Performance enhancement of TiO$_2$-based dye-sensitized solar cells by carbon nanospheres in photoanode

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Abstract. The conversion efficiency of dye-sensitized solar cells (DSSCs) is optimized by modifying the optical design and improving absorbance within the cell. These objectives are obtained by creating different sized cavities in TiO$_2$ photoanode. For this purpose, carbon nanospheres with diameters 100-600 nm are synthesized by hydrothermal method. A paste of TiO$_2$ is mixed with various amounts of carbon nanospheres. During TiO$_2$ photoanode sintering processes at 500$^\circ$C temperature, the carbon nanospheres are removed. This leads to random creation of cavities in the DSSCs photoanode. These cavities enhance light scattering and porosity which improve light absorbance by dye N719 and provide a larger surface area for dye loading. These consequences enhance performance of DSSCs. By mixing 3% Wt. carbon nanospheres in the TiO$_2$ pastes, we were able to increase the short circuit current density and efficiency by 40% (from 12.59 to 17.73 mA/cm$^2$) and 33% (from 5.72% to 7.59%), respectively.

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1. introduction

Since the fabrication of dye-sensitized solar cells (DSSCs) in 1991 [1], many researches have been done for enhancing the performance and stability of these cells. During the last two decades, DSSCs have taken a lot of attention because of their low cost and ease of manufacturing. The efficiency of DSSCs can be influenced by various characters such as charge recombination [2, 3], light absorption by dye [4], specific surface area and porosity [5], electron transport [6] and so on. These parameters can be controlled by a variety of approaches like using different dyes [7], semiconductors [8] or electrolytes [9], changing morphology [10] or band gap of semiconductors [11], photon management for light scattering [12, 13, 14], etc [15, 16]. Among these methods, photon management is used to enhance the photon path length in order to increase the probability of light absorption by dye.

The most successful implementation of photon management in DSSCs is usage of diffuse scattering layer [17]. This scattering layer, which is deposited on the top of photoanode main layer, is consisted of large size particles with sizes between 300-1000 nm. These particles are made of transition metal oxide with high refractive index such as TiO$_2$. In recent times, disordered structures such as one, two or three dimensional photonic crystals (1DPC, 2DPC, 3DPC) [18, 19] and TiO$_2$ hollow spheres [20] have been used as scattering layer instead of TiO$_2$ filled spheres. The replacement of TiO$_2$ hollow spheres with TiO$_2$ filled spheres has leaded to increment of light absorbance as is shown in Ref. [20].

In another implementation of photon management, a mixture of both small and large particles is employed in photoanode in order to scatter light [21]. Usage of porous structures in photoanode is another possibility for light scattering and improving dye absorption [22]. Many researches have been carried out to create porosities and cavities in the photoanode thin film. Recently, polystyrene ball embedded in a paste of TiO$_2$ has created cavities during sintering process. The role of these cavities is to scatter light and increase light absorption by dye [23].

In this research, carbon nanospheres powder was synthesized by hydrothermal method that is a facile and low cost method. Different amounts of carbon nanospheres were mixed with a paste of TiO$_2$ nanostructure consisted of ~ 20 nm TiO$_2$ nanocrystals as describe below. Consequentially, effect of TiO$_2$ porosity in photoanode on absorption of dye, light scattering, charge recombination, and chemical capacitance are investigated. Ultimately, an energy conversion efficiency up to 7.59% achieved for 3 %Wt. of carbon nanospheres mixed with TiO$_2$. 
2. Experimental details

2.1. Synthesis of carbon nanospheres

Synthesis of carbon nanospheres was done with polycondensation reaction of glucose under hydrothermal conditions described in Ref. [24]. A 0.5 M aqueous solution of glucose was prepared. 50 mL of this solution was kept in 60 mL Teflon lined autoclave and heated for 14 h at 160°C. The black or brown products were centrifuged and washed with ethanol and water three times and dried at 80°C for more than 4 h.

