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Functionalized C@TiO₂ hollow spherical architectures for multifunctional applications

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SI.1 DSSC fabrication with THS

Fluorine doped tin oxide (FTO) coated glass substrate with sheet resistance 15 Ω cm⁻² (TechInstro, India) was thoroughly cleaned with detergent, de–ionized (DI) water and ethanol. It was then dried at 100 °C for 30 min. To fabricate the photoanode film, a paste was prepared with the calcined THS powder along with ethyl cellulose as binder and ethanol as solvent following the procedure reported by Grätzel et al.⁵¹ The viscous TiO₂ paste was uniformly spread over the FTO by doctor blading technique. It was then heated at 150 °C for 30 min followed by sintered at 450 °C for another 30 min. The same process was repeated to get the film of proper thickness (~6–7 µm) for effective light absorption. The active area of the cell was 0.08 cm² (0.4×0.2 cm²). The prepared film was then soaked with N719 dye solution for 24 h at room temperature. The Pt coated FTO counter electrode was prepared by drop casting 5 mM ethanol solution of hexachloroplatinic acid (H₂PtCl₆) solution followed by annealing it at 450 °C for 30 min. These two electrodes was filled up with electrolyte solution containing 0.03 (M) I₂, 0.05 (M) LiI and 0.3 (M), 1, 2-dimethyl-3-propylimidazolium iodide in acetonitrile.



Fig. S1 Digital image showing the ethanol dispersion of C^F@THS under normal light.



Fig. S2 Electron microscopic images (FESEM and TEM) of CA– TiO_2 (a, b) and TU– TiO_2 (c, d) showing the formation of non-hollow spheres.



Fig. S3 Time dependent FESEM and TEM studies towards the growth of C^{F} @THS after 1.5 h (a, b) and 5 h (c, d).



Fig. S4 STEM images of as prepared C^{F} @THS showing the stacking of nanoflakes/sheets to form the hollow architecture.



Fig. S5 Reaction under the hydrothermal conditions between citric acid and thiourea produces functionalized C dots and different gaseous products.



Fig. S6 TEM image of the filtrate part of the hydrothermal product C^F @THS showing the presence of C dots.



Fig. S7 EDS area mapping of C^F@THS showing the uniform distribution of the elements present.



Fig. S8 N_2 adsorption-desorption isotherms and pore size distribution (inset) of C^F @THS



Fig. S9 UV-vis spectral studies of MB adsorption by (a) CA–TiO₂ and (b) TU–TiO₂.



Fig. S10 A comparative FTIR analyses of $C^F@THS$, CA–TiO₂ and TU–TiO₂. The study reveals significantly low content of functional groups with TU-TiO₂ and CA-TiO₂ in compare to $C^F@THS$. The spectra are normalized with respect to the Ti–O–Ti absorbance peak.



Fig. S11 Thermogravimetric analyses (TGA) of $C^F@THS$, CA–TiO₂ and TU–TiO₂. The study shows significantly less weight loss of TU-TiO₂ and CA-TiO₂ in compare to $C^F@THS$. Initial weight losses up to 100 °C are due to the elimination of adsorbed water. The loss of water was not considered in the indicated weight losses (5, 10 and 44%) of the respective samples.



Fig. S12 Control experiments on the dye adsorptions using MV, MO, CR $(0.50 \times 10^{-4} \text{ M})$ and RhB $(2.5 \times 10^{-5} \text{ M})$ by C^F@THS. Optical absorption spectra at different time intervals and the digital photos (in the insets) of the initial and final dye solutions are shown.



Fig. S13 Chemical structures of the dyes used for adsorption studies.



Fig. S14 (a) FTIR spectrum and (b) XRD pattern of THS obtained after calcination of dye adsorbed C^F@THS. O-H stretching peak shown in (a) is originated from Ti-O-H groups with some contribution of adsorbed water.



Fig. S15 (a) N_2 adsorption-desorption isotherm of THS and (b) its pore size distribution obtained from desorption branch of isotherm.



Fig. S16 Comparative study showing the photodegradation of MB using THS, TU–TiO₂ and CA–TiO₂ under UV–A (λ =365 nm) irradiation.