Supporting Information

for

Facile Synthesis of Carbon Doped TiO_2 Nanowires without External Carbon Source and Its Opto-Electronic Properties

*Vankayala Kiran and Srinivasan Sampath**

Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore -560012

Contents

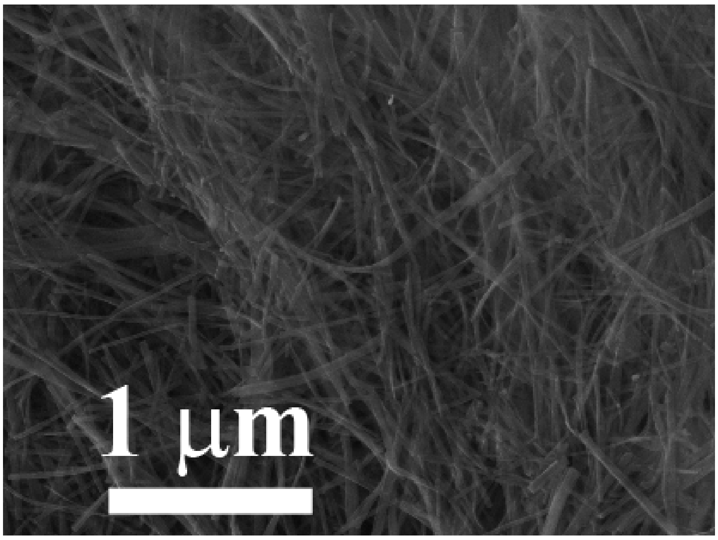

Figure S1. SEM image of hydrothermally treated TiC sample.

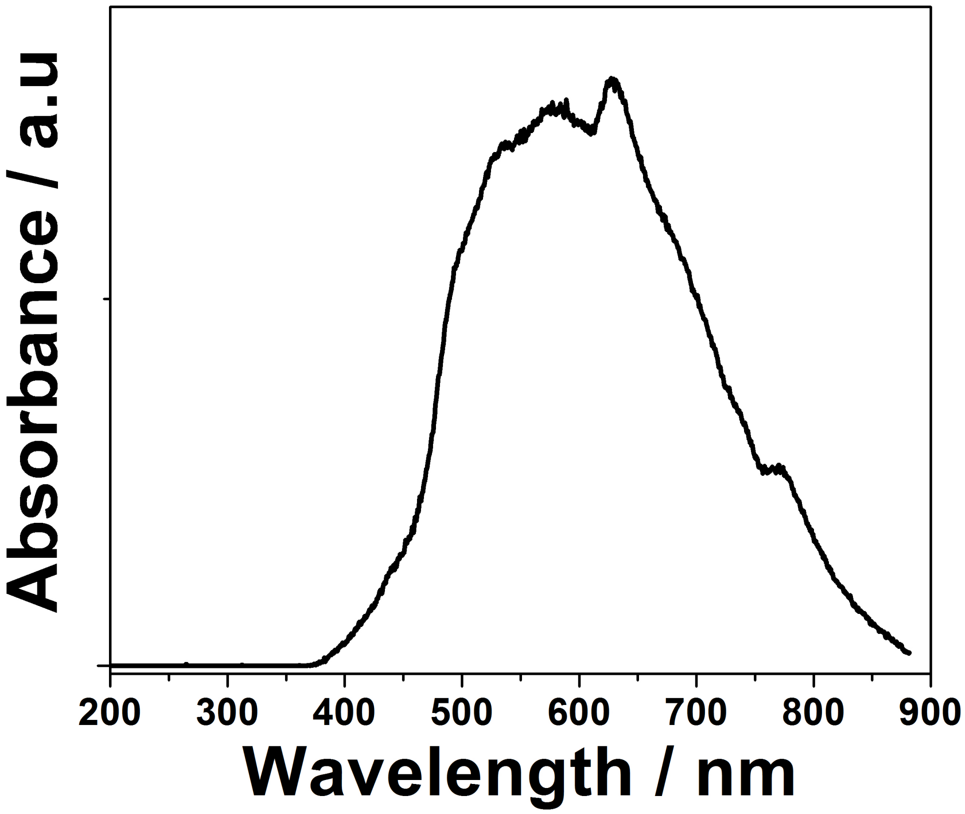

Figure S2. Spectral output of halogen lamp used in the present study, obtained using ocean optics spectrophotometer.

