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Supplementary Information

Microwave-assisted synthesis of $NaYF_4:Yb^{3+}/Tm^{3+}$ upconversion particles with tailored morphology and phase for the design of UV/NIR-active $NaYF_4:Yb^{3+}/Tm^{3+}@TiO_2$ core@shell photocatalysts

Sajjad Ullah[a,b], Chanchal Hazra[a], Elias Paiva Ferreira Neto[c], Tárcio de Castro Silva[a], Ubirajara Pereira Rodrigues-Filho[c], Sidney Jose Lima Ribeiro[a*]

[a]Instituto de Química de Araraquara, Universidade Estadual Paulista (Unesp), 14800-060, Araraquara, SP Brazil

[b]Institute of Chemical Sciences, University of Peshawar, 25120, Peshawar, KP Pakistan

[c]Instituto de Química de São Carlos, Universidade de São Paulo, 13560-970, São Carlos, SP Brazil

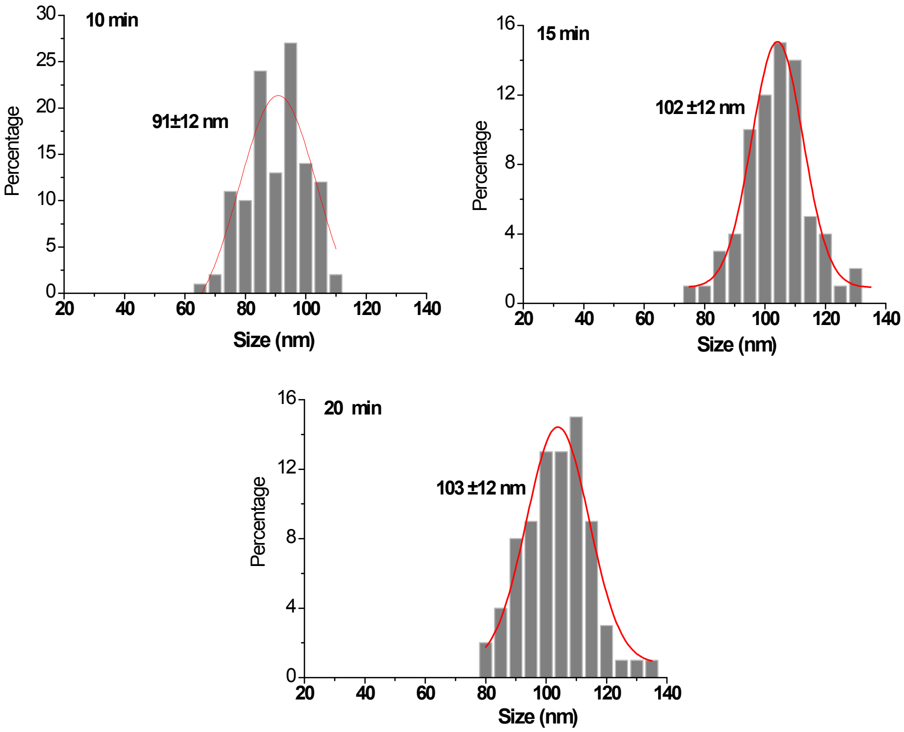


Figure S1: Particle size distribution of UCPs prepared using microwave treatment time of less than 30 minutes. The sizes are denoted as *average size±SD* where SD shows the width of size distribution

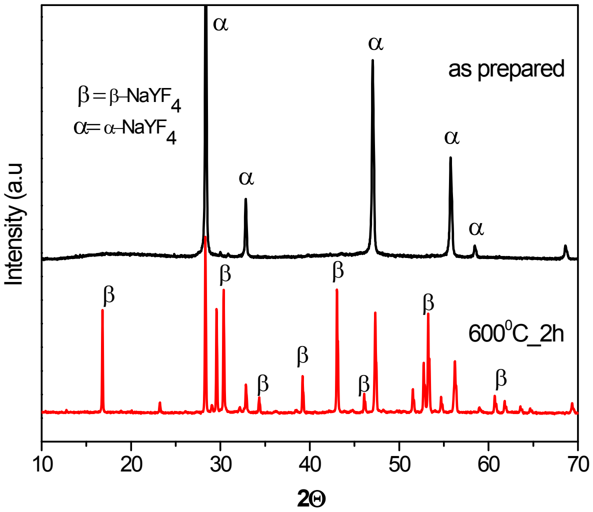


Figure S2: XRD pattern of the $NaYF_4$:Yb^{3+}/Tm^{3+} sample prepared using 15 min MW irradiation (upper curve) and after calcination at 600˚C for 2h (lower curve).

