

## Electronic Supplementary Information

for

Ionic liquid mediated synthesis of nitrogen, carbon and  
fluorine-codoped rutile TiO<sub>2</sub> nanorods for improved UV  
and visible light photocatalysis

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## METHODS

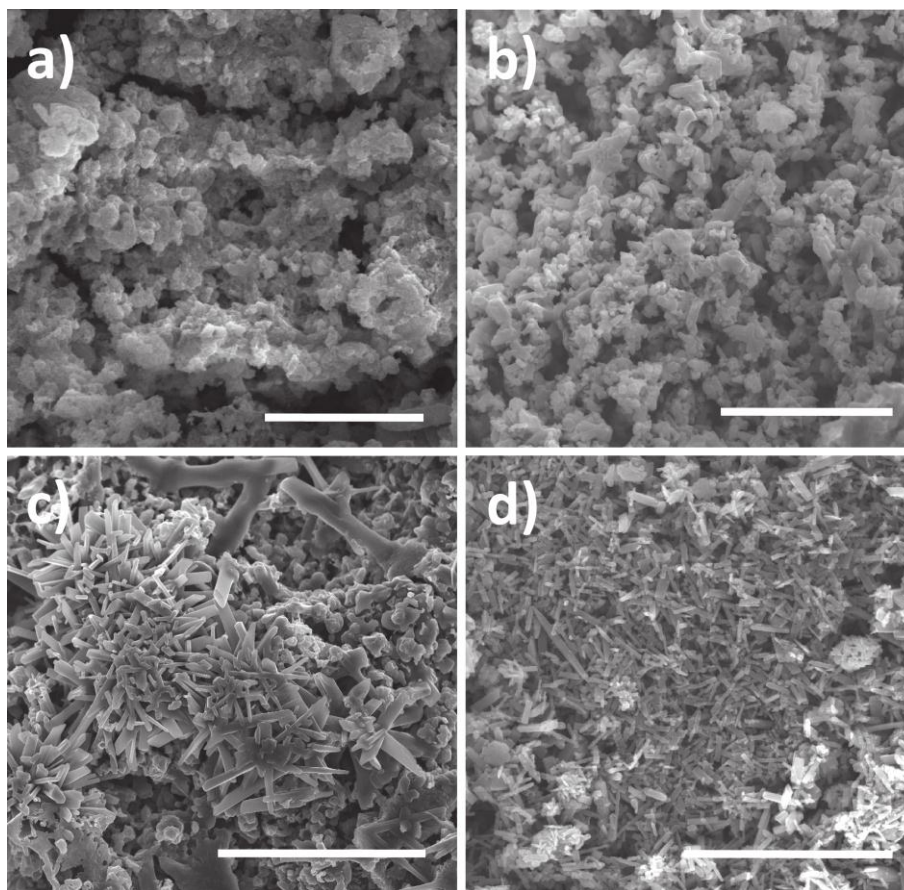
**Materials.** Titanium trichloride, Congo red, ammonia solution (28 %) and acetonitrile were obtained from Sigma-Aldrich. Anatase titanium dioxide ( $\text{TiO}_2$ ) powder was obtained from BDH Chemicals. Ionic liquid [BMIM][BF<sub>4</sub>] was obtained from Ionic Liquid technologies (IoLiTec). All chemicals were used as received. Deionized MilliQ water was used throughout the study.

**Synthesis of multiple nonmetal-codoped rutile NCF-TiO<sub>2</sub> nanorods.**  $\text{TiCl}_3$  stock solution was prepared in IL. The final 1 mL reactions consisted of 1 mM  $\text{TiCl}_3$  and varying concentrations of ammonia concentrations (0%, 0.56 %, 0.28 %, 0.14 % and 0.06 %) added using a constant volume of 20  $\mu\text{L}$  water. Notably, water volumes were kept to the minimum possible levels to avoid a potential change in the properties of ILs with admixtures. The reactions were pursued for 24 h at  $25 \pm 0.1^\circ\text{C}$  under stirring condition at 1,200 rpm during which all the reactions involving ammonia became turbid. However, no turbidity was observed in the control reaction containing only water (0% ammonia). The reaction products in IL were centrifuged at 10,000 rpm for 15 min and thoroughly washed with acetonitrile to remove the viscous IL before further characterization. To synthesize multiple nonmetal-codoped rutile  $\text{TiO}_2$  nanorods, this as-synthesized material was heated at  $1100^\circ\text{C}$  under air with a ramp rate of  $10^\circ\text{C}$  per minute. The temperature was held at  $1100^\circ\text{C}$  for 15 min followed by cooling to room temperature. The reaction products were used for further characterization and for photocatalysis experiments.