Preparation of C-TiO_2-NW (800°C)

Experiments were performed using C-TiO_2-NW which is prepared by thermal annealing of TiC-NW at 800°C for 5 h. It is reported that annealing at high temperatures results in loss of relatively high amount of carbon, as CO_2.[1,2] Hence, it is reasonable to assume that C-TiO_2-NW prepared at 800°C possesses relatively less amount of carbon as compared to the one prepared at 350°C. The sample prepared at 800°C (C-TiO_2-NW800) was characterized using TEM. As shown in figure S3, the sample retains its 1D morphology and the HRTEM image indicates that the sample possesses high crystallinity. Energy dispersive X-ray spectroscopy (EDS) mapping analysis is performed in scanning transmission electron microscopy (STEM) mode and the data reveal the existence of carbon along with Ti and O, as evident from the respective elemental maps. This observation reveals that the obtained material is carbon doped titania (C-TiO_2), though it is heated at high temperature.

Further, the C-TiO_2-NW800 is characterized using Raman spectroscopy (figure S4). The bands observed at 235 cm^{-1}, 442 cm^{-1} and 609.6 cm^{-1} are characteristics of TiO_2 in rutile phase.[3] The presence of varied amounts of carbon is also evidenced, as shown in reduced intensities of the D and G modes of carbon (figure S4). The presence of D (1375 cm^{-1}) and G (1596 cm^{-1}) bands represents the existence of carbon, in C-TiO_2. The intensity of D band decreases and G band gets more prominent, due to improved graphitization of carbon when annealed at high temperature. Difference in intensities of G band further reveals that the sample prepared at 800°C possesses relatively less amount of carbon as compared to that prepared at 350°C. Similar observations have been noted in earlier studies.[1,2]

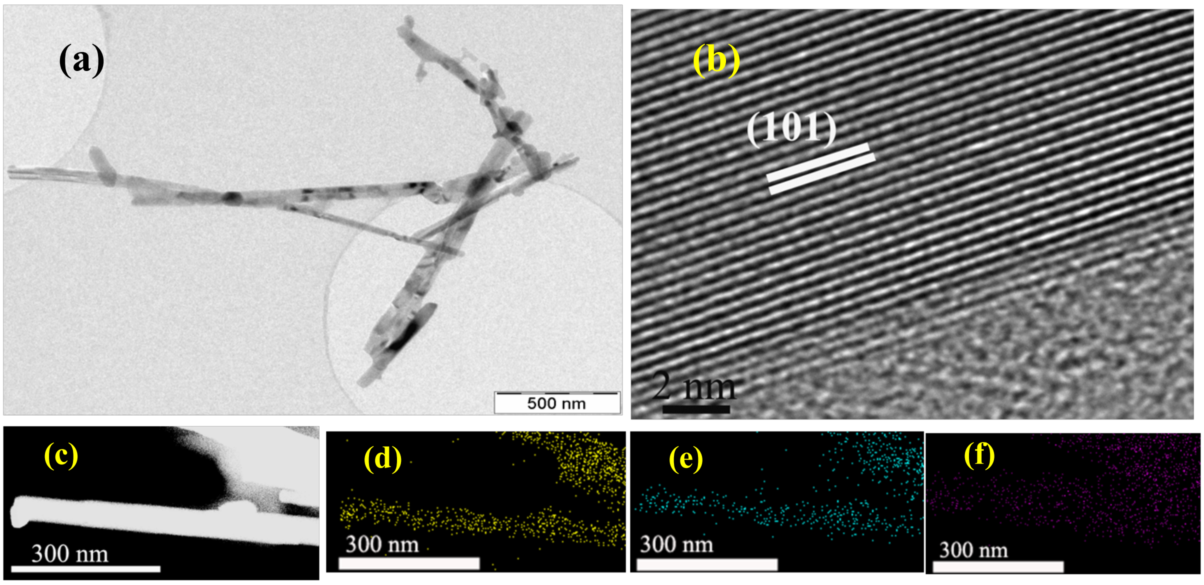

Figure S3. (a) TEM and (b) HRTEM images of C-TiO_2-NW prepared at 800°C. (c) represents STEM-DF image of isolated C-TiO_2-NW and (d)-(f) correspond to elemental mappings for Ti, O and C respectively.

