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Characterization and properties of anatase TiO_2 film prepared via colloidal sol method under low temperature

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Abstract Nanocrystalline titanium dioxide particles and films with anatase structures have been prepared via solvothermal method under low temperature. The products were characterized by X-ray diffraction and transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The optical properties were characterized in the ultraviolet-visible region by optical absorption measurement. The relationship between the optical band gaps and the structures was studied.

Keywords Anatase · Film · Chemical synthesis

1 Introduction

TiO_2 is a n-type, wide-band gap semiconductor, which is transparent in visible light. Its electrical properties critically depend on its stoichiometry [1], the nature and amount of dopants, as well as its nanostructure [2, 3]. Recently, the high-quality TiO_2 films have attracted much interesting from the viewpoints of basic science and applications. Especially interesting is photocatalysis [4], which can be used to decompose toxic gases into safe gaseous compounds by using solar energy, electrodes for solar energy conversion [5, 6], and gate oxides of metal-oxide-semiconductor field transistor [7]. Moreover, nanocrystalline thin TiO_2 films also have some advantages in solar cell where TiO_2 has been successfully used [8, 9].

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Various different methods have been employed for deposition of nanocrystalline TiO_2 thin films [10, 11]. The size of crystallites in the films depends on the deposition techniques used as well as on the deposition conditions and the thickness of films.

The solvothermal method is a promising approach to obtain many kinds of nanocrystalline oxide materials under comparatively low temperature [12]. In this study, a solvothermal process under mild temperature was used to synthesize nano-films of anatase TiO_2.

2 Experimental procedure

Tetrabutyl titanate was used as the titania precursor. The matrix sol was prepared by mixing with absolute ethanol, acetic acid, acetylacetone, and deionize water. Here the acetic acid and acetylacetone acts as a catalyst controlling the hydrolysis/condensation reactions in sol-gel solution. After that the sol was put into a Telfon-lined autoclave up to 90% of its capacity, which was maintained at 210 °C for a requisite time, and then cooled to room temperature naturally.

The products were washed with distilled water and absolute ethanol in sequence, and then uniformly dispersed in absolute ethanol. The substrate of quartz glass and silicon were cleaned by ultrasonic agitation in distilled water, acetone and ethanol. After being spun cast, the samples were heated under vacuum at 80 °C for 1 h to bake out solvents and other impurities. Thermal annealing was performed at 400 °C for 1 min.

Before preparing the film samples, some precursors were dried at 80 °C in vacuum to get TiO_2 powder for characterization. Powder X-ray diffraction (XRD) patterns were taken by employing CuKα radiation to characterize the powder and film. The average crystallite size was calculated using Scherrer's equation.

