Microporous and Mesoporous Materials 221 (2016) 182–186

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Short communication

Surfactant-assisted ultrasonic spray pyrolysis of hematite mesoporous thin films

C. Henrist [a, b, *], C. Toussaint [a], J. de Vroede [a], D. Chatzikyriakou [a], J. Dewalque [a], P. Colson [a], A. Maho [a], R. Cloots [a, b]

[a] GreenMAT, University of Liège, Allée du Six-Aout, 13, 4000 Liège-Sart Tilman, Belgium
[b] Center for Applied Technology in Microscopy, University of Liège, 4000 Liège-Sart Tilman, Belgium

ARTICLE INFO

Article history:
Received 1 July 2015
Received in revised form
22 September 2015
Accepted 26 September 2015
Available online 9 October 2015

Keywords:
Ultrasonic spray pyrolysis
Hematite
Templating
Mesoporous film

ABSTRACT

Mesoporous crystalline hematite is a material difficult to prepare by soft-templating with conventional techniques, because of its high crystallization temperature associated to the crystal-to-crystal goethite-to-hematite phase transition. In a previous work, it has been reported that with very careful calcination steps, it is possible to prepare mesoporous hematite films with the spin-coating technique. However, with less conventional techniques such as surfactant-assisted ultrasonic spray pyrolysis, the deposition usually leads to non-porous oxide films or to films with interstitial porosity.

In this work, we demonstrate for the first time the proof-of-concept of block-copolymer templating of hematite thin films by the ultrasonic spray pyrolysis technique. Despite the fast thermal decomposition during spray deposition, a regular, monodisperse packing of spherical pores is observed after deposition on pre-heated substrates (250 °C) and after a careful post-annealing step at 470 °C. Moreover, with the use of a silica scaffold, we successfully preserved porosity up to a temperature as high as 800 °C. These films are highly crystalline and they are composed by randomly oriented nanocrystallites with sizes as small as 25 nm. Furthermore, we show that the crystallization evolution with temperature is influenced by the presence of the templating agent and also by the preparation technique.

1. Introduction

Mesoporous iron oxide films offer promising potentials as material for electrodes, magneto-optical devices and catalysts. Specifically, hematite (α-Fe_2O_3) has received increasing attention for use as water splitting photoanode, because of its high stability in water, cheapness, environmental compatibility, abundance and its band gap of 2.2 eV which lies in the visible region [1]. However, the main drawback which restrains the performance of hematite as a photoanode is its short diffusion length of holes which leads to a fast electron–hole recombination and subsequently to limited efficiencies. Nanostructuration (introduction of porosity and/or tuning particles' morphology to form nanowires, cauliflowers …) of the photoanode can address this issue by reducing the distance between the photogenerated holes and the semiconductor-liquid junction [1,2].

Different techniques, such as colloidal solution deposition [3], electrochemical nanostructuration [4], hydrothermal method [5] and atmospheric pressure chemical vapor deposition (APCVD) [2], etc have been used to structure hematite films. Other promising nanostructuration routes rely on the soft-templating method which introduces porosity inside a material. It consists in combining sol–gel process and surfactant-assisted self-assembly to produce a mesostructured film. After calcination, the typical porous mesostructure is obtained with a regular packing of spherical pores with uniform diameters, constituting the imprints of surfactant micelles.

Mesoporous, crystalline hematite is a material difficult to prepare by templating because of its high crystallization temperature, associated to the crystal-to-crystal goethite-to-hematite phase transition that requires temperature up to 350 °C to be completed [6,7]. The Pluronic surfactants, usually employed as efficient templates for most metal oxide mesoporous thin films, are completely decomposed at this temperature and therefore do not ensure the preservation of the mesostructure during the crystallization of hematite. Specially designed block-copolymers with high thermal

* Corresponding author. GreenMAT, University of Liège, Allée du Six-Aout, 13, 4000 Liège-Sart Tilman, Belgium.
E-mail address: catherine.henrist@ulg.ac.be (C. Henrist).

http://dx.doi.org/10.1016/j.micromeso.2015.09.046
1387-1811/

stability and ultra hydrophobic features have been developed to ensure the robust templating of mesoporous hematite films [7–9].

Additionally, for the water-splitting application, Fe_2O_3 requires chemical doping in order to increase its charge carriers mobility. Recently, we have shown that it was possible to prepare mesoporous hematite films (with activated dopant) at a temperature as high as 850 °C by surfactant-assisted spin-coating with the help of a transient encapsulation by a silica scaffold [10].

However, most of those batch processes are not likely to fit with upscaling requirements. Continuous deposition techniques, like spray pyrolysis [11,12], open therefore exciting perspectives for the preparation of larger-scale hematite thin films. Ultrasonic spray pyrolysis (USP) is a promising and versatile technique to produce homogeneous thin films on large area substrates. Some papers report the addition of surfactants in the injected solution of oxides precursors. However, they usually do not result in a well-defined porous structure in the film [13,14], unlike what is observed for solution-processed films at room-temperature (dip-coating, spin-coating) followed by calcination. So far, porous hematite films prepared by USP only show irregular porosity related to interstitial voids [11,12,15].

