing the nature of the substrate (i.e. surface charge density, hydrophobicity) using the same amphiphilic solution. For example, CTAB in aqueous solution can form spherical, flat, and hemicylindrical aggregates on silica, mica, and graphite surface, respectively [20].

The surface charge of the solid surface is one of the major determining factors of the surface properties and therefore dictates the most stable surface amphiphilic phase [24,25]. Lipkowski and coworkers [25] demonstrated that applying a positive external bias to the substrate can transform a surface hemimicellar structure of SDS on a Au (1 1 1) surface to a condensed state (e.g. monolayer or bilayers). They directly observed this transition by combining atomic force microscopy (AFM) and scanning tunneling microscopy (STM) with electrochemical measurements. This experiment indicates that the interfacial assembly of surfactants is solely determined by the nature of the interface and that it can be altered by modifying the chemical and electrochemical conditions at the solid–liquid interface.

3. Electrochemical interfacial surfactant templating

The novelty of electrochemical interfacial surfactant templating lies in exploiting the aforementioned amphiphilic phenomena for inorganic synthesis by combining it with electrodeposition [13]. In this method, the plating solution contains surfactant molecules as structure directing agents, and the working electrode serves as a substrate for both the organic assemblies and inorganic deposition. In order to use interfacial amphiphilic assemblies formed on the working electrode as a template to deposit mesoporous inorganic films, amphiphiles are selected based on the types of metal species to be deposited (e.g. charge and coordination preference) and compositions of plating solution (e.g. pH and supporting electrolyte). The goal is to ensure strong interactions between the metal ions and the hydrophilic groups of the amphiphiles so that the metal ions can be tightly bound on the surface of the surfactant micelles serving as counter ions. Once well-ordered inorganic-amphiphilic assemblies are formed on the working electrode, this organization directly becomes the skeleton of the inorganic deposits when the deposition process is initiated (Fig. 2). Continuous reconstruction of interfacial inorganic–organic assemblies can be maintained during the deposition process by adjusting the deposition rate, which results in incorporation of homogeneous mesoporous structures throughout the films. To date, films containing lamellar structures, two-dimensional hexagonal structures, and three-dimensional worm-like structures have been produced by the electrochemical interfacial templating method [12–18].

4. Comparison with prior methods

4.1. Comparison with sol–gel based dip-coating methods

The mechanisms of inorganic wall construction and amphiphilic assembly during electrochemical interfacial surfactant templating are significantly different from those during sol–gel based dip-coating methods. In the electrochemical surfactant templating method, construction of inorganic frameworks is achieved by electrodeposition and surfactant assemblies are induced by surface forces at the solid–liquid interface (i.e. the working electrode surface). However, in the sol–gel dip-

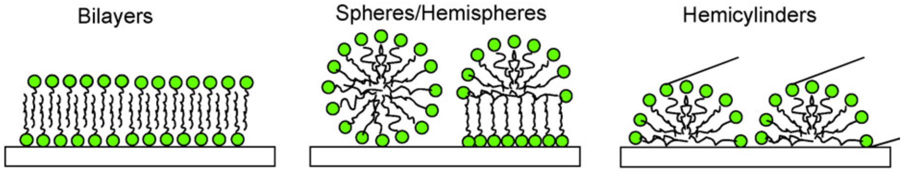

Fig. 1. Schematic representations of possible surfactant assemblies at the solid–liquid interface [12].