Electronic Supplementary Information

# A 'One Pot' Gel Combustion Strategy towards $Ti^{3+}$ Self-Doped 'Black' Anatase $TiO_{2-x}$ Solar Photocatalyst

Sanjay Gopal Ullattil[a] and Pradeepan Periyat [a,b*]

[a]*Department of Chemistry, University of Calicut, Kerala, India-673 635.*

[b]*Department of Chemistry, Central University of Kerala, India-671314.*

*pperiyat@uoc.ac.in/pperiyat@cukerala.ac.in, Ph: +91-9746602652.*

## Experimental

### Materials

Titanium (IV) butoxide, 97% (Sigma-Aldrich), Diethylene Glycol, extrapure (Ranbaxy, India) were all used as received without further purification. Deionized water was used in the experiment.

### Synthesis of $Ti^{3+}$ Self Doped Black $TiO_{2-x}$

0.2 M Titanium (IV) butoxide (6.8 g) was mixed with 50 ml diethylene glycol (DEG) followed by 30 minutes stirring at 1200 rpm leading to the formation of yellow titanium glycolate gel. 14.4 ml (8 molar times) of water was added to facilitate sufficient hydroxylation, since the excess hydroxylation can direct towards black $TiO_2$. In addition, the aqueous mediated reactions lead to crystal phase formation at relatively low calcination temperatures. Stirring was continued for further 15 minutes. The hydrated titanium glycolate gel that has been formed was kept in a muffle furnace at 300 °C for 2 hours. The black solid crystals obtained after rapid cooling to room

temperature was washed using 100 ml each of ethanol, ether and water to remove the organic and inorganic impurities.

**Photocatalysis**

0.0015 g of methylene blue ($10^{-5}$ M) was made up to 500 mL in a standard flask to get an intense blue coloured dye solution. 50 mL of the prepared methylene blue dye solution was taken in a beaker. 0.1g of the $TiO_2$ nanoparticles was added to the dye solution and stirred for 30 minutes in dark to obtain adsorption-desorption equilibrium that can eliminate any error due to initial adsorption effect. After stirring, it was irradiated under direct sunlight with constant stirring. The sunlight intensity was found 60,000-80000 lux intensity. The standard measurement of sunlight intensity was performed using Lutron, LX-107HA lux meter at Calicut University Campus, Kerala, India (Altitude: 11° 7′ 34″ North 75° 53′ 25″ East, Time: 13.00-15.30, Temperature: 26 ± 1 °C) on 23rd January 2016.

The degradation was monitored by taking 3 ml aliquots at certain time intervals. To eliminate the error due to scattering the solution taken were centrifuged for 30 minutes prior to the photocatalytic activity measurements.

**Characterization**

The $TiO_2$ samples were characterized using XRD, Raman spectroscopy, FTIR spectroscopy, XPS, UV-Visible spectroscopy and TEM. X ray diffraction pattern was recorded using Miniflex-600-X-ray diffractometer in the diffraction angle range $2\theta$ = 20-70° using Rigaku Miniflex X ray diffractometer. Raman spectrum was recorded using Bruker-MultiRam Raman spectrophotometer. FTIR spectrum measurement was done using Jasco-FT/IR-4100 spectrophotometer. XPS measurements were carried out by using Axis Ultra, Kratos Analytical, UK with an Al-Kα (1486.6 eV) source The UV-Visible absorbance spectra were obtained from Jasco-V-550-UV/VIS

spectrophotometer and particle morphology was examined by TEM using JEOL/JEM 2100 transmission electron microscope.

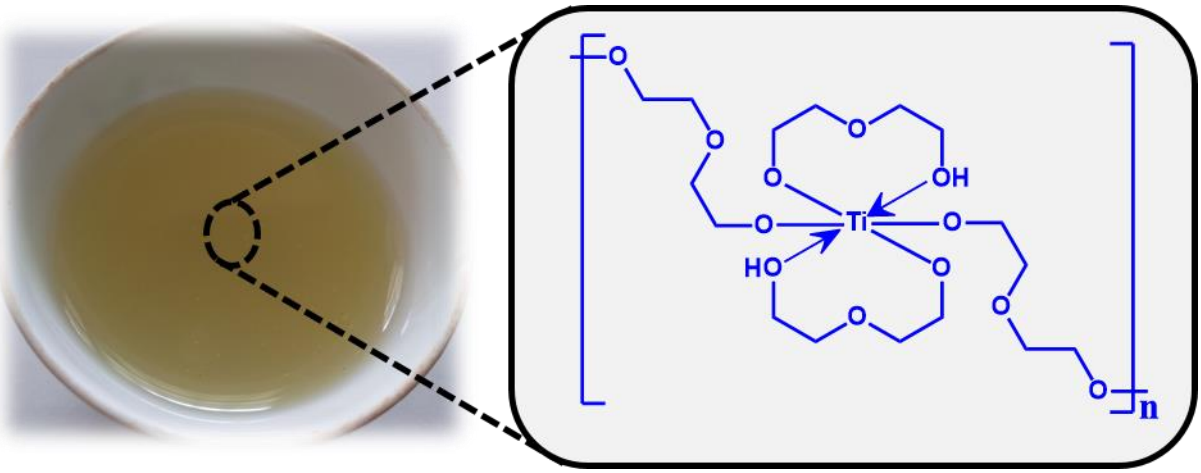


Figure S1. Digital photograph of the $TiO_2$ gel precursor and its proposed structure.

