Sol–gel synthesized mesoporous anatase titanium dioxide nanoparticles for dye sensitized solar cell (DSSC) applications

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Abstract. Hierarchically structured titanium dioxide nanoparticles were successfully synthesized by the sol–gel method. The synthesized nanoparticles were subjected to powder X-ray diffraction, UV–Vis DRS spectroscopy, Brunauer–Emmett–Teller method, Barrett–Joyner–Halenda analysis, field emission scanning electron microscopy, high-resolution transmission electron microscopy and energy-dispersive X-ray analysis. The powder X-ray diffraction pattern shows that the obtained particles are of anatase phase with good crystallite nature. The nitrogen adsorption and desorption isotherms show that the prepared material has surface area of $31.71 \text{ m}^2 \text{ g}^{-1}$ and the pore size distribution analysis shows the average pore diameters of mesoporous TiO_2 nanostructures to be 7.1 and 9.3 nm. The UV–Vis DRS spectrum shows that the TiO_2 nanoparticles are having absorption in the ultraviolet region. The optical band gap of the nanoparticles is 3.2 eV. The morphological studies show the morphology of the particles as spherical in shape. The elemental compositions of TiO_2 nanoparticles were confirmed by energy-dispersive X-ray spectrum analysis. The conversion efficiency of the solar cell was 3.415% with open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor (FF) of 0.607 V, 13.206 mA cm^{-2} and 42.56%, respectively.

Keywords. Semiconductors; sol–gel; solar cells; TiO_2 .

1. Introduction

Fujishima and Honda¹ first discovered the phenomenon of photocatalytic splitting of water over a TiO_2 electrode under ultraviolet light in 1972. The effective utilization of clean, safe and abundant solar energy through the TiO_2 photocatalysis provides promising solutions to the energy crisis and serious environmental challenges. TiO_2 has been widely used commercially in pigments,² sunscreens,^{3,4} paints,⁵ toothpaste,⁶ etc. Mesoporous materials^{7,8} have a wide range of applications, including their important role in photoelectrochemical cells, photocatalysts and sensors.

Dye sensitized solar cells (DSSCs) as alternatives to traditional silicon-based solar cell devices have attracted widespread attention due to their clean and pollution free nature, easy fabrication and powerful harvesting efficiency.⁹ One of the key elements in DSSC is the mesoporous TiO_2 photoanode, which transfers the charge carriers from the sensitizer (dye) to the fluorine-doped tin oxide (FTO) electrode and concurrently allows the electrolytes (redox couples) to diffuse to the anchored dyes. Typically, nanoparticles are used for the fabrication of the mesoporous TiO_2 layers on the FTO to obtain high surface areas and generate nanopored structures.^{10,11} In general, upon decreasing the size of TiO_2 nanoparticles, the surface area of the fabricated nanoporous

TiO_2 film is increased, and thus more dye molecules can be adsorbed. However, the average pore size is decreased simultaneously, and more defect sites and grain boundaries can be generated in the fabricated TiO_2 film. These defects will affect efficiency of DSSC. Kim *et al.*¹² reported that nanoporous spherical structures will provide both high adsorption of dye molecules and efficient electrolyte diffusion. In addition, the spherical TiO_2 structures offer a considerable scattering effect in the long-wavelength region. Generally, TiO_2 contains three different phases (anatase, rutile and brookite). Among them anatase and rutile phases are having several applications. The optical band gap of TiO_2 nanostructures with anatase phase is 3.2 eV, whereas for the rutile it is 3.0 eV.¹³ The anatase conduction band is 0.2 eV more negative than that of rutile if the same redox material is employed. This will cause more open-circuit voltage in DSSC than rutile phase.

In this work, we have synthesized hierarchically structured anatase TiO_2 nanoparticles with moderate surface area by the sol–gel method. The resulting materials have the spherical morphology via aggregation of anatase phase particles. The obtained products were characterized by powder X-ray diffraction (PXRD), UV–Vis DRS spectroscopy, Brunauer–Emmett–Teller (BET) method, Barrett–Joyner–Halenda (BJH) analysis, field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM).

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Figure 1. Hydrolysis and polycondensation reaction mechanism of sol-gel process.

2. Experiment

2.1 Synthesis procedure

The synthesized product was obtained from titanium (IV) isopropoxide, $\geq 97\%$ (Sigma Aldrich) dissolved in ethanol (Merck) and deionized water was added to the solution in molar ratio of $\text{Ti}:\text{H}_2\text{O} = 1:4$. The mixed solution was vigorously stirred for 1 h in order to form sols. After aging for a day, the sols were transformed into gel form. The hydrolysis and condensation mechanism is given in figure 1. The obtained gels were dried at 120°C for 24 h to remove the water and organic materials. After that, the dried gel was sintered at 450°C for 2 h in homemade high temperature programmable furnace. Finally the pure TiO_2 nanoparticles were obtained. Figure 2 shows the synthesis procedure of TiO_2 nanoparticles given in flow chart.

