Supporting Information

Efficient Dye-sensitized Solar Cells Based Hierarchical Rutile TiO_2 Microspheres by Hydrothermal Process

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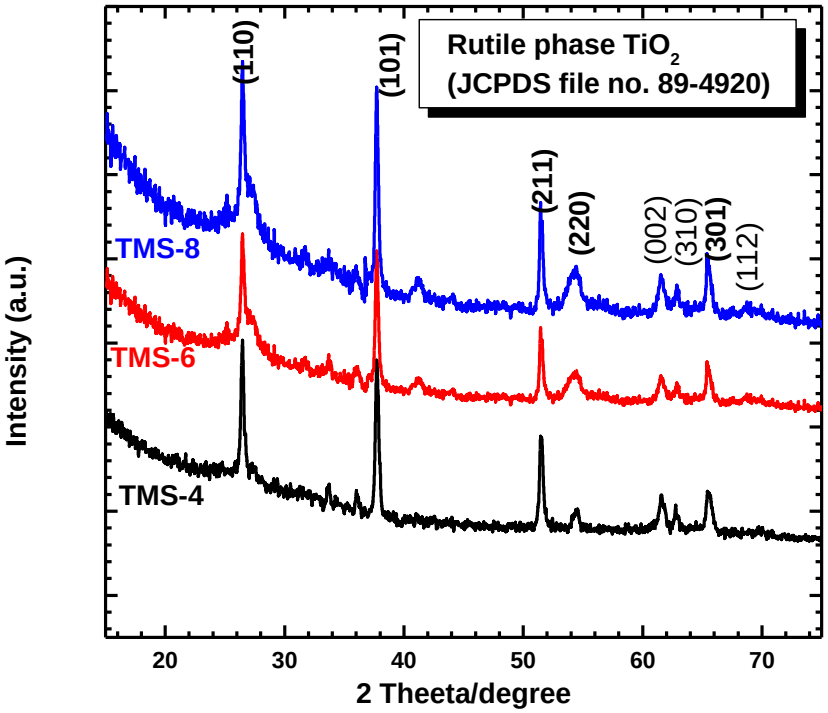

Figure S1 XRD spectra of TMS-4, TMS-6 and TMS-8 thin film deposited on glass substrate.

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

[1] S. S. Mali, C. A. Betty, P. N. Bhosale, P. S. Patil, *CrystEngComm*, 2011, **13 ,** 6349.

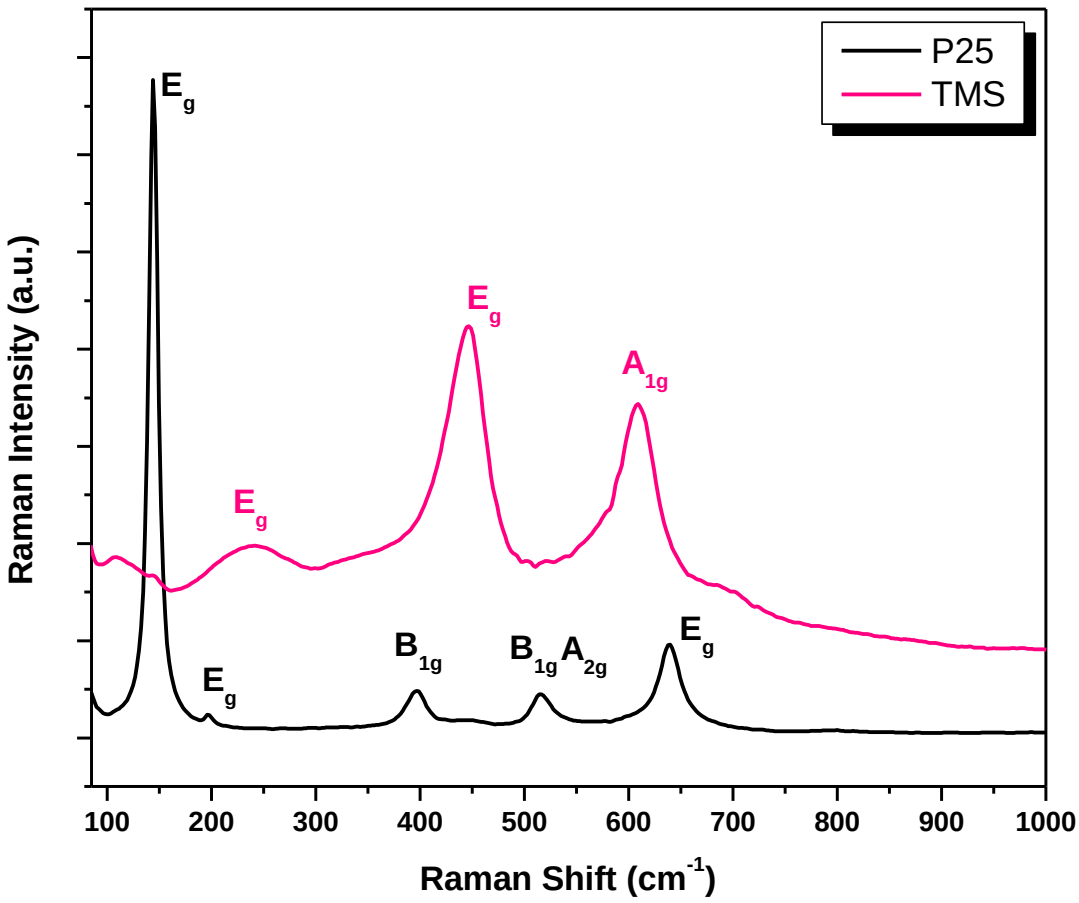

Figure S2 FT-Raman spectra of P25 and TMS sample.

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 A1g+B1g+B2g+Eg. The first Eg peak at ~144 cm^{-1}, a characteristic of anatase TiO_2 was formed in the P25 sample. The peaks at 516 (corresponding to B1g, A2g) and 635 cm^{-1} (correspond to Eg) modes of anatase TiO_2 are observed. The rutile phase of TiO_2 is tetragonal and exhibits symmetry characters of the space group with two TiO_2 molecules per unit cell. The TMS sample show four Raman active fundamental modes reveals rutile TiO_2 at 143cm^{-1} (B1g), 447cm^{-1} (Eg), 612cm^{-1} (A1g), and 826cm^{-1} (B2g) expressed as A1g+B1g+B2g+Eg. For the rutile phase two prominent maxima at 445 cm^{-1}(Eg) and 609 cm^{-1} (A1g), 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 ~237 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 ~237 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.