

Supporting Information

Characteristics of Dye-Sensitized Solar Cells Based on the TiO₂ Nanotube/Nanoparticle Composite Electrode

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The TiO₂ nanoparticles were prepared by the sol-gel procedure. The titanium (IV) isopropoxide (30 ml) was rapidly added to the stirring distilled water (60 ml) and then stirred for 30 min. The white precipitate formed immediately after addition of the titanium (IV) isopropoxide. The colloid was filtered and washed with distilled water and ethanol, then added to a closed vessel containing 30 ml 0.6 M teramethylammonium hydroxide aqueous solution and stirred at 90 °C until the slurry became a translucent blue-white liquid. The solution was moved to a Teflon-lined autoclave and treated hydrothermally at 220 °C for 8 h. After growth, the anatase nanoparticles formed. The nanopartilces were washed with distilled water and ethanol, and then dispersed in ethanol to make the paste. Fig. 1 shows the XRD patterns of the TiO₂ nanoparticles after sintering at 400 °C. The crystal diameter was 12.80 nm from the intensity of (101) peak.

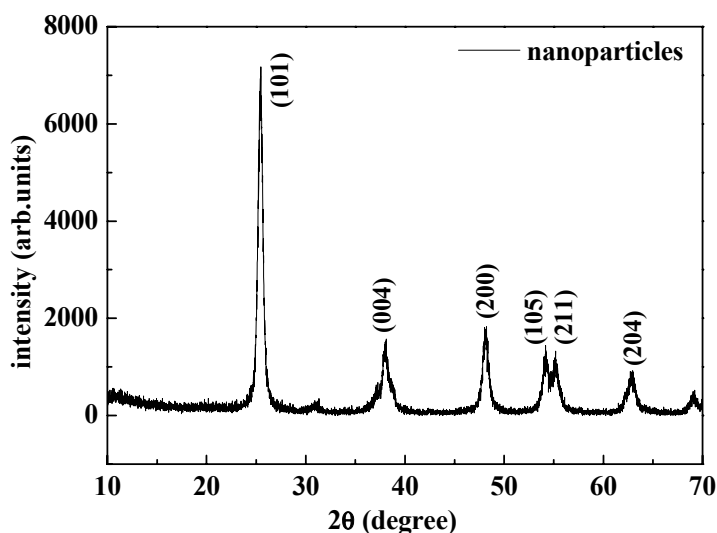


Fig. 1 X-ray diffraction (XRD) patterns of the annealed TiO₂ nanoparticles.

The intercalated sodium was removed by washing with 0.1 M HCl solution. The presence of sodium is observed by energy dispersive X-ray analysis (EDX), shown in Fig. 2a, which reveals that the sodium content is substantial in the nanotubes without HCl washing, up to ~9-10 at%. The EDX

measurement also revealed that the sodium content is almost zero in the nanotubes with HCl washing. So through HCl solution washing, the intercalated sodium of nanotubes was almost removed.

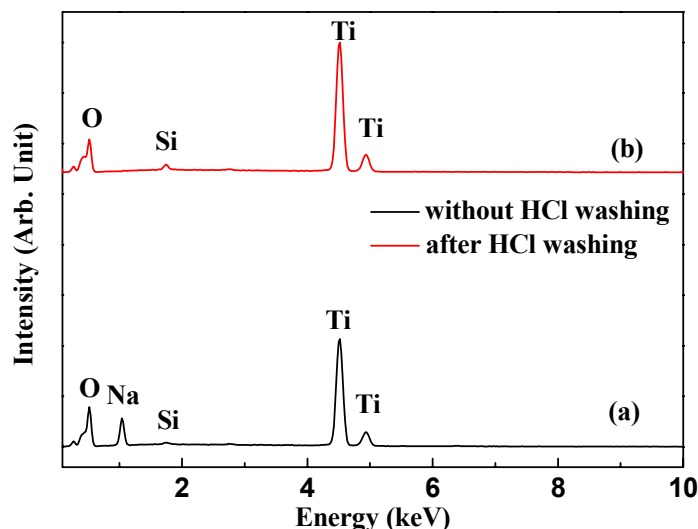


Fig. 2 EDX spectra of (a) as-synthesized titanate nanotubes without HCl solution washing, (b) the nanotubes after HCl solution washing.