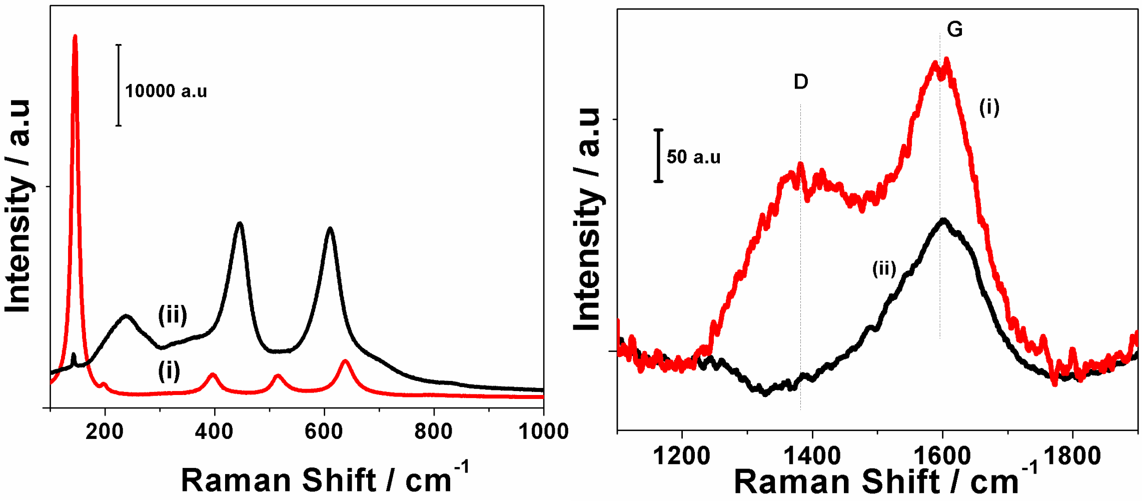

Figure S4. Raman spectra of C-TiO_2-NW prepared at (i) 350°C and (ii) 800°C from TiC-NW for 5 h.

Preparation of pristine TiO_2-NW

TiO_2 nanowires were prepared by alkaline hydrothermal method as reported earlier.[4] Briefly, 200 mg of TiO_2 powder was dispersed in 10 M NaOH and placed in telfon lined autoclave. The sample was subsequently heated at 200°C for 24 h. The obtained material was washed with HCl and water until the filtrate became neutral. Later on, the residue was annealed at 400°C for 2 h. Devices were fabricated by drop casting ethanolic dispersions of TiO_2-NW onto pre-cleaned Si/SiO_2 substrates. Figure S5 (inset) shows SEM image of the device fashioned using TiO_2-NW with FIB technique. As shown in figure S5, a silent effect of TiO_2-NW towards visible light is observed, indicating the inability of TiO_2 to respond to visible light.

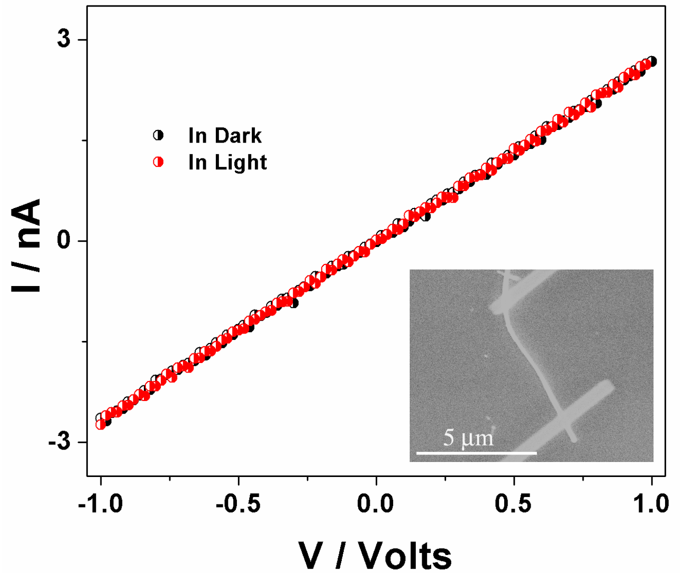

Figure S5. I-V characteristics of single TiO_2-NW based device recorded at 25°C. Inset show SEM image of the device fabricated using FIB technique.

