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Application of tetrahydrofuran dispersant in microemulsion for fabricating titania mesoporous thin film

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Abstract

A new strategy was used to fabricate titania mesoporous thin film by incorporating tetrahydrofuran (THF) into the CTAB/*n*-butyl alcohol/cyclohexane/water reverse microemulsion as a micelle disperser. Highly dispersed and congregated TiO_2 particles in the microemulsion with and without THF were observed by transmission electron microscopy (TEM), respectively. The photographs observed by field-emission scanning electron microscopy (FE-SEM) show that a uniform titania mesoporous thin film with monodisperse TiO_2 spherical nanoparticles of ca. 20 nm was obtained using the microemulsion with THF.

Keywords: Microemulsion; Titania; Tetrahydrofuran; Dispersant; Reverse micelle; Mesoporous thin film

1. Introduction

A mesoporous thin film composed of nanometer-sized semiconducting metal oxide particles, such as ZnO, SnO_2, and TiO_2, has been extensively investigated due to its special properties and potential applications in optical and electronical areas, such as photoelectrode in dye-sensitized solar cells (DSCs), highly efficient photocatalysts, and gas sensors. Great effort has been made in the preparation of titania mesoporous thin film composed of sintered TiO_2 nanoparticles. There are some methods to fabricate the thin film, such as the sol–gel method, hydrothermal synthesis, and a microemulsion method. However, the resulting thin film tends to crack and flake off during sintering and even the drying process, after the colloidal precursor solution is coated straight onto a substrate, especially in the case of repeated coatings. In order to improve the coating properties, the colloidal solution is generally centrifuged, filtered, and dried to form powder, and then mixed with solvent and nonionic surfactant, such as polyethylene glycol (PEG), to form a viscous slurry which is coated on a substrate to fabricate the thin film. The most important factor affecting the coating property is the inner structure of the thin film, especially the interfacial structure between the nanoparticles, which is influenced by the size distribution, shape, and gathering state of the nanoparticles in the colloidal solution. Thus the main issues in the preparation of homogeneous nanometer-sized titania mesoporous thin film are carefully controlling the size distribution and shape of the nanometer-sized particles as well as keeping a high dispersancy and stability of the colloid system.

Microemulsions have been used as chemical reactors because of their special interfacial properties, allowing an intimate contact, at the nanoscale level, of hydrophilic and hydrophobic domains. Surfactant molecules with polar and nonpolar regions will accumulate at the oil–water interface of microemulsions, orienting at the interface in such a way that the polar part of the molecule extends into the water domain and the nonpolar part extends into the oil domain [1], which allows the surfactant molecules to self-assemble into thermodynamically stable micelles with well-defined structures, such as spherical, rod-like, and layered. In the core of the micelle, water or oil is solubilized to form water-in-oil or oil-in-water microemulsions,

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in which the chemical reaction occurs. Thus the size and morphology of resulting particles are controlled by the components and structure of the microemulsion system, which offers the most convenient method for the synthesis of nano-sized materials [2].

The microemulsion method is now widely used to prepare nanometer-sized material because of its easy control in particle size and the simplicity of the process [3]. However, the aggregation of the nanoparticles synthesized in the microemulsion system is still unavoidable, which leads to a bad coating property and the surface morphology of the resulting thin film, such as cracking and flaking off. The dispersancy and stability of the nanoparticles in microemulsion still need to be improved.

Tetrahydrofuran (THF) is generally used in the microemulsion method after the chemical reaction occurs in the micelles to remove the surfactants adsorbed on the resulting nanoparticles, which facilitates the treatments, such as centrifuging and filtering, about the colloidal solution. In this paper, THF was added into the microemulsion before the chemical reaction occurred in the micelles. Experimental evidence of homogeneous TiO_2 mesoporous thin films prepared in a water-in-oil microemulsion which incorporates THF as a dispersant in the quaternary microemulsion system, by coating the colloidal precursor solution straight onto a substrate, is presented. The dispersion effect of THF on the micelles, which improves the dispersancy and stability of the nano-sized TiO_2 particles in the microemulsion, is demonstrated.

2. Materials and methods

All chemicals were analytically pure and were used without further purification. The reverse (water-in-oil) microemulsion system comprises CTAB (cetyltrimethylammonium bromide), *n*-butyl alcohol, water, cyclohexane, and THF. The reactant was the mixture of tetrabutyl titanate and diethanolamine.