2.2. Mixing TiO$_2$ paste and carbon nanospheres powder

For mixing carbon nanospheres powder and commercial TiO$_2$ paste consisting of ~20 nm TiO$_2$ nanoparticles, carbon nanospheres were dissolved in ethanol to obtain 1, 2, 3, and 4 Wt.% solutions. These solutions were sonicated to disperse completely and then mixed with TiO$_2$ paste with a weight ratio of 1:2. The resultant mixture was dispersed with ultrasonic titanium probe and then was concentrated with rotary-evaporator to remove ethanol. Five different TiO$_2$ pastes were prepared with various weight percentages of ethanolic solutions of carbon nanospheres about 0%, 1%, 2%, 3%, and 4% and named T0, T1, T2, T3 and T4, respectively.

2.3. Fabrication of TiO$_2$ photoelectrode

For preparing DSSC working electrode, FTO glass (3 mm thickness, 15Ω/□, Dyesol) was first washed with detergent and rinsed with DI water. Then it was cleaned by using an ultrasonic bath with DI water, 0.1 M HCl solution in ethanol, acetone, and ethanol for 15 min each. The washed FTO was heated up to 450°C for 15 min. Afterwards a compact blocking layer of TiO$_2$ was deposited onto FTO by immersing FTO into 40 mM aqueous TiCl$_4$ solution for 30 min at 70°C and washed with DI water and ethanol. The next layer was a porous TiO$_2$ layer (T0, T1, T2, T3 or T4) deposited by doctor blade technique with ~10 μm thickness. After drying the doctor bladed films for 6 min at 125°C, the films were heated at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min, and at last at 500°C for 30 min. Finally, for depositing last layer, the films again were treated in 40 mM aqueous TiCl$_4$ solution as described previously and sintered at 500°C for 30 min. After cooling naturally to 80°C temperature, TiO$_2$ electrodes were immersed into a 0.4 mM N719 (Dyesol) dye solution in ethanol for 20-24 h. In this research five different working electrodes (T0, T1, T2, T3, and T4) were prepared corresponding to the different TiO$_2$ pastes.

2.4. Preparation of counter electrode

For preparing DSSC counter electrode, a hole with diameter about 6-7 mm was drilled on the FTO glass. Then the FTO glass was washed as described above for FTO working electrode but instead for 6 min. After that, the FTO was heated to 470°C for 15 min.
The thermal decomposition method was employed to deposit the Pt catalyst on the FTO glass. With this purpose, a drop of 0.3 mM H₂PtCl₆ solution in ethanol was applied on the FTO glass and annealed at 470°C for 15 min.

2.5. Electrolyte

The electrolyte I⁻/I₃⁻ consisted of 0.1 M LiI, 0.1 M I₂, 0.5 M 4-tert-butylpyridine, and 0.6 M Tetrabutylammonium iodide in acetonitrile.

2.6. DSSC assembly

The dye loaded porous TiO₂ photoanode and the Pt counter electrode were sealed together with a 30 µm Surlyn (Dyesol) spacer around the TiO₂ active area (0.25 cm²). The liquid electrolyte (I⁻/I₃⁻) was injected into assembled cells. At the end, the hole of counter electrode was covered by a glass (1cm*1cm) and sealed by a spacer.

The morphology of carbon nanospheres and TiO₂ nanoparticles and the thickness of the layer were observed by field-emission scanning electron microscope (Hitachi S-4160). The current-voltage (I-V) characteristics of the fabricated DSSCs were measured under solar simulator illumination of AM 1.5 (100 mW/cm²). The electrochemical impedance spectroscopy (EIS) measurements of the cells were performed with an Iviumstat. The EIS measurements were carried out in dark conditions and in room temperature, by applying a sinusoidal potential perturbation of 10 mV with the frequency ranging between 1 MHz and 0.05 Hz at different applied forward biases. Incident photon to current conversion efficiency (IPCE) spectra were recorded on a Jarrell Ash monochromator using a 100 W halogen lamp and a calibrated photodiode (Thorlabs). Diffuse reflection spectra of the films have been collected by Avaspec2048-TEC UV-Vis-NIR spectrophotometer with integrating sphere Avaligh-DHS. UV-Vis spectra of the dye loaded TiO₂ films were determined with a UV-Vis spectrophotometer (PG instrument, T80+). The concentration of absorbed dyes was determined by first desorbing the dyes from the dye-sensitized TiO₂ films in 0.1 M NaOH aqueous solution and then analyzing by UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION