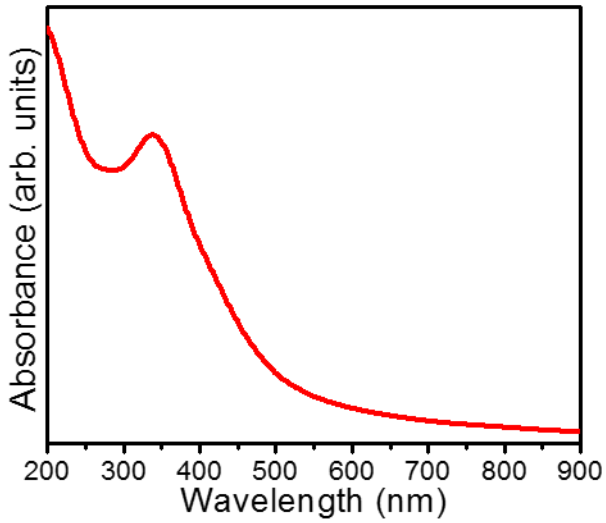


Figure S2. UV-Visible spectrum of gel precursor.

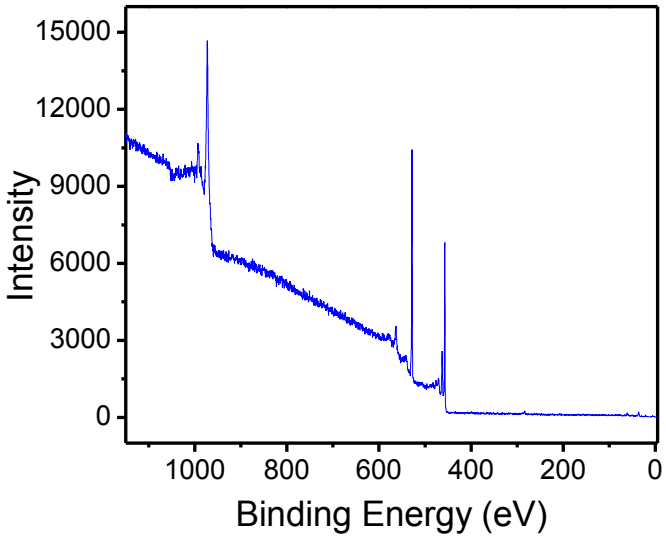


Figure S3. Wide XPS of black anatase $TiO_{2-x}$.

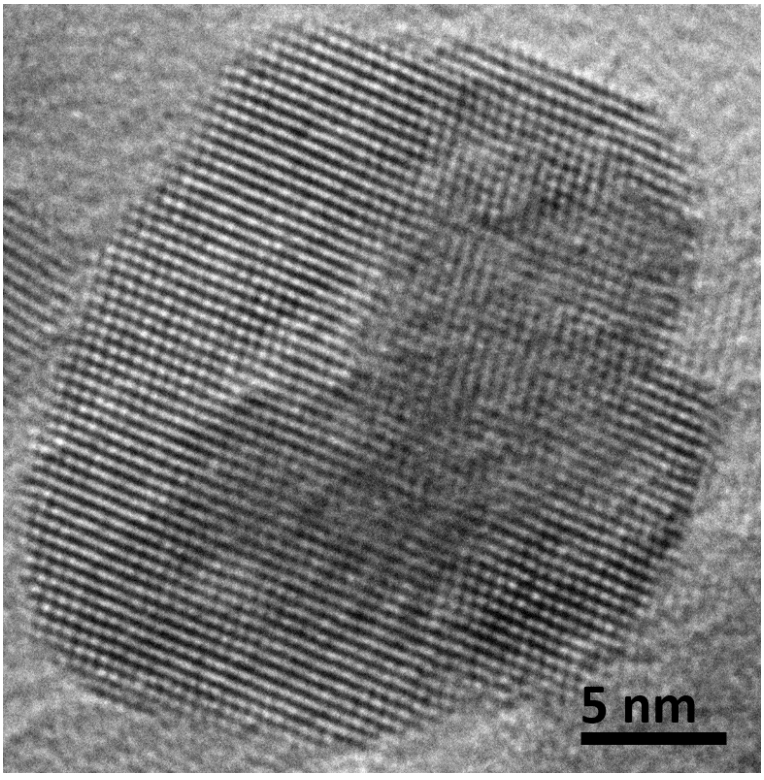


Figure S4. HRTEM image of black anatase $TiO_{2-x}$