2.2 Fabrication of DSSCs

The electrodes were prepared as follows: 1 g of prepared TiO_2 powder was mixed with 0.1 ml of acetylacetone and ground mechanically. During vigorous stirring, 5 ml of mixture of water and ethanol (1:1 vol%) was added and 0.4 ml of polyoxethylene (10) octylphenyl ether (Triton X-100) was added with the above solution to form a paste. The obtained colloidal paste was coated on the FTO

(sheet resistance, $8 \Omega/\square$) substrate by the doctor-blade technique. After coating, the resulting film was sintered at 500°C for 1 h. The sintered electrodes were soaked in 0.3 mM of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II) (known as N3) dye in an ethanol solution. The counter electrode was prepared by the doctor-blade technique using Platisol T/SP (Solaronix SA) precursor and thermally decomposed at 400°C for 30 min. Finally both electrodes are sandwiched together to form a cell. The small amount of electrolyte (Iodolyte AN-50) was injected into cell.

3. Results and discussions

3.1 PXRD

The phase composition and the crystallite size of the prepared TiO_2 nanoparticles were evaluated by PXRD analysis. Figure 3 shows the PXRD pattern of TiO_2 nanoparticles obtained by sintering at 450°C which shows preferred orientation corresponding to the plane (101). All the diffraction peaks in the diffraction patterns can be indexed as anatase phase of TiO_2 nanoparticles and the diffraction pattern was in good agreement with JCPDS files # 21-1272.¹⁴ Crystallite size was calculated by Debye-Scherrer's formula given by

$$D = K\lambda/\beta \cos \theta,$$

where D is the crystallite size, λ the wavelength of the X-ray radiation ($\lambda = 0.15406 \text{ nm}$) for $\text{CuK}\alpha$, K the constant ($K = 0.89$) and β the full-width at half-maximum of (101) plane. The crystallite size of TiO_2 nanoparticles is 17 nm.

3.2 UV-Vis DRS spectroscopy

Optical properties were studied by UV-Vis DRS spectroscopy. Figure 4a shows the optical absorption spectra of TiO_2 nanoparticles. The absorption edge of TiO_2 nanoparticles is 396 nm. The optical absorption coefficient (α) of a semiconductor is expressed by the following equation:

$$\alpha = A(h\nu - E_g)^n/h\nu,$$

Here α is the absorption coefficient, E_g the band gap, A is a constant depending on the transition probability, n depends on the nature of the transition, i.e., allowed direct, allowed indirect, forbidden direct and forbidden indirect. In our case, for an indirect band gap, the value of n is $1/2$.¹⁵ The variation of $(\alpha h\nu)^{1/2}$ with photon energy is shown in figure 4b. The band gap is found to be 3.2 eV.

3.3 BET and BJH analysis

The specific surface area and porosity of the mesoporous anatase TiO_2 were evaluated by using the nitrogen adsorption and desorption isotherms after sintering at 450°C as

Figure 2. Flow chart: preparation methodology of spherical shape TiO₂ nanoparticles by the sol-gel process.

Figure 3. Powder X-ray pattern of sol-gel synthesized anatase phase TiO₂ nanoparticles sintered at 450°C.

shown in figure 5. The isotherm of sample reveals the stepwise adsorption and desorption branch of type IV curve, indicating the presence of mesoporous material having a

three-dimensional (3D) intersection according to the IUPAC classification. A hysteresis loop with a stepwise adsorption and desorption branch is observed at wide range of pressure (P/P_0). The BET surface area of TiO₂ nanoparticles is 31.76 m² g⁻¹ as shown in figure 5a. This result indicates that the synthesized material has wider mesoporous structure. To analyse pore size, the plots of the pore size distribution are investigated by desorption branch of the BJH method as shown in figure 5b. The average pore diameters of mesoporous TiO₂ nanostructures are 7.1 and 9.3 nm. This kind of bimodal porous structure can be useful for efficient electrolyte diffusion into the photoanode in DSSC.