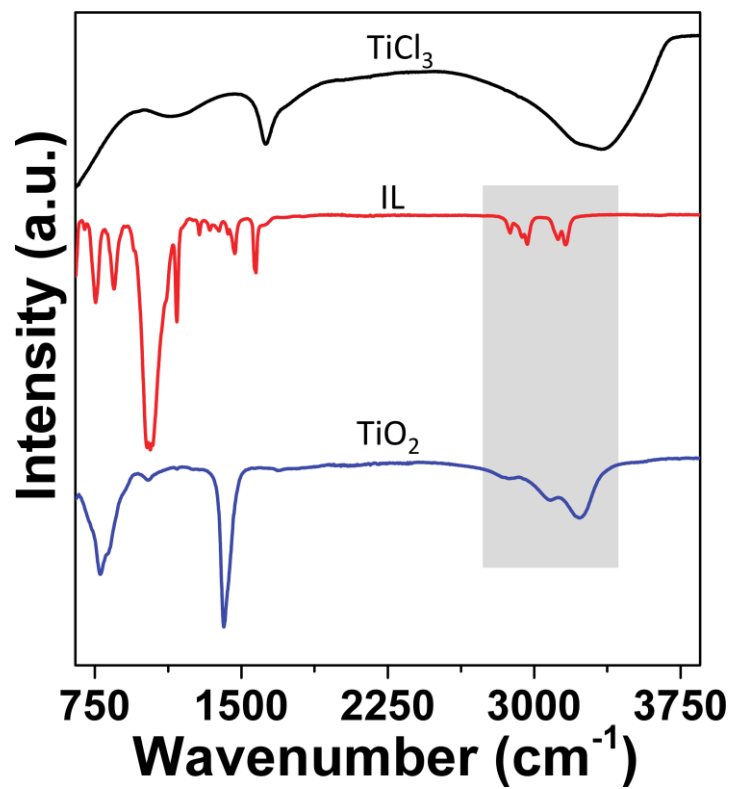
**Materials characterisation.** The samples for SEM were prepared by drop casting the sample on an aluminum stub and coating with a thin layer of platinum prior to imaging to minimize surface charging. SEM images were obtained using FEI Nova NanoSEM instrument operated at an accelerating voltage of 30 kV. The samples for TEM were prepared by drop casting the nanorods on to a carbon-coated copper grid, followed by TEM and SAED measurements using a JEOL 1010 TEM instrument operated at an accelerating voltage of 100 kV. High temperature XRD (HT-XRD) measurements were carried out on a Bruker D8 Advance XRD instrument operated at a voltage of 40 kV and a current of 40 mA with  $\text{Cu K}\alpha$  radiation. The heating rate during XRD measurements were constant at  $5^\circ\text{C}/\text{min}$ . Samples for XPS measurements were prepared by drop casting on Au-coated Si wafers, and measurements were carried

out using Thermo K-Alpha XPS instrument at a pressure better than  $1 \times 10^{-9}$  Torr (1 Torr =  $1.333 \times 10^2$  Pa). The general scan and C 1s, N 1s, O 1s, F 2p, Ti 2p, Cl 2p and B 1s core level spectra were recorded with un-monochromatized Mg K $\alpha$  radiation (photon energy of 1253.6 eV) at a pass energy of 20 eV and electron take off angle of 90°. The overall resolution was 0.1 eV for XPS measurements. The core level spectra were background corrected using Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure. The core level binding energies (BE) were aligned with adventitious carbon binding energy of 285 eV. BET surface area analysis was obtained at 77.25 K on a Micromeritics ASAP 2010 instrument. Prior to analysis, the samples were degassed at 423 K for 12 h and flushed with Ar gas for 2 h. For analysis, the samples were heated from ambient temperature to 1073 K with a heating rate of 10 K min<sup>-1</sup> under the flow of N<sub>2</sub> gas. The surface area was then calculated using the instrument micromeritics software.