Transport properties of various TiO_2-NW

Electrical measurements using isolated nanowires of (1) undoped TiO_2-NW and (2) C-TiO_2-NW which was prepared by thermal annealing of TiC-NW at 800°C for 5 h, are performed. The electrical response to light are shown in figure S6. As expected, the response for the sample heated at 350°C is maximum. The undoped TiO_2-NW does not respond to visible light while the 800°C treated C-TiO_2-NW shows weak response towards visible irradiation.

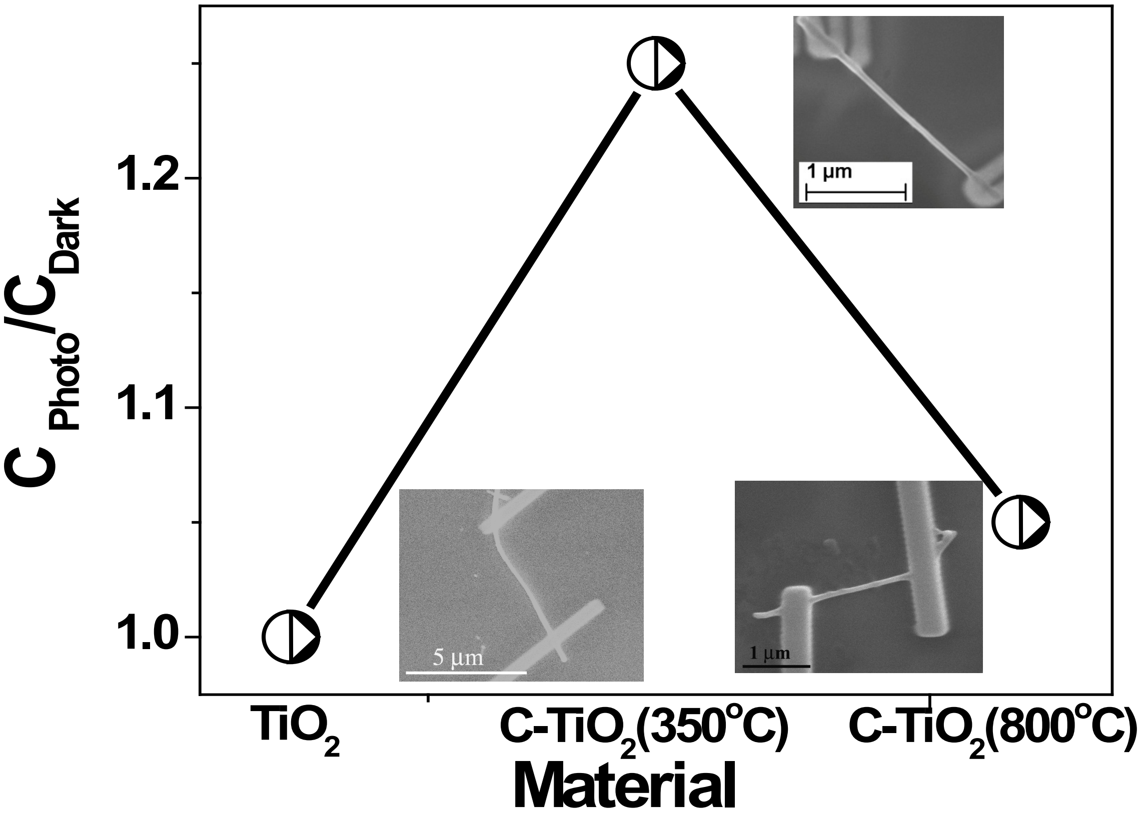

Figure S6. Ratio of conductivity at 0.5 V in presence and absence of light for pristine TiO_2 and C-TiO_2 prepared under two different conditions. SEM images of devices fabricated using FIB are also shown.

