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Synthesis of highly ordered and worm-like mesoporous TiO_2 assisted by tri-block copolymer

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Abstract

A highly ordered and worm-like mesoporous TiO_2 materials have been prepared by evaporation-induced self-assembly method (EISA) using different concentrations of tri-block copolymer Pluronic F127 as a structure-directing agent and inorganic chlorides as precursors in a non-aqueous medium. The characterization of the mesoporous TiO_2 was carried out using small angle X-ray diffraction (SAXD), transmission electron microscopy (TEM) and N_2 adsorption/desorption. The well-ordered mesoporous TiO_2 showed average pore size of 2.8–3.7 nm and high specific area of 263 m^2/g. From TEM observation, the pore pore-wall is composed of nano-crystalline TiO_2 domains after successfully synthesized at 573 K. The pore morphology changed from well-ordered to worm-like as the concentration of Pluronic F127 increased beyond 8.35%.

Keywords: Mesoporous TiO_2; Tri-block copolymer; Nano-crystallite

1. Introduction

In 1992, scientists from the Mobil Corp. introduced a new concept in the synthesis of porous materials. The silica-based mesoporous M41S materials have been well investigated [1,2]. Mesoporous TiO_2 has attracted particular attention because of the expectation of potential applications such as highly specific chemical sensor, photocatalysts, lithium batteries and solar cell [3–17]. Until recently, only a few successful syntheses have been reported. In 1995, Antonelli and Ying [8] synthesized a thermally stable mesoporous TiO_2 materials with a hexagonal pore structure. Ulagappan and Rao [9] prepared mesoporous TiO_2 using neutral amine as the surfactant. However, the mesostructure was destroyed during the removal of the amine surfactant. Fröba et al. [10] even succeeded in synthesizing various types of mesoporous TiO_2 materials using different surfactants, but the mesostructures also collapsed during the removal of the templates. Yang et al. [11,12] restrained the crystallization reaction of TiO_2 to prepare the mesostructure TiO_2 materials with hexagonal and cubic pore arrangement. Dai et al. [13] used alkylphosphate and alkylamine surfactants with different chain lengths to synthesize hexagonally ordered TiO_2 and successfully retain the mesoporous structure.

However, these studies about mesoporous TiO_2 did not emphasize the relationship between the specific surface area, pore volume, pore structure and the concentration of structure-directing agent. These parameters are particularly important in order to prepare the highly surface area and desired pore structure for electronic and photonic application.

In this study, we reported the synthesis of mesoporous TiO_2 using various concentrations of tri-block copolymer surfactant in the synthesis of ordered and worm-like mesoporous TiO_2.

2. Experimental

The mesoporous TiO_2 was prepared by evaporation-induced self-assembly(EISA) method [18–21]. $TiCl_4$ (99.9%, ACROS) was added to ethanol solution where different amount of poly(alkylene oxide) block copolymer Pluronic F127

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Table 1
The sample number and their F127 weight % and BET test results

Item	S-1	S-2	S-3	S-4	S-5	S-6	S-7
F127 wt. %	2.61	5.56	6.51	7.46	8.35	9.27	11.82
BET surface area (m^2/g)	67	116	170	205	263	235	170
Pore volume (cm^3/g)	0.028164	0.095445	0.140765	0.227282	0.326351	0.2649	0.208986
Pore size (nm)	2.8947	3.2161	3.3092	3.5143	3.7305	3.6382	3.6971

($EO_{106}PO_{70}EO_{106}$) (where EO is ethylene oxide and PO is propylene oxide) was dissolved in ethanol with fixed volume (from 2.61% to 11.82%, Table 1). The resulting sol solution was gelled in an open Petri dish and underwent solvent evaporation at 30 °C in air for 24 h while the inorganic precursor hydrolyses and polymerizes into a metal oxide network. The as-made bulk samples were then calcined at 350 °C for 2 h with heating rate of 1 °C/min.

Thermogravimetric analysis (TGA) using Setaram, Setsys Evolution Version 16 was carried out to investigate the decomposition temperature. The sample was heated with a rate of 10 °C/min from 25 °C to 1200 °C in air. Small-angle X-ray diffraction (SAXD) was performed on the beam line 17A at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan operated at an energy of 9.3 keV (λ=1.33320 Å). The phase identification was performed by wide-angle powder X-ray diffraction (XRD) using a Rigaku, Model Rad II diffractometer with Cu K_α radiation (λ=1.5406 Å) and Ni filter, operated at 30 kV, 20 mA with scanning rate of 4°/min. Transmission electron microscopy (TEM) was collected using a FEI E.O Tecnai F20 G2 MAT S-TWIN Field Emission Gun Transmission Electron Microscope. The nitrogen adsorption and desorption isotherms were measured using a Micromeritics ASAP 2010 system at 77 K after the samples were vacuum-dried at 150 °C for 12 h.