3.4 Morphological studies

Figure 6 shows the FESEM and HRTEM images of mesoporous TiO₂ calcined at 450°C. The morphology of synthesized material is spherical in shape. Discernable pores are present at the surface of samples. The pore structure is observed at the space between the nanoparticles, indicating that the interparticle porosity is due to the mesoporosity. From the FESEM analyses, the mechanism for the formation of mesoporous TiO₂ nanoparticles can be analysed. As

Figure 4. (a) Optical absorption (UV-Vis DRS) spectrum of anatase TiO₂ nanoparticles and (b) plot of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$) for indirect transition.

can be seen from the FESEM images, the mesoporous structure probably arises from the aggregation of nanocrystallite TiO₂ particles. When the titanium precursor was dissolved in ethanol, TiO₂ nanoparticles can be formed via hydrolysis and condensation process. Further hydrolysis and condensation of titanium precursors lead to the growth of larger TiO₂ nanoparticles, which are slowly aggregated to one another. As TiO₂ nanoparticles are further aggregated, the TiO₂ particles become microscopic particles, and finally form microspheres as shown in figure 6a and b. HRTEM images of sol-gel derived nanoparticles are shown in figure 6c. It confirms the clear spherical and homogeneous formation of nanoparticles. Selected area electron diffraction is shown in figure 6d which clearly indicates that TiO₂ nanoparticles are highly crystalline in nature with anatase phase ($d_{(101)} = 0.35$ nm). Figure 6e shows the individual particle of TiO₂. As can be seen from the HRTEM images the average particle size is ~ 20 nm, which is in agreement with the crystallite size obtained from XRD. The elemental composition of TiO₂ nanoparticles was verified with EDAX spectrum.

Figure 5. (a) Nitrogen adsorption and desorption isotherm analysis of TiO₂ nanoparticles sintered at 450°C and (b) pore size distribution of TiO₂ nanoparticles sintered at 450°C.

Figure 6f shows the EDAX spectrum of sol-gel synthesized TiO₂ nanoparticles.

3.5 I-V measurement

The photovoltaic performance of solar cells (active area – 0.25 cm²) was examined by using an Oriel Class AAA solar simulator equipped with AM 1.5 G filter. The incident light intensity of the simulated light was calibrated to 100 mW cm⁻² by using a reference Si reference solar cell. The applied potential and cell current was measured using Keithley model digital source metre.

The overall efficiency of the DSSC can be obtained as product of the photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), the fill factor (FF) and the intensity of the incident light (I)

$$\eta = V_{oc} \times J_{sc} \times FF / I.$$

The fill factor (FF) is derived from the I - V curve

$$FF = I_m \times V_m / J_{sc} \times V_{oc},$$

Figure 6. (a, b) FESEM image of porous TiO_2 aggregates, (c) HRTEM image of TiO_2 nanoparticles dispersed in ethanol, (d) SAED pattern of TiO_2 nanoparticles, (e) HRTEM image of an anatase TiO_2 nanoparticle with lattice fringes pattern of (101) plane and (f) EDX spectrum of TiO_2 nanoparticles.

Figure 7. Photocurrent–voltage (I – V) characteristics of dye sensitized solar cells.

where V_m is the maximum output voltage and I_m the maximum output current.

As depicted in figure 7, the conversion efficiency (η) of the DSSCs was 3.415% with open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor (FF) of 0.607 V, 13.206 mA cm⁻² and 42.56%, respectively. This may be due to the effective light scattering and porous nature of the large size spherical nanoparticles. Kim *et al*¹² reported, the maximum efficiency of the cell as 10% with the 776 mV based on spherical-shaped nanostructures. In the present case, the conversion efficiency and open-circuit voltage of the cell are lower than existing report, which may be due to the increased electron recombination rate in the interface of photoanode/electrolyte.¹⁶ However, this drawback can be solved by introducing the blocking layer on the photoanode and optimizing the thickness of the films.

4. Conclusions

The hierarchically structured anatase TiO₂ nanoparticles were successfully synthesized by the sol–gel method without adding any surfactant. The powder X-ray studies show that synthesized materials are highly crystallite with anatase phase. The UV–Vis DRS spectrum shows that TiO₂ nanoparticles absorption occurred at UV region. The band gap was evaluated to be 3.2 eV. The type IV isotherm shows mesoporous nature of the TiO₂ nanoparticles. The BET isotherm shows the surface area of the nanoparticles

as 31.76 m² g⁻¹. The pore sizes are 7.1 and 9.3 nm (bimodal-like pores), which are evaluated from the BJH method. The morphological result shows that the synthesized particles are spherical in shape. The mesoporous order of spherically shaped sol–gel synthesized TiO₂ nanoparticles reached 3.415% conversion efficiency. Finally, we claim that the spherical shape and bimodal-like pores of the TiO₂ nanostructures can be used as a photoanode in DSSCs.

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