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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.

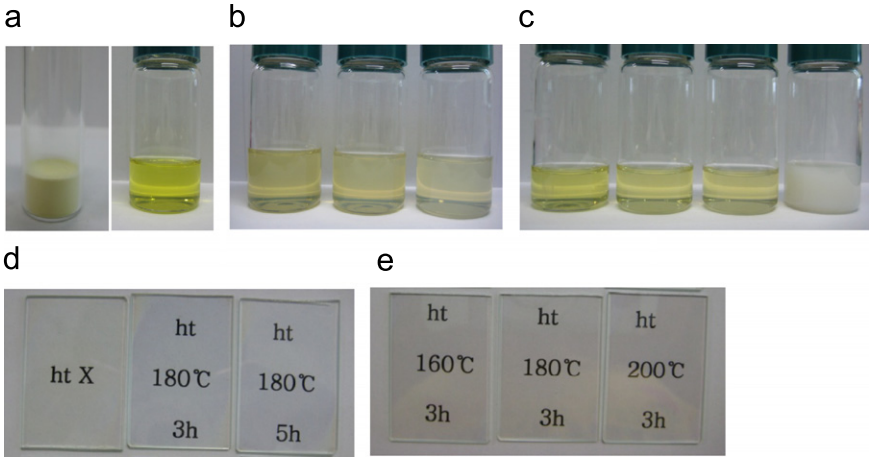

Fig. 1. Non-aggregated titania nanoparticles synthesized in this study (a) As-synthesized TiO_2 powder, and 5 wt% dispersion in 1-butanol. (b) Solvothermally treated dispersions at 180 °C for different reaction time 3, 5, and 10 h, from left. (c) Solvothermally treated dispersions for 3 h at different 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.

Table 1
Physical properties of TiO_2 nanoparticles.

Solvothermal condition	Reaction time varied at fixed temperature (180 °C)				Reaction temperature varied at fixed time (3 h)			
	0 h (as-synthesized)	3 h	5 h	10 h	160 °C	180 °C	200 °C	240 °C
Organic content (%)	30	14	13	11	x	x	x	x
Average size (nm)	5.3	8.8	9.0	9.3	8.4	8.8	8.9	x
Refractive index	1.82	1.89	1.92	x	1.85	1.88	1.91	x
Transmittance (at λ=500 nm, %)	98.2	96.9	95.4	95.3	98.2	98.3	97.7	14.4

x: not measured.

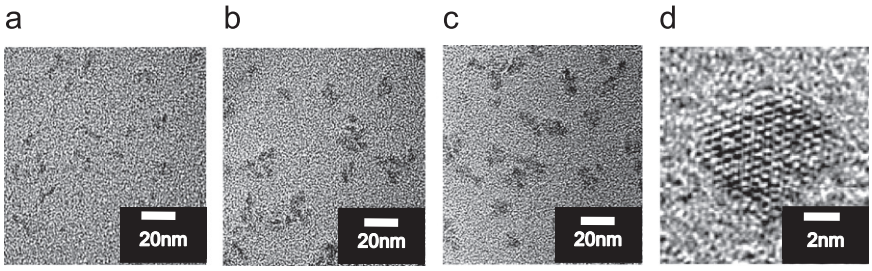

Fig. 2. HR-TEM images of TiO_2 nanocrystals obtained from solvothermal reactions at 180 °C for different reaction time. (a) As-synthesize particles, (b) after 3 h, (c) after 5 h, and (d) individual TiO_2 nanocrystal enlarged from (b).

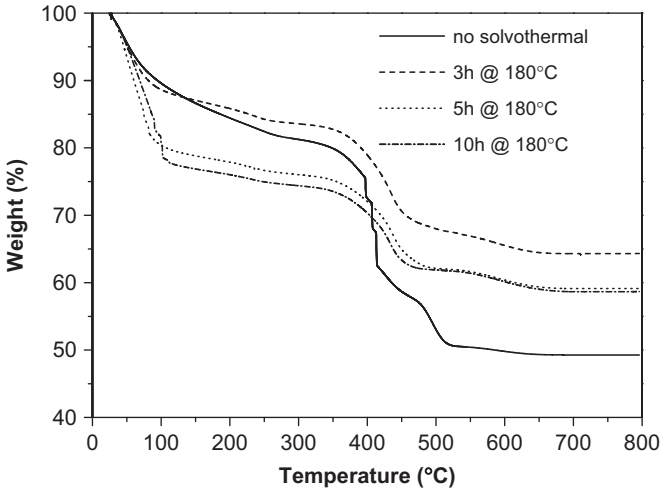

Fig. 3. TGA thermograms of TiO_2 nanocrystals obtained from solvothermal reactions at 180 °C for different reaction time.

After plateaus up to 400 °C, degradation of organic groups occurred for respective samples. Organic content of pristine TiO_2 sample was measured to be 30%, while those of the samples after solvothermal treatment gradually decreased down to 11%. The results are summarized in Table 1. The decrease in organic content can be attributed to the decreased surface area of TiO_2 nanoparticles due to the particle size growth after solvothermal reaction.