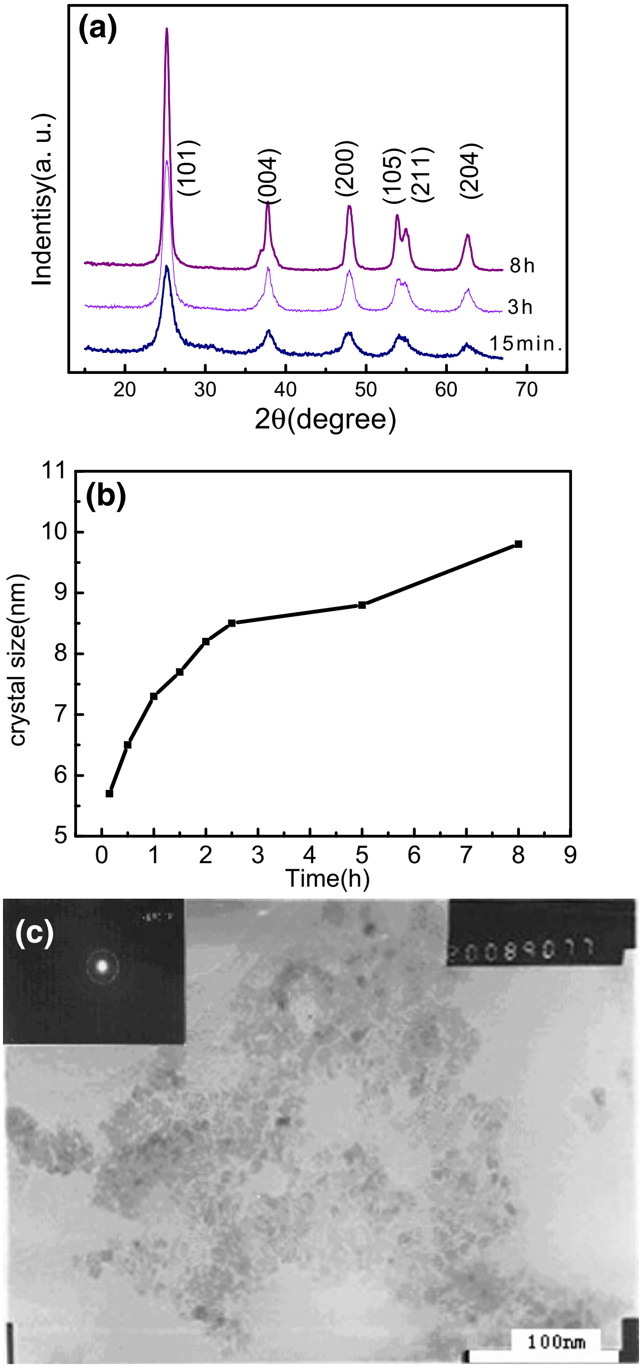

Fig. 1 TiO_2 nanoparticles prepared by using solvothermal method. (**a**) X-ray diffraction patterns for samples, (**b**) dependence of grain size on reaction time, and (**c**) a TEM image

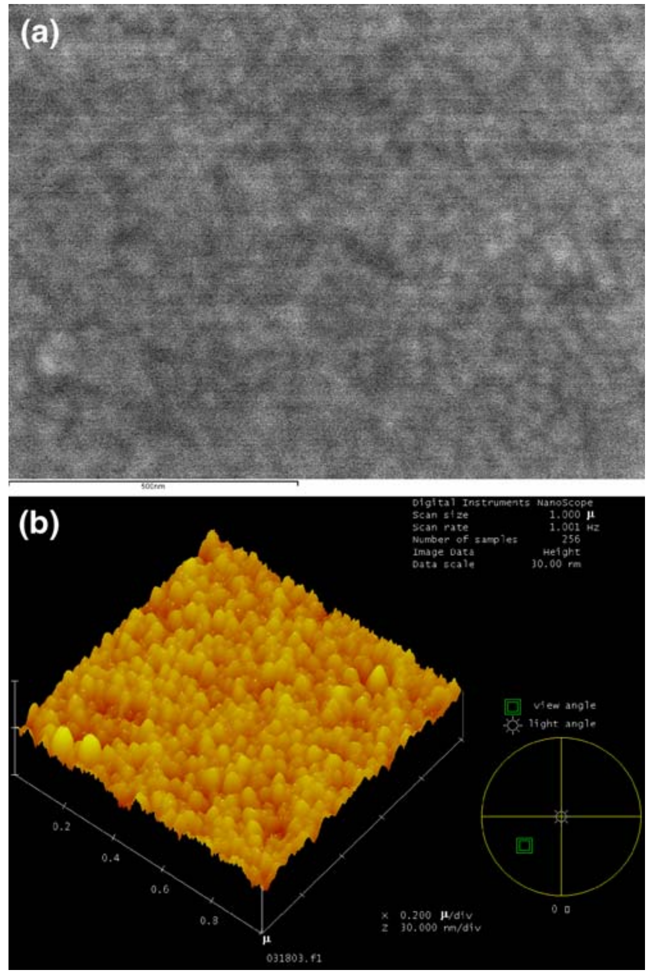

Fig. 2 Typical (**a**) SEM and (**b**) AFM micrographs of TiO2 films prepared by spin casting