3. Results and discussion

The TGA curve of the as-synthesized mesoporous TiO_2 precursor consisting of F127 surfactant and metal chloride is shown in Fig. 1. The decomposition temperatures at which the highest weight reduction rate with a drastic weight loss in TG curve was were observed before 300 °C. The weight loss is due to the removal of residual water and surfactant molecules through the decomposition or oxidation process. From the TGA analysis,

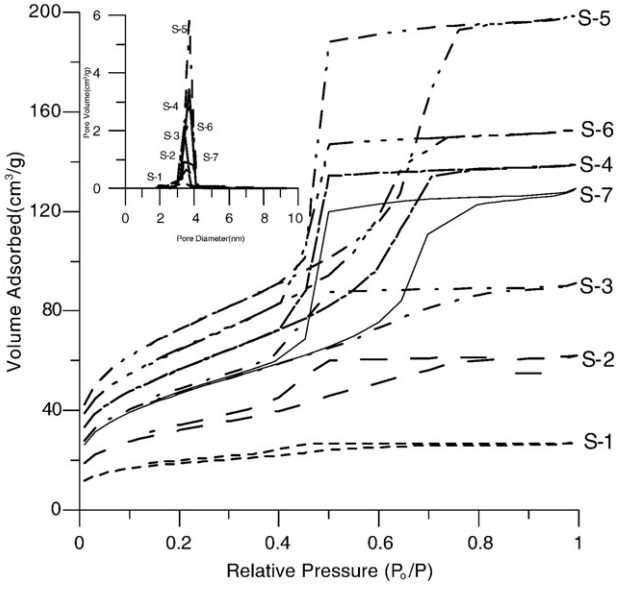

Fig. 2. Nitrogen adsorption/desorption isotherms of mesoporous TiO_2 calcined at 350 °C for 2 h. Inset shows pore volume plotted a function of pore diameter for samples S-1 to S-7.

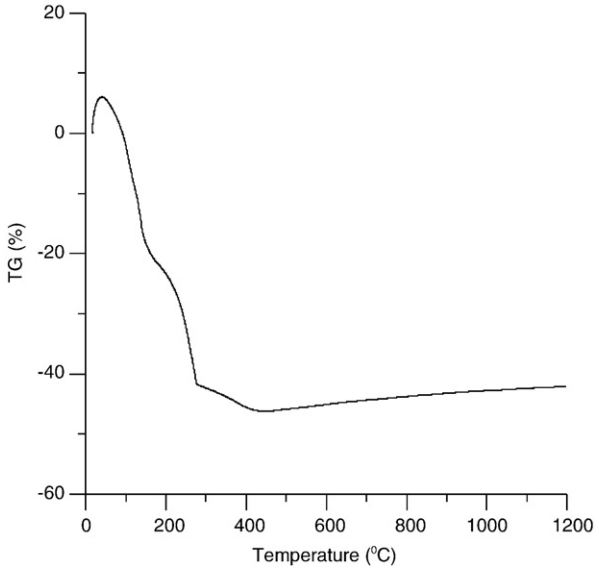

Fig. 1. The TG curve of mesoporous TiO_2 precursor with heating rate of 10 °C/min.

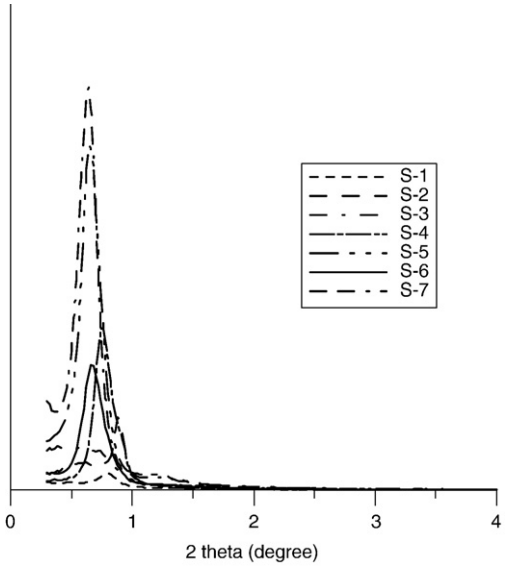

Fig. 3. SAXD patterns of ordered mesoporous TiO_2 calcined at 350 °C for 2 h.