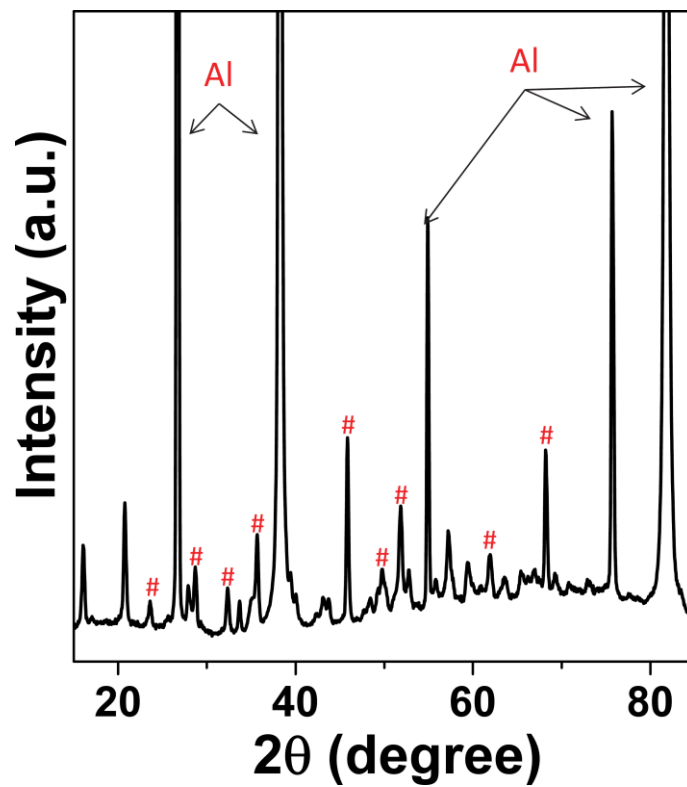
**Photocatalytic degradation of Congo red (CR) dye:** The photocatalytic activity of multiple nonmetal-codoped rutile TiO<sub>2</sub> nanorods was studied by adding 12 mg of nanorods to a 10 mL aqueous solution of 10  $\mu$ M CR dye in quartz tubes and recording the intensity of the characteristic absorption maxima ( $\lambda$  max = 500 nm) after exposure to UV (15 min) and visible-light (15 and 30 min) conditions. Control experiments were performed in which either no TiO<sub>2</sub> or equivalent amount of Degussa P25 commercial TiO<sub>2</sub> was used. For UV and visible light excitations, at an operating distance of 10 cm, 30 W UV lamp ( $\lambda$  max = 253 nm; RPR-2537 A) and visible lamp ( $\lambda$  max = 575 nm; RPR-5750 A), respectively were used. These lamps were obtained from Southern New England Ultraviolet Co. After photoirradiation, samples were centrifuged to remove the nanomaterial, and the remaining solutions were examined by UV-visible absorbance spectroscopy. For reusability experiments, TiO<sub>2</sub> nanorods were separated from the CR solutions after each reaction by centrifugation at 8,000 rpm for 20 min, followed by the exposure of the used TiO<sub>2</sub> nanorods to a fresh CR solution and recording the dye photodegradation by UV-vis spectroscopy for five cycles.



**Figure S1.** Additional SEM images of titania nanostructures obtained in [BMIM][BF<sub>4</sub>] by hydrolysing 1 mM TiCl<sub>3</sub> using different concentrations of ammonia (a) 0.56% , (b) 0.28%, (c) 0.14% and (d) 0.06%. Scale bars correspond to 20  $\mu$ m.



**Figure S2.** FTIR spectra of the TiCl<sub>3</sub> precursor, [BMIM][BF<sub>4</sub>] as the IL solvent and titania nanorods synthesised in IL.



**Figure S3.** XRD pattern obtained from the as-synthesised nanorods formed by hydrolysing  $\text{TiCl}_3$  precursor with 0.06% ammonia in  $[\text{BMIM}][\text{BF}_4]$  as a solvent. (#) correspond to XRD features arising from brookite phase of titania while peaks arising from aluminium (Al) XRD substrate are also indicated.