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Solution processed thin films of non-aggregated TiO_2 nanoparticles prepared by mild solvothermal treatment

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ABSTRACT

In this report, non-aggregated anatase TiO_2 nanoparticles were synthesized by mild solvothermal process in 1-butanol. By varying solvothermal reaction temperature and time, TiO_2 particle size was controlled from 5.3 to 9.0 nm, while maintaining pure anatase phase and optical clearance in the concentrated dispersion (5 wt%). Spin coating of TiO_2 dispersions resulted in transparent thin films with thickness controllability, and it was confirmed that the mild solvothermal reaction significantly increased the refractive index of the thin films without post-thermal treatment. In addition to the fabrication of low-temperature processed thin films, the inverse opal TiO_2 films were also fabricated by the colloidal templating method followed by thermal calcination to reveal the improved volume shrinkage of the mesoporous TiO_2 films.

1. Introduction

Due to the unique photophysical properties, nanosized titania (TiO_2) is an attractive material towards various applications such as solar energy harvesting [1–5], photocatalysis [6–8], antibacterial coating [9], and photonic crystals [6,10]. Among other crystalline morphologies of TiO_2, anatase TiO_2 is regarded as the most efficient crystalline phases to be used as electron transporting materials for dye sensitized solar cell (DSSC) which are of great interest these days [1–5]. Thin films of nanocrystalline TiO_2 can be obtained either by dry-process [4] or wet-process [9]. Compared to dry-process, wet-process is often preferred owing to the flexibility and cost-effectiveness of the process [11]. In order to assure pure anatase TiO_2 nanoparticles in the thin film, the coating process is followed by calcination at the temperature below 450 °C [5]. Instead of calcination, hydrothermal [9,12], or non-aqueous solvothermal [8,13] treatment of TiO_2 sol at an elevated temperature can also produce highly crystalline anatase TiO_2 nanoparticles. The solution processability of TiO_2 nanoparticle such as coating property depends on its particle size, size distribution, and surface functional groups. Scolan and Sanchez [14] synthesized highly dispersed anatase TiO_2 nanoparticles in organic solvent by introducing organic modifier at nanoparticle surface. The organically modified TiO_2 showed promising applicability to the photonic devices such as 3-D photonic crystal structure [11], and DSSC photoelectrode [5].

In this study, we investigated various solvothermal reaction conditions in order to control the particle size and the crystallinity of the organically modified TiO_2 nanoparticle system which can be processed into the transparent films.

2. Experimental

The synthesis of organically modified TiO_2 nanoparticle was carried out following the method reported elsewhere [14]. As-synthesized TiO_2 nanoparticle was redispersed in 1-butanol, which was sealed in a stainless steel bomb reactor (4744 Parr instrument). In a temperature stabilized oven, mild solvothermal reaction was carried out at the temperature ranging from 160 to 240 °C for 3–10 h, followed by precipitation and drying.

The crystal structure of TiO_2 powder was characterized by X-ray diffractometer (XRD, Rigaku D/Max-2500). High-resolution transmission electron microscopy (HR-TEM) (tecnai F20, FEI) analyses were carried out to observe the nanoparticles' shape and morphology.

Organic contents in TiO_2 nanoparticles were characterized by thermogravimetric analysis (TGA, TA Instrument). The thin films of TiO_2 were prepared by spin coating the butanol dispersion on

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the pre-cleaned substrate. After spin coating, the films were dried in convection oven at 70 °C. The thicknesses and the refractive indices of the TiO_2 thin films were characterized by ellipsometry (SE MF-1000, Nano-view) without calcinations.

Inverse opal structures composed of TiO_2 nanoparticles before and after solvothermal process were prepared, and analyzed. First, the colloidal crystals exhibiting 3D opal structure with ~5 μm thickness were prepared on slide glass using narrowly dispersed polystyrene (PS) microspheres which were synthesized by standard emulsion polymerization [15]. A detailed fabrication method for the colloidal crystal is reported elsewhere [1–5]. The dispersions of TiO_2 nanoparticles at 5 wt% in 1-butanol were infiltrated within the colloidal crystals by spin coating at 500 rpm. Once dried in air overnight, PS colloidal crystal template was removed by calcination at 450 °C using a furnace (LK-Lab Korea). The resulting inverse opal structures were analyzed by SEM.

3. Results and discussion

From the previous literatures, non-aggregated TiO_2 nanoparticle system used in this study showed unique solution processibility toward thin film applications [11]. As-synthesized TiO_2 nanoparticle was obtained as a fine yellowish powder as shown in Fig. 1(a), and it was readily dispersed in 1-butanol solution up to 30 wt% without necessity for heating to promote solvation. Such an excellent dispersibility of TiO_2 originates from its narrow size distribution and surface modification by AcAc.

