Chapter 8

Facile Carbonate Doping in Mesoporous TiO$_2$ Microspheres for Dye Sensitized Solar Cell with Enhanced Efficiency

8.1. Introduction: The marathon race for the ultimate goal of commercialization of an alternative silicon-free solar cell technology to achieve lower cost-per-watt level with grid parity versus fossil fuel technologies, started with the seminal demonstration of a prototype dye sensitized solar cell (DSSC) in last century with 7% efficiency [1]. Since then many efforts are dedicated to enhance the efficiency of the cells by a variety of following ways [2]: (i) selection of strongly absorbing donor-pi-acceptor sensitizing dyes [3-5] (ii) use of redox couples to achieve higher open circuit voltage [6-8] (iii) better thin film (composition and morphology) on the photoanode [9-11]. Apparently first two points look independent of the third one. However, given the amount of dye adsorption, electron injection from the dye to the photoanode and redox coupling, the parameters are found to be key factors for the optimum DSSC efficiency. Successful design of the photoanode again relies on the four key parameter: (a) light trapping via scattering of incident solar radiation (b) very high surface area of the oxide film in the photoanode for dye adsorption (c) ultrafast electron injection from excited dye to the oxide layer (d) efficient transport of charge carriers with minimal recombination loss of electrons [2].

A mammoth of literature on the various ways of controlling above four parameters for the efficient DSSC is existing [2, 12-13]. For example, plasmonic nanoparticles (Ag, Au) are integrated into photovoltaic devices for light trapping [14-16]. However, use of plasmonic nanoparticles on the photoanode is reported to
generate a negative influence named Fano effect due to destructive interference between scattered and unscattered light below the plasmon resonance of nanostructure causing reduced light absorption in DSSC at short wavelength [17]. Application of Aluminum (Al) nanoparticles is reported to overcome such limitation due to Fano effect [17]. Use of porous oxide layer in the photoanodes are reported to be efficient strategy for the layer with higher surface area [18]. Ultrafast electron injection in the DSSC were achieved by doping plasmonic metals [15, 19] and atomic layer deposition (ALD) of TiO$_2$/Al$_2$O$_3$ after dye adsorption [20]. The use of unidirectional nanotube arrays is shown to exhibit a faster electron diffusion time ($\tau_d$) along the tube axis [21]. In principle, charge collection efficiency ($\eta_{cc}$) can be enhanced by reducing $\tau_d$ [22]. However, it has been shown that the nanostructure based photoanodes exhibit an undesired porous structure and thereby offer poor solar light harvesting [23]. Alternatively, a particular submicron sized TiO$_2$ structure called beads was used in photoanode or as scattering layer in order to increase charge collection efficiency [9].

From the brief overview of different synthesis strategies for the optimization of photoanode to account different important parameters for the betterment of the DSSC efficiency, it is most likely that optimization of one parameter may compromise others. Thus finding one-shot optimization strategy of all the parameters for the betterment of solar cell efficiency is “most wanted” and is the motive of the present study. In this work, we have used a particular TiO$_2$ structure called carbonate doped mesoporous microstructure (doped MS) in photoanode of a N719 dye containing solar cell. The doped MS prepared using two step non-aqueous solvothermal method in the photoanode essentially satisfies all the key requirements for the enhancement of efficiency of the DSSC. While scattering and electronic band modification increase light trapping, porosity enhances the dye adsorption. The ultrafast electron injection and minimization of
electron recombination leading to better solar cell efficiency compared to DSSC with photoanode using undoped MS are also demonstrated.

8.2. Results and Discussion:

8.2.1. Carbonate Doping in TiO$_2$ Microsphere: The Key Parameter Influencing Others for Efficient Dye Sensitized Solar Cell [24]: The control TiO$_2$ MS and doped MS were prepared according to modified procedures reported earlier [25-27]. The positive influences of the doped MS in DSSC performance are schematically shown in Scheme 8.1. Figure 8.1-A-a shows scanning electron

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme81.png}
\caption{Scheme 8.1. Schematic presentation. Synthesis of doped TiO$_2$ MS and their advantages in the dye-sensitized solar cells.}
\end{figure}
**Figure 8.1.** Characterization of TiO$_2$ MS and doped TiO$_2$ MS. (A) SEM images (a and b); EDAX spectrum (c); SEM image of a single particle (d) and Ti, O elemental mapping images of that particle (e, f) of TiO$_2$ MS. (B) SEM images (a and b); EDAX spectrum (c); SEM image of a single particle (d) and Ti, O, C elemental mapping images of that particle (e, f, g) of doped TiO$_2$ MS.

