Supplementary Information

Supplemetary Information 1

Indirect band gap from UV-Vis. Absorption

$$(\alpha h\nu)^n = k(h\nu - E_g)$$

Where k is the absorption constant for an indirect or direct transition,
n = ½ for an indirect transition and n= 2 for a direct transition
E_g is the band gap [1]

The x-intercept (energy axis) i.e. for $(\alpha h\nu)^n = 0$.

Supplementary Information 2

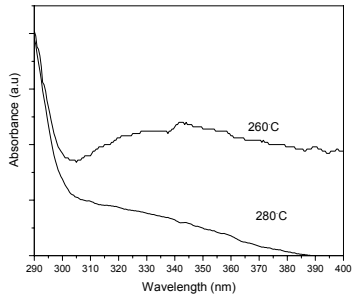
B-TiO_2 E_g = 3.76 eV, T-TiO_2 E_g = 3.6 eV
$E_{g,b}$ = 3.2 eV
The radius of particle from the onset of absorption can be calculated by the following Brus relation [2],

$$E_g - E_{g,b} = \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1.8e^2}{\varepsilon R}$$

Where ε is the dielectric constant of TiO_2, μ is the reduced mass of the exciton ($\mu^{-1} = m_e^{-1} + m_h^{-1}$), m_e and m_h are the effective masses of the electron and hole respectively. E_g and $E_{g,b}$ are the band gap of the TiO_2 in the present case and band gap of bulk TiO_2 respectively. $\mu = 0.74\ m_e$ and ε= 184 for TiO_2 [3]. But caution must be excercised while using the effective mass for the charge carriers in TiO_2 as there is a considerable controversy regarding the exact value in the literature.

Supplementary Information 3

Absorption spectrum for samples prepared at lower temperatures

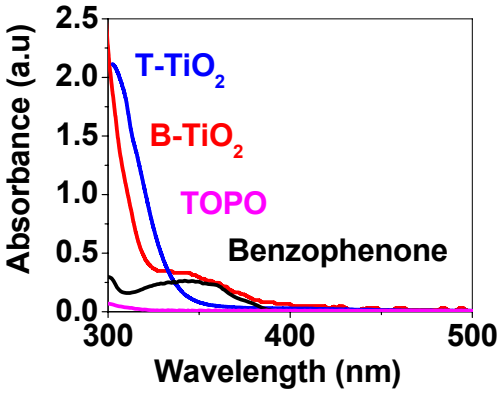


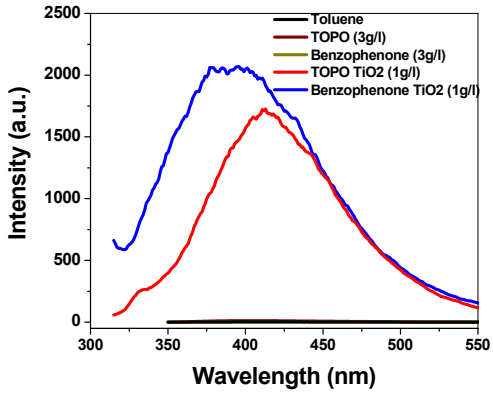
References

(1) Pankove, J. I. *Optical Processes in Semiconductors;* Dover Publoications, Inc.: New York, 1971.
(2) Brus, L., *J. Phys. Chem.,* **1986**, 90, 2555.
(3) Enright, B.; Fitzmaurice, D., *J. Phys. Chem,* **1996**, 100, 1027.

Supplementary Information 4

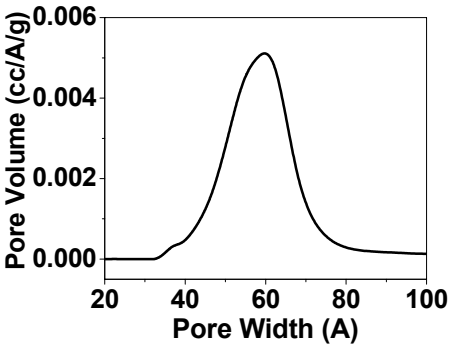
1. Optical absorption and emission spectra of TOPO-TiO2, Benzophenone-TiO2, Toluene, TOPO and Benzophenone. Emission spectra has been collected after exciting the sample at 300 nm

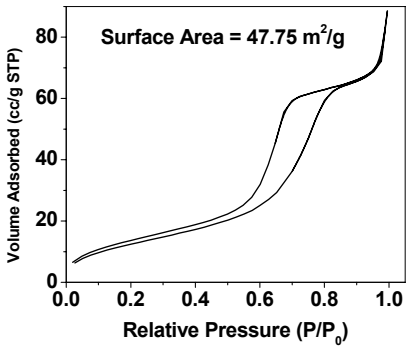




Supplementary Information 5:

N_2 adsorption-desorption thermal curves and pore size distribution of B-TiO_2 particles



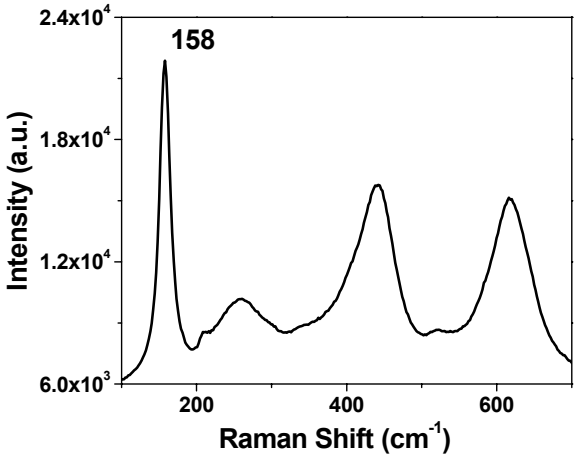


A **B**

From N_2 absorption and desorption thermal curves it is clearly seen that the surface area is 47.75 m^2/g and pore size distribution is ~ 60 Aº The pore size distribution is very less as evidenced from the distribution curves.

Supplementary Information 6:

Raman spectrum of anatase B-TiO_2 nanoparticles:



The Raman spectrum clearly shows size quantization effect. The prominent raman peak shift at ~158 cm^{-1} belongs to the anatase phase. According to the literature (Phys. Rev., 71, 184302, 2005 and J. Mater. Chem. 13, 877, 2003) bulk anatase phase has raman shift 144 cm^{-1}. Also other frequency positions of Raman shift in the present investigation matches very close to the reported (Phys. Rev., 71, 184302, 2005 and J. Mater. Chem. 13, 877, 2003) value of TiO_2 anatase particles. However, in nanocrystalline samples of the present investigation these peak shift value shifted to higher wave numbers. Swamy et.al (Phys. Rev., 71, 184302, 2005) reported that 4 nm TiO_2 anatase particle has raman shift position at ~155 cm^{-1}. Our measurements confirmed that our particles are much smaller than 4 nm and which lie in the confinement region and with very high purity.