Figure 1 shows field-emission scanning electron microscopy (FE-SEM) images of carbon nanospheres (a), as well as cross section (b) and top view (c,d) of TiO₂ thin film. In figure 1a, the spherical morphology with the size range of 100-600 nm is indicated. Figure 1b shows cross sectional FE-SEM image of the TiO₂ thin film deposited on FTO substrate. This Figure confirms that the TiO₂ thin film had the thickness of about 10 µm. Figure 1c and d show the top view FE-SEM images of the sintered TiO₂ with and without carbon nanospheres for T0 and T3 photoanodes. These images make the point clear that adding carbon nanospheres to TiO₂ paste increases porosity of TiO₂ thin films. During TiO₂ sintering processes, carbon nanospheres were removed at 490°C
Figure 1. FE-SEM images of a) carbon nanospheres b) cross section of TiO$_2$ thin film c) top view of TiO$_2$ photoanode without carbon nanospheres (T0) and d) with 3 % Wt. carbon nanospheres (T3)

and led to the creation of cavities [20]. These cavities enlarged the surface area and thus increased the number of absorbed dye molecules (N719 dye) on the TiO$_2$ thin film. The I-V curves of the different DSSCs fabricated with the T0, T1, T2, T3, and T4 photoanodes are depicted in figure 2. Table 1 lists photovoltaic parameters of the T0, T1, T2, T3, and T4 DSSCs. As seen in Table 1, the absorbed dye molecules for T3 photoanode is maximum with an increment of about 85% compared to T0 photoanode. The effect of porosity on the cells has also improved the current density of the cells so that $J_{SC}$ has increased from 12.59 mA/cm$^2$ for T0 cell to 17.73 mA/cm$^2$ for T3 cell.

Figure 2. I-V curves of DSSCs fabricated with TiO$_2$ and TiO$_2$ mixed carbon nanospheres with different weight percentages 1, 2, 3 and 4 %Wt (T0, T1, T2, T3, and T4 cells).
This improvement of $J_{SC}$ stems from more dye loading and light scattering due to the presence of the porosity in the photoanode.

Table 1. Photovoltaics parameters of the DSSCs with different amounts of carbon nanospheres mixed with TiO$_2$.

| Sample | T0    | T1    | T2    | T3    | T4    |
|--------|-------|-------|-------|-------|-------|
| $J_{SC}$ (mA/cm$^2$) | 12.59 | 14.99 | 15.90 | 17.73 | 16.05 |
| $V_{OC}$ (V)     | 0.710 | 0.685 | 0.715 | 0.720 | 0.700 |
| FF              | 0.64  | 0.63  | 0.61  | 0.59  | 0.607 |
| $N_{dye}$ ($10^6$ cm$^{-2}$) | 4.44  | 6.17  | 6.91  | 8.23  | 6.11  |
| $\eta$ (%)      | 5.72  | 6.47  | 6.90  | 7.59  | 6.82  |

The porosity has a slight effect on the open circuit voltage ($V_{OC}$) as it is seen in Table 1. In the following, when we present the results of EIS analysis, we will describe these small changes in $V_{OC}$ as a consequence of charge recombination with electrolyte.

Now, we focus on the fill factor results presented in Table 1. The fill factor behaviour can be easily justified based on the change in current density. The increment of current density causes high electron concentration leading to a greater resistance of the cells and therefore decreases the fill factor.

To determine the absorbance of the dye-loaded porous TiO$_2$ layers, UV-Vis spectra were measured. Figure 3 shows UV-Vis spectra of the dye-sensitized T0, T1, T2, T3, and T4 photoanodes. As seen in figure 3, light absorbance by the dye-sensitized TiO$_2$ increases from T0 up to T3 sample and decreases from T3 to T4.

Diffuse reflectance was measured in order to investigate optical properties of T0, T1, T2, T3, and T4 electrodes in the absence of dye sensitization. Diffuse reflectance spectrum is an effective analysis for indicating the light scattering ability of samples.

![Figure 3. UV-Vis spectra of the dye-loaded TiO$_2$ layers T0, T1, T2, T3, and T4 photoanodes.](image-url)
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Figure 4. Diffuse reflectance spectra of T0, T1, T2, T3, and T4 photoanodes.