Microscopy (SEM) image of TiO$_2$ MS with a diameter range 1-1.1 μm obtained by solvothermal treatment at 180 °C for 12 h. Densely-packed, interconnected TiO$_2$ nanocrystals are clearly visible in the high resolution image as shown in Figure 8.1-A-b. Figure 8.1-A-c shows EDAX spectrum of the microspheres with the relative distribution of oxygen and titanium. The elemental EDAX mapping of the microspheres for Ti and O and their distribution in a microsphere are shown in Figure 8.1-A-(d-f), consistent with uniform distribution of the element in the sample. No signature of carbon in this sample is evident. In Figure 8.1-B-a, we have shown SEM images of the doped MS. The distribution lies in the range of 0.9-1 μm, which is slightly smaller than that of the undoped MS. Similar interconnection of the TiO$_2$ nanocrystals with a bit higher porosity is evident from Figure 8.1-B-b. The EDAX spectrum (Figure 8.1-B-c), the elemental mapping for Ti,
Figure 8.2. Characterization of TiO\(_2\) MS and doped TiO\(_2\) MS. TEM and HRTEM images (a-c), SAED patterns (d), powder XRD patterns (i) of TiO\(_2\) MS. TEM and HRTEM images (e-g), SAED patterns (h), powder XRD patterns (j) of doped TiO\(_2\) MS.

O and C (Figure 8.1-B-(d-g)) and their atomic percentages clearly show uniform C-doping in the microsphere. In an earlier report on the synthesis of such C-doped nanoparticles, X-ray photoelectron spectroscopy (XPS) was performed and obtained two distinct peaks at 284 eV and 288 eV consistent with C 1s binding energy. While the peak at 284 eV was assigned to carbon adsorbed on the TiO\(_2\) surface as contaminant, the later peaking at around 288 eV was concluded to be the result of Ti-C bonds [27]. Although high resolution microscopy on the samples was out of the scope of the report, the absorption spectrum of the C-doped samples is consistent with our result (see later). The high resolution transmission
electron microscopy (HRTEM) images of the MS before and after doping are shown in Figure 8.2. Relatively higher porosity and similar nanoparticle size of 10-20 nm in the case of doped MS compared to undoped counterpart are clear. The additional porosity and surface roughness in the case of doped MS could be result of surface adsorbed carbon as concluded in the earlier XPS study [27]. As the materials were annealed at 450 °C for the preparation of working electrode of the DSSC, we have examined the crystalline condition of the materials after the annealing as shown in Figure 8.2 (i, j). We have obtained negligibly small difference in the diffractograms after and before annealing. The diffraction peaks of the undoped and doped samples are not only consistent with that reported in the literature [28], also consistent with the selected area electron diffraction (SAED) patterns of the corresponding samples as shown in Figure 8.2 (d, h).

The absorption spectrum of the doped MS is found to be significantly different from that of undoped counterpart as shown in Figure 8.3a. The main electronic band of TiO$_2$ at ~360 nm is found to be red-shifted to 410 nm upon carbonate doping in addition to significant scattering across the absorption spectrum of N719 in the entire visible solar spectrum. In a recent computational study the density of states (DOS) of undoped and carbonate doped TiO$_2$ have been performed [26]. The study showed that the carbonate-doping produced band tail states near the valence and conduction band edges of TiO$_2$ decreasing the band gap by about 0.2 eV. The calculation also demonstrated that the band gap in doped TiO$_2$ is smaller than that of the undoped one. As shown in Figure 8.3b, the red-shift in the absorption spectrum of the doped MS has significant spectral overlap with green light (~500 nm) emission from two coumarin dyes namely C343 and C500 covalently and non-covalently adsorbed at the TiO$_2$ surfaces. The ability of absorbing direct sunlight and contributing to the total photoinduced charge carrier in the doped MS are additional advantages over its undoped
Figure 8.3. Optical studies of TiO₂ MS and doped TiO₂ MS attached to C343 and C500 dyes. (a) UV-VIS absorption spectra of TiO₂ MS and doped TiO₂ MS. (b) Shows the overlap of C343, C500 emission and doped TiO₂ MS absorption. (c) The picosecond-resolved fluorescence transients of C500 (excitation at 375 nm) in the absence (pink) and in the presence of TiO₂ MS (green) and doped TiO₂ MS (red) collected at 490 nm. (d) The picosecond-resolved fluorescence transients of C343 (excitation at 375 nm) in the absence (cyan) and in the presence of TiO₂ MS (green) and doped TiO₂ MS (red) collected at 480 nm.