The purpose of the present study is to establish the proof-of-concept of block-copolymer templating of hematite thin films by USP deposition technique.

We demonstrate that a regular, monodisperse packing of spherical pores can be obtained in hematite thin films after deposition on pre-heated substrates (250 °C) and that the porosity is preserved after calcination and crystallization at 470 °C. Additionally, the open mesoporosity has been preserved at high temperature (800 °C) thanks to the silica scaffold strategy, which opens the route towards dopant activation.

2. Materials and methods

2.1. Preparation of the solutions

First, a solution of template is prepared by dissolving 145.9 mg of poly(isobutylene)-block-poly(ethylene oxide) (PIB_{125}-PEO_{120} from PolymerSource) in 2.765 g of ethanol (Sigma Aldrich). The solution is covered and kept at 40 °C under sonication for at least 15 min to ensure complete dissolution. Besides, the iron precursor solution is prepared by dissolving 1.165 g of iron (III) chloride hexahydrate (Sigma Aldrich) in a mix of H_2O (58.8 μL), ethanol (5.53 g) and tetrahydrofuran (1.557 g). The surfactant solution is then poured into the iron solution under stirring and aged at room temperature under stirring for at least 6 h.

2.2. Substrate pre-treatment and film deposition

Aluminoborosilicate glass/FTO substrates (Solaronix, 10 Ω/sq) were cleaned by successive sonication in ethanol and acetone, during 5 and 10 min respectively. They were then blow-dried with a compressed air stream. The iron oxide films were deposited by spin-coating or USP. For TEM imaging, the films were deposited onto passivated Si substrates (100-oriented, LG Siltron Korea) to facilitate sample preparation.

2.3. Spin-coating

50 μL of solution were deposited onto the substrate. The spinning process was applied in two steps: 500 rpm for 5 s followed by 3500 rpm for 30 s. During the whole process, the relative humidity was maintained between 15 and 20%. After deposition, samples were stabilized at 250 °C for 15 min on a hot plate then calcined under air at 470 °C for 10 min in a preheated tubular furnace. The deposition protocol is repeated six times.

2.4. Ultrasonic spray pyrolysis

The precursor solution was continuously sprayed with an ultrasonic spray pyrolysis device (ExactaCoat, Sonotek) through the ultrasonic AccuMist nozzle (operated at 120 kHz) onto pre-heated substrate (T = 250 °C, 2 min pre-heating), which is located 5.5 cm below the nozzle. The solution's flow rate was 0.25 mL/min and dry air was used as a carrier gas (6205 Pa). To obtain a full surface coverage, the ultrasonic nozzle was moved in x and y directions following a S-shaped pattern (4 mm spacing) at a constant speed (40 mm/s). Eight passes were needed, with a lateral shift in x direction of 2 mm for each even pass, to obtain a quantity of active material similar to spin-coated films. The substrates were maintained on the hotplate for a total time of 10 min after deposition to reach the desired temperature at the surface of the substrate. As in spin-coating, this stabilization step is necessary in order to initiate precursor's decomposition and to consolidate the inorganic network around the template.

Finally, all samples (spin-coated and USP) were calcined under air at 470 °C for 10 min in a preheated tubular furnace.

2.5. Porosity preservation at high temperature

All the films were finally submitted to an additional heat treatment at very high temperature, placing them in a pre-heated furnace at 800 °C for 10 min.

Prior to this final heat treatment, the mesoporous films were reinforced by a silica scaffold [3,20]. In order to achieve that, the films were immersed for 1 h in a stirred solution maintained at 0 °C containing 195 μL tetraethylorthosilicate (TEOS), 0.211 g hexadecyltrimethylammonium chloride (C_{16}TAC), 17.7 mL distilled water, 100 mL methanol and 8 mL NH_3 25%. After withdrawing, the samples were washed with water and dried before the final heat treatment at 800 °C. In order to remove SiO_2 after the final heat treatment, the samples were soaked in NaOH 5 mol/L for 10 min, washed with distilled water and dried.

2.6. Characterization

Transmission electron micrographs were collected at an acceleration voltage of 200 kV (FEI, Tecnai G2TWIN, LaB6 cathode) on films scratched off the silicon substrate and dispersed in ethanol under ultrasonication, then deposited on carbon-coated copper grids.

The films deposited on glass/FTO substrates were characterized by X-ray diffraction with a Bruker D8 grazing incidence diffractometer (CuKα radiation, incidence angle of 0.5°). The presence of hematite was checked from the (104) peak at 33.2° 2θ. The size of the coherent crystal domain, further called “crystallite size”, was evaluated using the Scherrer equation:

$$D = \frac{k.\lambda}{B.cos\theta}$$

where D is the crystallite size (nm), λ is the wavelength of Cu Kα radiation (nm), θ is the Bragg angle (°), k is a constant (0.89) and B the full width at half-maximum intensity (rad).

The morphology of the samples was examined by atomic force microscopy (AFM) under ambient conditions using a Adigital Instruments Nanoscope III microscope (Veeco). The image acquisition was perfomed in tapping mode with a super sharp improved super cone (Team Nanotec).