The flatband potential of mesoporous TiO_2 composite film electrode was measured by spectroelectrochemical method. The electrode consisted of a $4.5 \mu\text{m}$ thick titania composite layer was supported by the conducting glass substrate (F doped SnO_2). The composite electrode formed the working electrode of a closed three electrode signal compartment cell, the counter electrode being platinum and the Ag/AgCl reference electrode. The electrolyte solution was composed of tetrabutylammonium perchlorate (TBAP) and acetonitrile (MeCN). Absorbance was measured at 780 nm, the applied potential being scanned at $0.005 \text{ V} \cdot \text{sec}^{-1}$. For each determination of V_{fb} a new working electrode and freshly prepared electrolyte solution were used.

In general, the impedance spectra of dye-sensitized solar cells presented three semicircles in Nyquist plots, which were assigned to the charge transfer at the counter electrode (R_{ct1} between the Pt/electrolyte interface) in the high frequency region, to electron transfer at the TiO_2 electrode (R_{ct2} between the TiO_2 /dye/electrolyte interfaces) in the middle frequency region, and to the Warburg diffusion process of I^-/I_3^- in the electrolyte (R_{diff}) in the low frequency region. The sheet resistance of the TCO (R_s) was in the high frequency range over 10^6 Hz .

According to the Mie theory, the particles should have a large size to scatter light. Ferber et al¹ through computer simulation found that the large TiO_2 particles 250-300 nm in diameter as scattering centers mixed in a TiO_2 matrix containing 20 nm particles could scatter light efficiently. Many

groups²⁻⁵ have confirmed that the use of large particles as scattering centers or an upper scattering layer is more favorable for enhancing light harvesting. Fig. 3 shows the UV-vis reflectance and transmittance spectra of different nanotube content films (thickness $5 \pm 0.5 \mu\text{m}$) in the range of visible light. With the nanotube content increasing, the reflectance of films increased and the transmittance decreased. The 50 wt% film had around 0% transmittance at the wavelength range from 400 to 600 nm. If the light illuminated the front of cell with 10 μm film, the dye in upper 5 μm film hard absorb the light at these wavelength (from 400 to 600 nm). So the nanotube content should not be high.

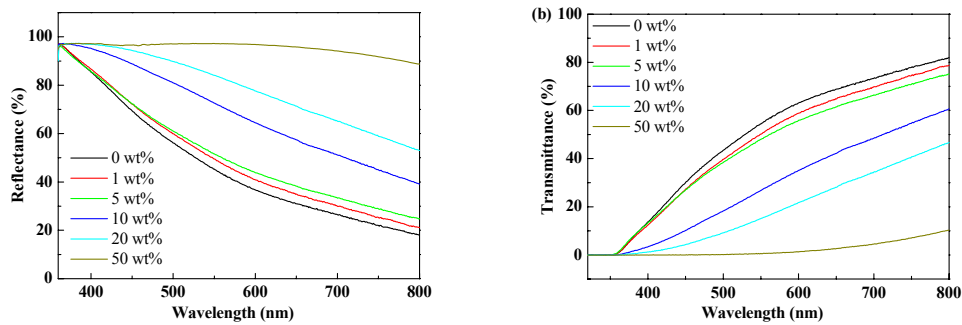


Fig. 3 UV-vis spectra of (a) absorbance and (b) transmittance for different nanotube content films.

Table 1 shows the performance of the DSCs based on the various amount of nanotubes under simulated AM 1.5 light. At the comparable film thicknesses, the photocurrent densities increased from 14.47 mA/cm^2 of the 0 wt% DSC to 17.05 mA/cm^2 of the 5 wt% DSC, and decreased to 14.09 mA/cm^2 of the 50 wt% DSC. Meanwhile, there were essentially no substantial differences in the photovoltages and fill factors. The improvement in J_{sc} would increase the photovoltaic conversion efficiency. The photovoltaic conversion efficiency of the 5 wt% DSC received the highest value, which was 7.80%.

Table 1. The photovoltaic parameters of the DSC as a function of the nanotubes amount under AM 1.5 light (100 mW/cm^2).

Nanotubes (wt%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
0	14.47	0.701	0.664	6.73
1	15.28	0.696	0.664	7.06
5	17.05	0.691	0.663	7.80
10	16.05	0.702	0.662	7.46
20	14.94	0.705	0.682	7.18
50	14.09	0.693	0.671	6.55

References

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