Fig. 1(b) shows the solvothermally treated dispersions at 180 °C for 3 different reaction times. Although the reaction temperature of 180 °C was regarded as a mild condition for solvothermal treatment, longer reaction time apparently caused the increased opaqueness to the dispersions. At a fixed reaction time (3 h), the temperatures above boiling point of 1-butanol (117 °C) were surveyed for each 5 wt% TiO_2 dispersion in 1-butanol. The solvothermally treated dispersions at 4 different reaction times are shown in Fig. 1(c). The clearance of the dispersion was maintained up to 200 °C solvothermal temperature, though the dispersions treated at 200 °C showed a slight increase in turbidity. It was found at the solvothermal temperature above 200 °C, the dispersion turned very turbid. Since the aim of this study was to improve refractive index of TiO_2 film while maintaining optical transparency, optimized solvothermal condition was concluded to be the temperature of 180 °C, and reaction time of 3–5 h.

The 1-butanol dispersions of TiO_2 samples except for that treated at 240 °C were spin-coated on the glass slide which had been pre-cleaned by piranha solution. The concentration (5 wt%) and the spin rate (2000 rpm) have been optimized to give ~100 nm film thickness on the glass substrate or Si wafer. As shown in Fig. 1(d) and (e), all the coated TiO_2 films are optically clean without dewetting or any visible aggregates, exhibiting shiny reflection color depending on the thickness. Optical clarity of the solvothermally treated TiO_2 dispersions was further confirmed by UV–vis transmittance measurement. The TiO_2 dispersions of 0.5 wt% in butanol showed a good transmittance above 400 nm wavelength except that treated at 240 °C [6–8]. Similarly, the dispersions prepared at different solvothermal reaction time up to 10 h showed good transmittance above 400 nm. As shown in Table 1, the transmittance of as-synthesized sample measured at 500 nm was 97%, but it slightly decreased as solvothermal reaction time gets longer. Such a tendency is mainly attributed to the increased turbidity by solvothermal reaction. XRD data for the powdered samples revealed the characteristic peaks from pure anatase crystal. By measuring FWHF of the peaks from (1 0 1), (0 0 4), (2 0 0), (2 0 4), and (2 1 5) plane, average particle size (d_{ave}) of each TiO_2 nanoparticle was calculated based on the Scherrer formula, and the calculated size was summarized in Table 1. The calculated d_{ave} clearly showed the increasing tendency of the particle size from 5.3 to 9.0 nm by increased solvothermal temperature and reaction time.

For the comparison of the particle size and the shape changes by solvothermal reaction, TiO_2 nanoparticles before and after solvothermal reaction were characterized by HR-TEM as shown in Fig. 2. Compared to Fig. 2(a) in which small-sized individual nanocrystals are shown, Fig. 2(b) and (c) shows the gradual increases in TiO_2 particle sizes by longer solvothermal reaction time. Overall, particle shapes were elliptical. Fig. 2(d) is the enlarged view of an individual nanocrystal after solvothermal treatment at 180 °C for 3 h, where anatase crystalline lattice structure is evidently shown. Although not shown, the anatase crystalline phase was again confirmed through selective area electron diffraction (SAED) on HR-TEM image of the nanocrystals.

For the characterization of organic contents in each TiO_2 sample, TGA thermograms of selected samples (reacted at 180 °C) were obtained as shown in Fig. 3. Every sample showed a typical weight loss below 100 °C due to evaporation of adsorbed water.

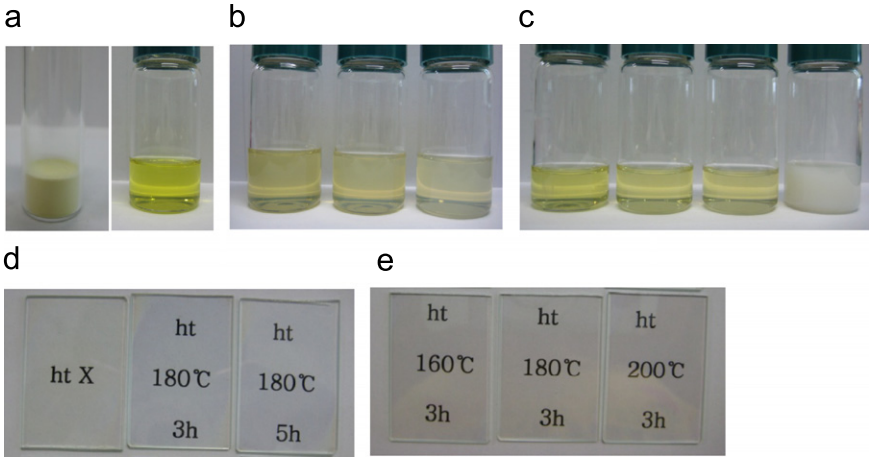

Fig. 1. Non-aggregated titania nanoparticles synthesized in this study (a) As-synthesized TiO_2 powder, and 5 wt% dispersion in 1-butanol. (b) Solvothermally treated dispersions at 180 °C for different reaction time 3, 5, and 10 h, from left. (c) Solvothermally treated dispersions for 3 h at different temperatures 160, 180, 200, and 240 °C from left. (d),(e) TiO_2 thin films spin-coated on the glass substrate. Hydrothermal conditions for each TiO_2 films are printed on the paper below each coated film showing optical clarity for all cases. All the films were obtained by spin coating 1-butanol solution of 5% TiO_2 at 2000 rpm.