One of the most important physical properties of TiO_2 nanoparticle controlled by solvothermal treatment is a refractive index. As mentioned earlier, a drawback of the organically modified TiO_2 nanoparticle was a low refractive index (<1.8) due to high organic content. It was confirmed that refractive indices of TiO_2 thin films were increased by solvothermal reaction. The increased reaction time up to 5 h and the increased solvothermal temperature up to 200 °C resulted in the refractive index as high as 1.92 without loss of optical clarity of the films (Δn variation is shown in the supporting data).

The tapping mode AFM images on the thin film of as-synthesized TiO_2 nanoparticle showed very even surface with root-mean-square (rms) roughness of 1.0 nm while the film of 3 h solvothermal treated TiO_2 exhibited a slightly rougher surface with rms roughness of 1.7 nm without visible agglomerates. Almost no trace of dewetting or large agglomerate after spin coating was observed by AFM analyses.

Towards the photocatalytic applications, there is growing interest in the fabrication of mesoporous TiO_2 nanocrystals [10]. Recently, TiO_2 inverse opal made from polymeric colloidal crystal template was used as a light-amplified photoelectrode for DSSC [1–5]. However, the fabrication process of TiO_2 inverse opal includes calcinations step which accompanies a large volume shrinkage of at an elevated temperature (~450 °C) resulting in a decreased solar cell efficiency.

In this study, non-aggregated TiO_2 nanoparticles were fabricated into the inverse opal structures on glass substrate using polymeric colloidal crystal of PS to investigate the volume shrinkage upon calcinations. Fig. 4 shows various inverse opal structures obtained from colloidal crystal templating method. After the colloidal templates were burned off by thermal calcinations at 450 °C, it was confirmed that the inverse opal from TiO_2 of 5 h solvothermal treatment exhibited the lowest reduction in volume shrinkage. A reduced shrinkage upon solvothermal treatment can be attributed to a lower organic content on the surface of TiO_2 nanoparticles. Non-aggregated property as well as small particle size of our TiO_2 resulted in an excellent inverse opal formation for various PS particle sizes without significant volume shrinkage as shown in Fig. 4(d)–(f).

The inverse opal TiO_2 shown in Fig. 4 can be directly used as a photoelectrode for DSSC. The conductivity of TiO_2 particles should be increased by calcination due to elimination of organic groups, although anatase TiO_2 is well known n-type semiconductor material.

In summary, mild solvothermal treatments on the organically modified TiO_2 system resulted in the precise control of the particle size and crystallinity without significant agglomeration of the nanoparticles. The spin-coated TiO_2 film showed the refractive index as high as 1.91 without thermal treatment. The non-aggregated TiO_2 nanoparticles were successfully infiltrated into

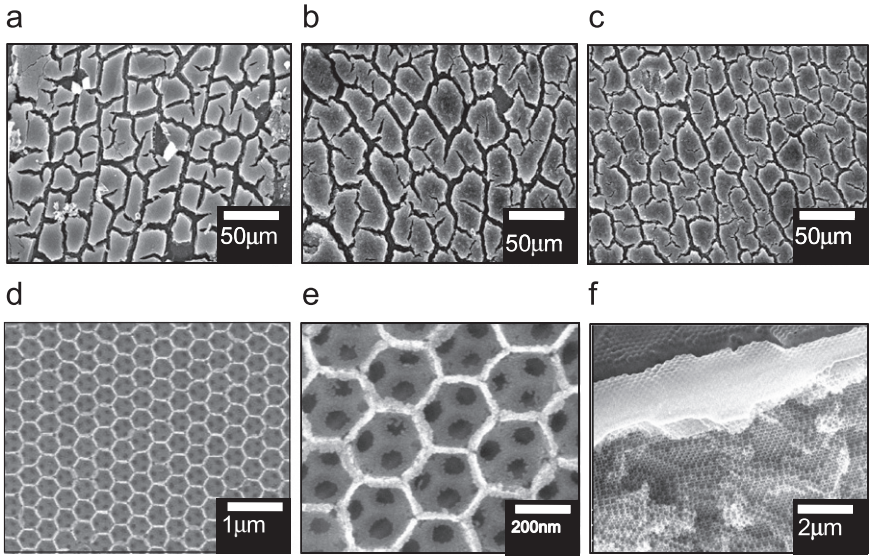

Fig. 4. SEM images of inverse opal films (thickness ~5 μm) prepared using TiO_2 nanoparticles with different solvothermal treatment time, (a) 0 h, (b) 3 h, and (c) 5 h. PS microsphere with 500 nm particle diameter was used for sacrificial colloidal template. Inverse opals made of PS template with different particle sizes of (d) 500 nm, (e) 350 nm, and (f) 280 nm are also shown.

colloidal crystal template, which were consequently converted to the inverse opal structure which can be directly utilized as a photoelectrode of light-amplified DSSC.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2010.05.023.

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