counterpart. N719 dye does not have emission, thus the coumarin dyes are used to study the electron and energy transfer processes. We have quantified the light absorption in terms of Förster resonance energy transfer (FRET) from the green emitting dye C500 adsorbed to the host surface of the MS. As shown in Figure 8.3c, the dye C500 at the doped MS shows faster fluorescence decay compared to C500 at the undoped MS surface revealing resonance energy transfer in the former case [29]. The estimated distance between the dye and the host surface of doped TiO₂ is found to be 1.53 nm, consistent with the surface adsorption of the dye C500. The ultrafast electron injection of the covalently attached coumarin dye
C343 is evident from Figure 8.3d. The spectroscopic and fitting parameters are shown in Table 8.1. It is well known that the covalently adsorbed dye C343 undergoes electron transfer to host TiO$_2$ upon photoexcitation [30]. The apparent rate constant, $k_{nr}$, is determined for the nonradiative processes by comparing the lifetimes of C343 in the absence ($\tau_0$) and the presence ($\tau$) of MS, using the following equation [31]:

$$k_{nr} = \frac{1}{\tau} - \frac{1}{\tau_0} \quad (8.1)$$

we have estimated that electron transfer rate of the dye C343 at the doped MS (2.8X10$^{9}$ s$^{-1}$) is much faster than that at the undoped MS (1.1X10$^{9}$ s$^{-1}$). Although a significant spectral overlap of the C343 emission with the absorption band of the doped MS is evident from Figure 8.3b, the possibility of FRET in this case can be ruled out for the interference of much faster electron transfer dynamics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Excitation wavelength (nm)</th>
<th>Detection wavelength (nm)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\tau_{avg}$ (ns)</th>
</tr>
</thead>
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<tr>
<td>C343</td>
<td>375</td>
<td>480</td>
<td>3.88 (100%)</td>
<td></td>
<td></td>
<td>3.88</td>
</tr>
<tr>
<td>C343-TiO$_2$ MS</td>
<td>375</td>
<td>480</td>
<td>0.19 (80.7%)</td>
<td>3.04</td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td>C343-doped TiO$_2$ MS</td>
<td>375</td>
<td>480</td>
<td>0.08 (78.3%)</td>
<td>0.35</td>
<td>3.88</td>
<td>0.33</td>
</tr>
<tr>
<td>C500</td>
<td>375</td>
<td>490</td>
<td>3.25 (100%)</td>
<td></td>
<td></td>
<td>3.25</td>
</tr>
<tr>
<td>C500-TiO$_2$ MS</td>
<td>375</td>
<td>490</td>
<td>3.25 (100%)</td>
<td></td>
<td></td>
<td>3.25</td>
</tr>
<tr>
<td>C500-doped TiO$_2$ MS</td>
<td>375</td>
<td>490</td>
<td>0.35 (66.7%)</td>
<td>3.25</td>
<td></td>
<td>1.31</td>
</tr>
</tbody>
</table>

*Numbers in the parenthesis indicate relative weightages.*
Figure 8.4. Device performance. I-V characteristics without dye (a) and with N719 dye (c); (b) dye loading; (d) wavelength dependent photocurrent response curves and (e) open circuit voltage decay profiles of different DSSCs fabricated with TiO$_2$ MS and doped TiO$_2$ MS.