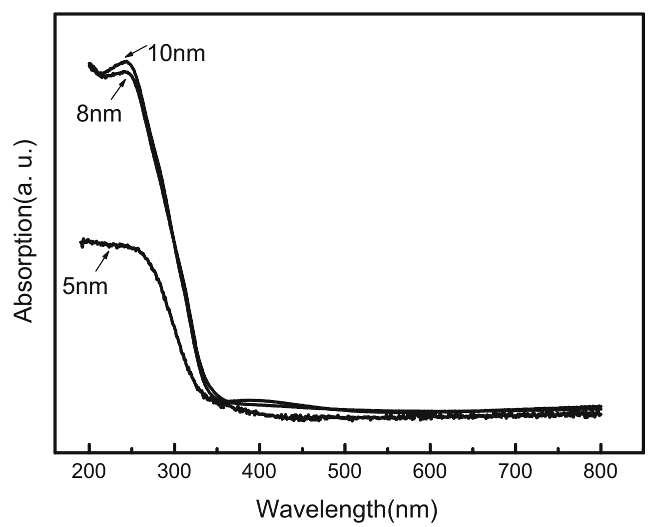

Fig. 3 UV-vis absorption spectra for TiO_2 films with different particle sizes

The particle morphology and size were determined by transmission electron microscopy (TEM, Hitachi H-800). Microstructure of the film samples was observed by scanning electron microscopy (SEM, Hitachi S-450) and atomic force microscopy (AFM). UV Absorption Spectra were recorded between 1.55 and 6.2 eV by exciting the TiO_2 films on quartz using Thermospectronic Unicam UV-500 spectrophotometer. The Van der Pauw four-probe

Table 1 Surface resistivity of nano TiO_2 films with different particle sizes.

Sample	1#	2#	3#
Grain size	5 nm	8 nm	10 nm
$\overline{\rho_s}/\Omega$	3.1×10^5	4.1×10^5	6.3×10^5

method with a dc power supply of 5–10 nA was employed to measure the electrical conductivity.

3 Results and discussion

The XRD patterns of the as-prepared products by solvothermal processing with different reaction times are shown in Fig. 1(a). All of the peaks labeled in the pattern have been indexed as from anatase TiO_2 phase. But each sample prepared with different time is different by the extent of crystallization and half-width.

The influence of reaction temperature and time on the synthesis of anatase TiO_2 nanoparticles was investigated. Anatase TiO_2 could form when the reaction temperature is in the range of 170 to 230 °C, but the temperature has little influence on the crystallite size. Here, the reaction time appears to be dominating. The crystallite sizes calculated by Scherrer's formula are shown in Figs. 1(b). In general the resultant particles become bigger with increasing reaction time. Fig. 1(c) shows the TEM images of as-prepared products. The shape of the TiO_2 nanoparticles is nearly spherical. The particle size is 5–12 nm, which is consistent to the result calculated via *Scherrer's* formula. The TEM results indicate that particles with smaller diameter appear rather monodisperse.

The resulting TiO_2 nanoparticles are insoluble in pure ethanol. No additional surfactants or ligands are needed to disperse the TiO_2 nanoparticles in these solvent mixtures to reach solubility up to 25 mg/ml. The solution of the anatase TiO_2 nanoparticles of 5–12 nm in diameter is deposited via spin casting and annealed at 400 °C for 1 min to prepare the TiO_2 nano-film.

Figure 2(a) shows SEM micrographs of typical microstructure of this TiO_2 nano-film. The average grain sizes measured from the SEM micrographs are distributed in the range from 5 nm to 12 nm. This result illustrates that the annealing process do not change the grain size. Figure 2(b) shows AFM measurement on the roughness of the TiO_2 films. The film is smooth, with variations on the order of only 2 nm.

Figure 3 shows the UV absorption spectrum of the TiO_2 nano-films on quartz glass. Because the extension of the electronic wave functions of semiconductor quantum dots is confined to the particle, their energy levels are size-dependent, and UV-vis spectroscopy can be used to determine the diameter of semiconductor nanoparticles. The observed $\lambda_{1/2}$ (the wavelength at which the absorption is 50% of that at the shoulder [exitonic peak]) corresponding to the films with particles with 5 nm in diameter displays a blue-shift obviously, while when the particle size reach 8 nm, the blue-shift can hardly be observed. This indicates that the quantum confinement effect in the UV absorption onset only appears in ultra-small particles.

The surface resistivity of these film samples were measured at room temperature as shown in Table 1. As the grain size increases, the values of conductivity decrease accordingly. The main reason is that the particles with smaller size can be dispersed in ethanol uniformly, therefore the quality of films with smaller particles is better than those with bigger particles, although much more grain boundaries exist in sample 1# resulting in a decrease in electrical conductivity [13]. By adding suitable amounts of less polar solvents such as dichloromethane, chloroform, or chlorobenzene into the samples with bigger particles, stable solutions should be obtained, and the electrical conductivity could be enhanced accordingly.

4 Conclusion

Anatase TiO_2 nanoparticles and films with different grain sizes have been synthesized via a solvothermal method under low temperature. Their surface morphology, optical absorption and conductivity are sensitive to the grain sizes. The results are extremely promising and further research is being carried out to refine solvothermal method for metal-oxide films and to better understand the intrinsic relationship between the physical properties of films and the processing.

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