Figure 5. Schematic diagram of light scattering in TiO$_2$ photoanodes.

figure 4 clearly reveals the effect of the carbon nanospheres on diffuse reflectance. As shown in figure 4, the ability of light scattering of the samples increases by increasing of the weight ratio of carbon nanospheres mixed with TiO$_2$. Increasing large cavities of size range 400-600 nm can be ideal for light scattering in visible region. figure 4 indicates that the light scattering monotonically increases from T0 to T4. On the other hand, the light absorbance by dye plotted in figure 3 becomes maximum for T3 and decreases by increasing the porosity of TiO$_2$ photoanode further. This behaviour can be explained based on the size of carbon nanospheres. Because the carbon nanospheres have the size range of 100-600 nm, the number of large cavities increase by increasing the weight ratio of carbon nanospheres. Consequently, the light scattering continues to increase from T3 to T4 while dye loading starts to decrease beyond the optimum amount of porosity 3 % Wt..

figure 5 schematically shows how the presence of large cavities leads to the light
scattering and enhances the optical path length in photoanode. These cavities increase multiple scattering of light and improve optical properties of the cell (better light trapping and less transmittance). Small cavities make high surface area which lead to more dye loading and light harvesting.

The incident photon-to-current conversion efficiency (IPCE) is plotted in figure 6 for T0 and T3 cells. This figure demonstrates that T3 cell has a higher IPCE than T0 cell confirming a higher short circuit current density $J_{SC}$ for T3 compared to T0 as it was also found from I-V figure (figure 2). It is also seen that the peak of IPCE curve is shifted from 30% to 60% and the IPCE spectrum is broadened over the 400-600 nm wavelength region which are due to the more dye loading and light scattering in T3 photoanode.

![Figure 6. Incident photon to current conversion efficiency for T0 and T3 cells.](image)

The EIS measurements were carried out to investigate the electron recombination and the band structure in fabricated cells. The results of EIS measurements were fitted using previously developed model. From this fitting the chemical capacitance $C_\mu$ and recombination resistance $R_{rec}$ were found. The results for $C_\mu$ and $R_{rec}$ are plotted versus voltage in figure 7.

As seen in figure 7a, the porosity in TiO$_2$ photoanode has no considerable effect on the chemical capacitance $C_\mu$. Since the slope of $C_\mu$ reflects the TiO$_2$ density of states [25], it can be concluded that the TiO$_2$ density of state distributions are identical for all the different porosity. Also there is no shift in the chemical capacitance of various cells and consequently no displacement for the TiO$_2$ conduction band edge has occurred.

The recombination resistance can be used as a criterion for the recombination rate so that a larger rate indicates a lower resistance and vice versa. figure 7b shows that T3 and T1 cells have the maximum and minimum recombination resistance, respectively. This behaviour can justify the maximum and the minimum values of $V_{OC}$ that we found from I-V analysis, see Table 1. Considering that increase of recombination reduces $V_{OC}$, a maximum and a minimum $V_{OC}$ is plausible for T3 and T1 cells. The seemingly
disputed $V_{OC}$ result that we found for T0 and T1 samples can also be justified by taking into account the role of recombination. Although the T1 sample in contrast to the T0 sample has a higher $J_{SC}$ and a higher dye loading but the increase in the recombination shown in figure 7b leads to a lower $V_{OC}$ for T1 compared to T0.

The recombination rate of T2 and T4 cells are almost the same as seen from figure 7b. This is compatible with the rather equal photovoltaic parameters, see Table 1 that we find from I-V figure for T2 and T4 cells.

4. Conclusion

The use of carbon nanospheres mixed with TiO$_2$ nanoparticles in DSSC photoanode with a facile method demonstrated a higher photovoltaic performance compared to the TiO$_2$ without any carbon nanospheres. By removing the carbon nanospheres, large and small cavities were created in the photoanode and enhanced the recombination resistance. The large cavities improved the light scattering and therefore an increase in the optical path was achieved. On the other hand the small cavities increase dye loading in the photoanode. These results are proven by DRS, desorption of dyes, and EIS measurements. As a consequence an enhancement of about 40% for current density and about 33% for the cell efficiency were obtained. Improving the photovoltaic performance with the method described in this article can be promising to fabricate high efficiency dye-sensitized solar cells.
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