The direct light harvesting ability and the better photoconductivity of the doped MS compared to those in its undoped counterpart is evident from I-V characteristics of the solar cell without sensitizing dye (Figure 8.4a). Figure 8.4b shows enhanced dye loading capability of the doped MS because of its better...
Table 8.2. Solar cell performance using different active electrodes

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Dye</th>
<th>J_sc (mA cm⁻²)</th>
<th>V_oc (V)</th>
<th>Fill Factor</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ MS</td>
<td>No dye</td>
<td>0.08</td>
<td>0.27</td>
<td>38.7</td>
<td>0.01</td>
</tr>
<tr>
<td>Doped TiO₂ MS</td>
<td>No dye</td>
<td>0.18</td>
<td>0.35</td>
<td>38.5</td>
<td>0.02</td>
</tr>
<tr>
<td>TiO₂ MS</td>
<td>N719</td>
<td>15.2</td>
<td>0.68</td>
<td>54.8</td>
<td>5.16</td>
</tr>
<tr>
<td>Doped TiO₂ MS</td>
<td>N719</td>
<td>16.6</td>
<td>0.76</td>
<td>65.6</td>
<td>7.65</td>
</tr>
<tr>
<td>TiO₂ NP P25</td>
<td>N719</td>
<td>15.6</td>
<td>0.72</td>
<td>63.2</td>
<td>6.49</td>
</tr>
</tbody>
</table>

*Short-circuit photocurrent densities (J_sc cm⁻²), open-circuit voltage (V_oc) and efficiency (η).*

porosity as discussed earlier. The betterment of all the key parameters ultimately enhances the solar cell efficiency as shown in Figure 8.4c. The corresponding values of the photovoltaic parameters, such as the short circuit photocurrent density (J_sc), open circuit voltage (V_oc), fill factor (FF), power conversion efficiency (η) values are presented in Table 8.2. The DSSC with doped TiO₂ MS shows higher energy conversion efficiency of 7.6% compared to that of the undoped MS (5.2%). The enhancement of photocurrent at the peak absorption of the dye N719 is also studied and shown in Figure 8.4d. The spectra collected from different cells show good agreement between the wavelength of photocurrent maximum and N719 absorption maximum (λ_max = 520nm). The temporal decay of the open circuit voltage has been monitored for different cells in the dark following a brief period of illumination as shown in Figure 8.4e, revealing reduced recombination in the case of DSSC with doped MS. The fitted timescales are presented in Table 8.3. The open circuit voltage decay reflects the timescales for the recombination processes of the electron at the conduction band of the semiconductor with the oxidized electrolytes [32]. The increase in V_oc as evident from Figure 8.4c is a consequence of reduction in the back electron transfer [33].
Table 8.3. Dynamics of photovoltage transients of DSSCs fabricated using different active electrodes:

<table>
<thead>
<tr>
<th>Active Electrode</th>
<th>$\tau_1$ (S)</th>
<th>$\tau_2$ (S)</th>
<th>$\tau_{avg}$ (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ MS</td>
<td>0.13 (38.8%)</td>
<td>1.60 (61.2%)</td>
<td>1.03</td>
</tr>
<tr>
<td>Doped TiO$_2$ MS</td>
<td>0.21 (33.7%)</td>
<td>2.21 (66.3%)</td>
<td>1.54</td>
</tr>
<tr>
<td>TiO$_2$ NP P25</td>
<td>0.11 (28.8%)</td>
<td>1.25 (71.2%)</td>
<td>0.92</td>
</tr>
</tbody>
</table>

*Numbers in the parenthesis indicate relative weightages.*

8.3. Conclusion: Carbonate doped TiO$_2$ microspheres were synthesized via two step facile solvothermal routes and used as photoanode of a N719 based dye sensitized solar cell (DSSC). Our single-shot modification in the solar cell design is shown to take care of several key parameters including porosity for dye loading, scattering for light trapping, electron injection for photocurrent and less electron recombination with redox coupling for the enhancement of the efficiency of the solar cell as schematically shown in Scheme 8.1. We have compared the efficiency of the DSSC with undoped TiO$_2$ microsphere and conventional TiO$_2$ nanoparticle (P25) and found significant improvement in the light harvesting efficiency upon doping. To our knowledge the realization of carbonate doping solar cells provides a novel pathway to control conversion efficiency in DSSC. Future investigations will focus on tailoring the absorption wavelengths of the sensitizing dye for the light trapping in the NIR region of solar radiation, where 49% power remains un-harvested.
References