A typical procedure for preparing TiO_2 mesoporous thin film was as follows. First, tetrabutyl titanate was mixed with diethanolamine which acted as a hydrolytic inhibiter with a molar ratio of 1:1. CTAB, *n*-butyl alcohol, cyclohexane, and water were mixed with a gram ratio of 1:1:8:2 to form transparent reverse microemulsions. Then THF was added into the microemulsion with a gram ratio of 1:3 to CTAB and the five-component microemulsion was stirred for a few minutes. A mixture of tetrabutyl titanate and diethanolamine was added into the reverse microemulsion and stirred at 60 °C. Several minutes later, an opalescent colloid formed. The resulting TiO_2 colloid solution was coated onto a glass substrate by a glass rod with Scotch tape as spacers, dried at 120 °C for 10 min, and then annealed at 450 °C for half an hour in air. The coating, drying, and annealing steps were repeated until a film with desired thickness was obtained. TiO_2 film synthesized by the same quaternary microemulsion without THF was also fabricated for comparison.

The morphology of the mesoporous TiO_2 film was characterized by field-emission scanning electron microscopy (FE-SEM; Leo; Supra35). The shape, size, and gathering state of TiO_2 nanoparticles in the reverse microemulsion were characterized by transmission electron microscopy (TEM; Philips; Tecnai 10).

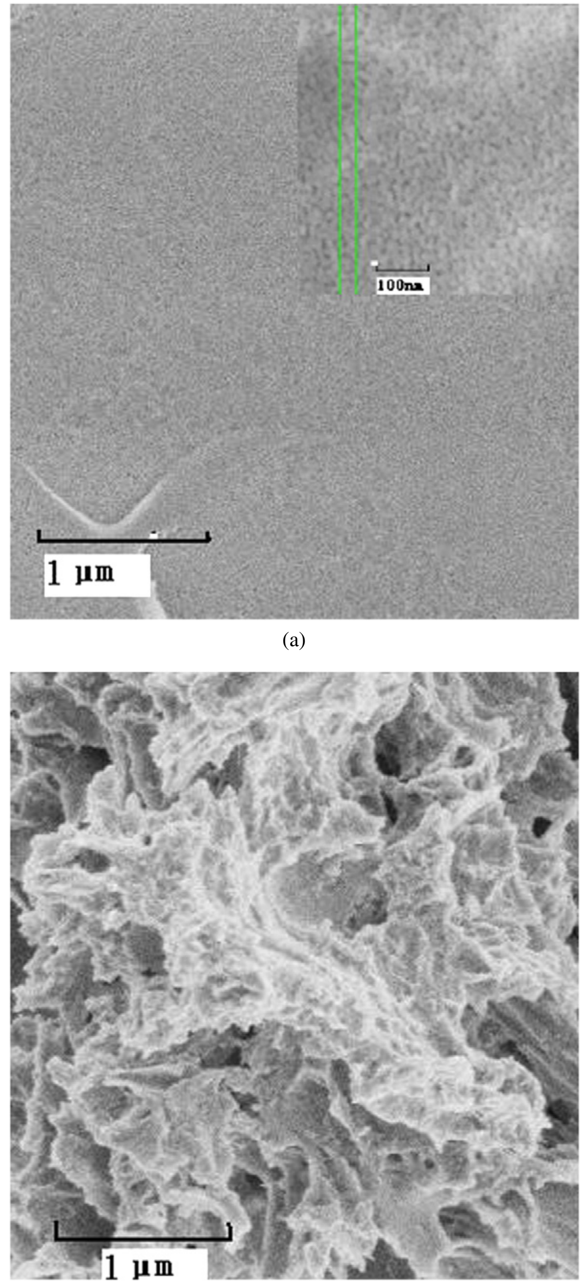

Fig. 1. FE-SEM photographs showing the surface morphology of TiO_2 mesoporous film prepared by reverse microemulsion (a) with and (b) without THF.

3. Results and discussion

The microemulsion method is a very convenient way to synthesis nano-sized materials. The size and shape of the nanoparticles can be controlled by the components and structure of the microemulsion system. When tetrabutyl titanate hydrolyzed in the quaternary reverse microemulsion, and then the precursor was coated straight onto a substrate, the resulting thin film tended to crack and flake off. The FE-SEM image of the TiO_2 mesoporous film (Fig. 1b), which was prepared by the qua-