**Supporting Information**

Efficient Dye-sensitized Solar Cells Based Hierarchical Rutile TiO$_2$ Microspheres by Hydrothermal Process

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![XRD spectra of TMS-4, TMS-6 and TMS-8 thin film deposited on glass substrate.](image)

**Figure S1** XRD spectra of TMS-4, TMS-6 and TMS-8 thin film deposited on glass substrate.

Figure S1 shows the XRD patterns of the TMS films deposited on glass substrates at various deposition times. The comparison of ‘d’ values in observed XRD patterns with those from the standard JCPDS data (89-4920) confirms the formation of Rutile TiO$_2$ phase having tetragonal crystal structure. The lattice parameter values “a” and “c” for tetragonal structure calculated for the deposited film is found to be in good agreement with the reported values. Seven distinct reflections such as (101), (211), (220), (002), (310) (301) and (112) besides a prominent (110), reflection are seen in the all TMS-4 to TMS-8 samples [1].

Reference

The FT-Raman of the P25, and TMS films are shown in Figure S2. The ‘tetragonal anatase structured’ TiO$_2$ belongs to D194h (I41/amd) space group (SG) and following normal lattice A$_{1g}$+B$_{1g}$+B$_{2g}$+E$_g$. The first E$_g$ peak at ~144 cm$^{-1}$, a characteristic of anatase TiO$_2$ was formed in the P25 sample. The peaks at 516 (corresponding to B$_{1g}$, A$_{2g}$) and 635 cm$^{-1}$ (correspond to E$_g$) modes of anatase TiO$_2$ are observed. The rutile phase of TiO$_2$ is tetragonal and exhibits symmetry characters of the space group $\bar{4}2m$ with two TiO$_2$ molecules per unit cell. The TMS sample show four Raman active fundamental modes reveals rutile TiO$_2$ at 143 cm$^{-1}$ (B$_{1g}$), 447 cm$^{-1}$ (E$_g$), 612 cm$^{-1}$ (A$_{1g}$), and 826 cm$^{-1}$ (B$_{2g}$) expressed as A$_{1g}$+B$_{1g}$+B$_{2g}$+E$_g$. For the rutile phase two prominent maxima at 445 cm$^{-1}$ (E$_g$) and 609 cm$^{-1}$ (A$_{1g}$), are comparable with
that found in the rutile TiO$_2$ single crystal. In addition, there are second-order scattering features, the most prominent one at $\sim237$ cm$^{-1}$ (Eg) peak due to the multiple-phonon scattering processes, which is also considered as a characteristic Raman peak of rutile type TiO$_2$. In the Raman spectra of TMS samples, the Eg and A1g modes, as well as the second-order effect at $\sim237$ cm$^{-1}$, are the major features; the B1g and B2g modes are extremely weak or absent. The second order Eg at 237 cm$^{-1}$, a characteristic of rutile TiO$_2$. 