Estimation of P_{otical}

Fresnel reflection of incident light is known to occur at the interface between materials of different refractive indices. The transmitted rate of incident light is given by $4n_1n_2/(n_1+n_2)^2$, where n_1 and n_2 are refractive indices of two media.[5-7] Thus, the intensity of light absorbed by C-TiO_2-NW is smaller than the actual intensity of illumination. It is estimated that around 41% of intensity of incident light is absorbed by C-TiO_2-NW by taking refractive index of TiO_2 as 2.488 into account.

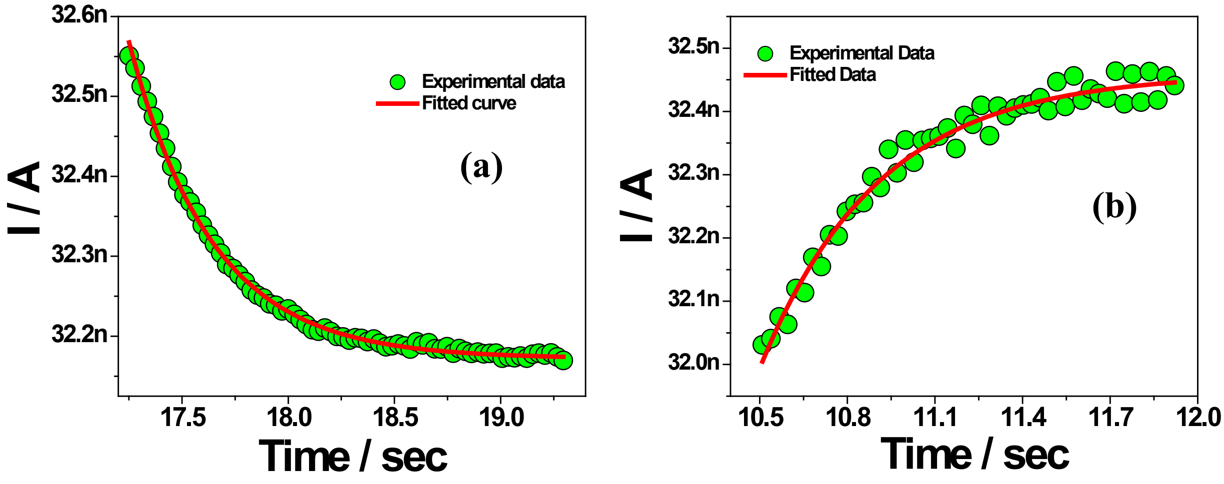

Figure S7 (a) Decay and growth transients recorded for single C-TiO_2-NW at 5 V bias with an intensity of 57.7 mW/cm^2. Single exponential fit (for decay process, $I = I_{dark} + A_1[\exp(-x/t_1)]$ and for growth process, $I = I_{dark} + A_1[\exp(x/t_1)]$ is used for the analysis.

References

(1) L. Zhang, M. S. Tse, O. K. Tan, Y. X. Wang, and M. Han, *J. Mater. Chem. A,* 2013, **1**, 4497.

(2) L. Zhang and R. V. Koka, *Mater. Chem. Phys.* 1998, **57***,* 23.

(3) J. Zhang, M. Li, Z. Feng, J. Chen and C. Li, *J. Phys. Chem. B* 2006, 110, 927.

(4) Y. X. Zhang, G. H. Li, Y. X. Jin, Y. Zhang, J. Zhang and L. D. Zhang, *Chem. Phys. Lett.*, 2002, 365, 300.

(5) P. Wu, Y. Dai, Y. Ye, Y. Yin and L. Dai, *J. Mater. Chem.,* 2011, **21**, 2563.

(6) H. K. Yadav, K. Sreenivas and V. Gupta, *J. Appl. Phys.,* 2006, **99**, 083507.

(7) R. R. Prabhakar, N. Mathews, K. B. Jinesh, K. R. G. Karthik, S. S. Pramana, B.Varghese, C. H. Sow, and S. Mhaisalkar, *J. Mater. Chem.,* 2012, **22**, 9678.