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Facile fabrication of rutile monolayer films consisting of well crystalline nanorods by following an IL-assisted hydrothermal route

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ABSTRACT

In this study, rutile films consisting of rectangular nanorods were facilely deposited on glass substrates from strongly acid solution of $TiCl_4$. The highly ordered array of nanorods was realized in presence of ionic liquid (IL) of [Bmim]Br by following a hydrothermal process. In this process, Degussa P25 nanoparticles served as seeds that were pre-deposited on the substrates to facilitate the array of rutile nanorods. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectrum were used to characterize the obtained nanorod films. The measurements showed that the nanorods were rectangular with width of 100–200 nm and length of more than 1 μm, and grew up typically along *c*-axis to form the arrays against the substrate. The presence of IL was found vital for the formation of rutile nanorods, and the suitable molar ratio of [Bmim]Br to $TiCl_4$ ranged from 500:1 to 1500:1. The excessive [Bmim]Br may hinder the precipitation of rutile particles.

1. Introduction

Titanium dioxide is a versatile material and has been investigated considerably due to its unique optoelectronic and photochemical properties, such as high refractive index, high dielectric constant, and excellent optical transmittance in the visible and near-IR region as well as high performance photocatalysis for water splitting and for degradation of organics [1,2]. Each phase of TiO_2 (anatase, rutile, brookite) presents different physical and chemical properties with different functionalities. In recent years, rutile nanostructure has received increasing attention because it has been demonstrated comparable to anatase in application to photocatalysis, dye-sensitized solar cells (DSCs) and so on [3–6]. However, the synthesis of rutile nanostructures usually requires time-consuming reactions at elevating temperature, even via hydrothermal processes [7–12]. Therefore, a feasible synthesis of rutile nanostructures at low temperature is still an attractive target.

Recently, a new solvent system, room-temperature ionic liquids (ILs), has been developed and widely used as a new kind of reaction media owing to their intrinsic properties such as negligible vapor pressure, wide liquid temperature range, high thermal stability, large electrochemical window, and high ionic conductivity, etc. [13] Many inorganic nanostructures [14–16], including titanium dioxide [17–21], have been fabricated via various ILs-involved processes. For titania nanomaterials, however, few works about the synthesis of rutile nanostructures have been reported in ILs solution [9,22].

In this work, we report a facile method to prepare rutile films, in presence of IL, 1-butyl-3-methylimidazolium bromide ([Bmim]Br), under mild hydrothermal condition. Reaction time and the ratio of [Bmim]Br to $TiCl_4$ were varied to optimize the condition. Highly concentrated HCl was used to control the hydrolysis of $TiCl_4$ and enhance crystallization of rutile phase [22]. The rutile films were facilely deposited, which consisted of rectangular nanorods that arrayed against the glass substrates.

2. Experimental and characterization

2.1. Materials

[Bmim]Br was synthesized and purified according to previous literature [23]. Other reagents were AR grade from local commercial suppliers and used as accepted without further purification. Hydrochloric acid serves as an acidic catalyst to control hydrolysis rate of the titanium source.

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2.2. Synthesis of rutile films

The synthesis was conducted in a 6 mol dm^{-3} of HCl solution containing $TiCl_4$ and [Bmim]Br. The rutile nanorods films were typically prepared as follows. 2.0 g of [Bmim]Br and 0.2 mL of $TiCl_4$ was dissolved in 20 mL of HCl with vigorously stirring at 0 °C. Correspondingly, the molar ratio of [Bmim]Br to $TiCl_4$ is 500:1. Then, the solution was transferred to a Teflon-lined autoclave when the solution became clear. The glass substrate was previously coated by Degussa P25 nanoparticles, through dip coating from P25 suspension, before it was immersed in the solution. The reaction was carried out at 100 °C for 3, 8, and 12 h, respectively. After the reaction, the films, which were deposited on the substrate, were washed by deionized water and ethanol several times in turn, till pH value of filtrate was about 7, and then dried at 80 °C overnight.

2.3. Characterization

XRD measurement was performed on a Rigaku D/max 2500 diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm) at 40 kV and 120 mA, using a nickel filter. SEM (scanning electron microscopy) was carried out by using Rigaku JEOL-6700F at 10 kV. TEM (transmission electron microscopy) and HRTEM images were recorded with a Tecnai G2 20 S-Twin transmission electron microscope operating at 200 kV. Raman spectra were measured in the frequency range 80–4000 cm^{-1} using Bruker RFS-100 FT-Raman spectrometer.

3. Result and discussion

3.1. Characterization of the films on seeded substrate

Typical SEM images of rutile nanorods films, deposited on seeded glass substrate for 3, 8, and 12 h are listed in Fig. 1. As shown by Fig. 1a, a large amount of small particles stick up against the substrate, and a few particles have presented rectangular shape by giving a careful observation, although others are still smoothly round on the tip. After 8 h deposition, the particles grow up towards rod shape against the substrate (Fig. 1b), most of which present obviously rectangular parallelepiped morphology. However, the width of the nanorods is not uniform but in a range from 30 to 350 nm. When the reaction time is prolonged to 12 h, the film made up of uniform nanorods is deposited. The low and high magnification images (Fig. 1c and d) give top images. The nanorods totally grow up with width of 100–200 nm, and the top presents regular squares. A cross-section image (Fig. 1e) reveals that the substrate is covered totally and continuously with the

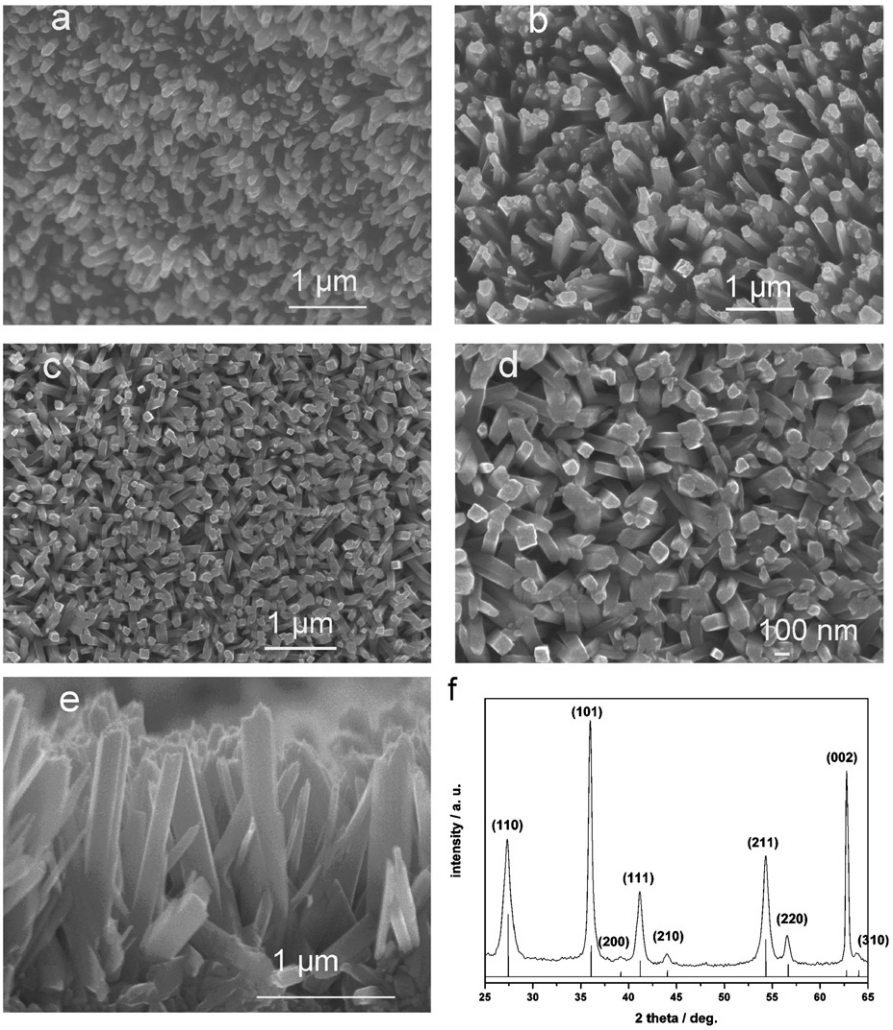

Fig. 1.