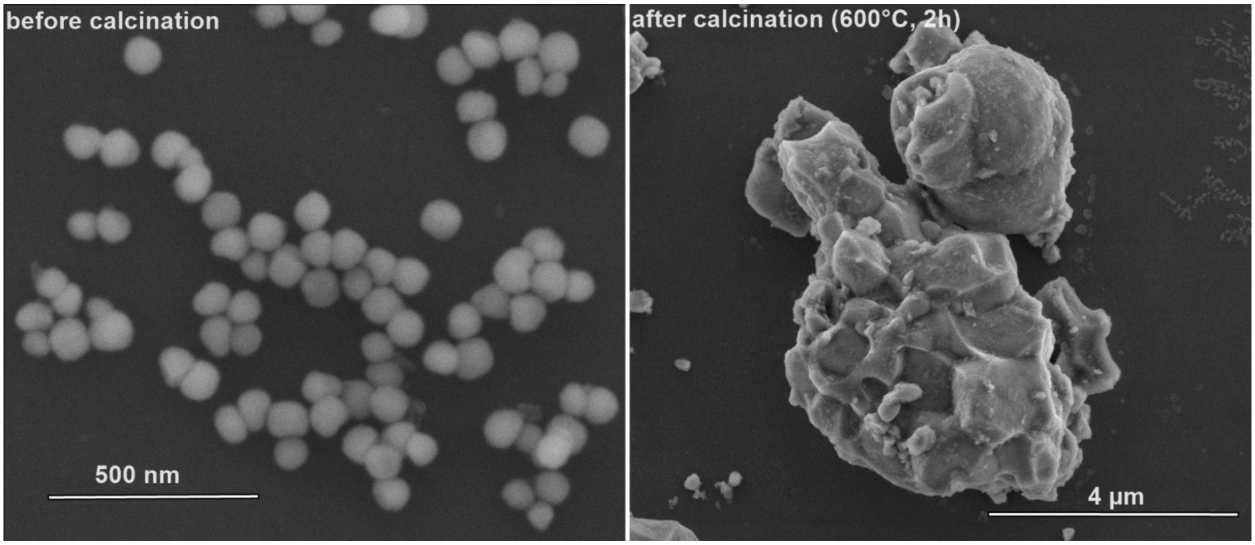
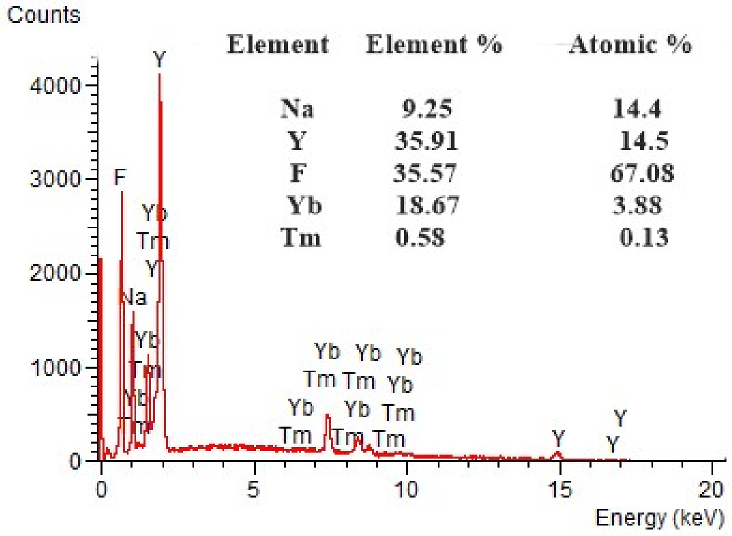


Figure S3: SEM images of the $NaYF_4$:Yb^{3+}/Tm^{3+} sample prepared using 15 min MW irradiation time before calcination (left) and after calcination at 600˚C for 2h (right).



Element	Element %	Atomic %
Na	9.25	14.4
Y	35.91	14.5
F	35.57	67.08
Yb	18.67	3.88
Tm	0.58	0.13

Figure S4: EDX spectrum of NaYF$_4$:Yb^{3+}/Tm^{3+} UCPs.

Photoluminescent Properties of UCPs

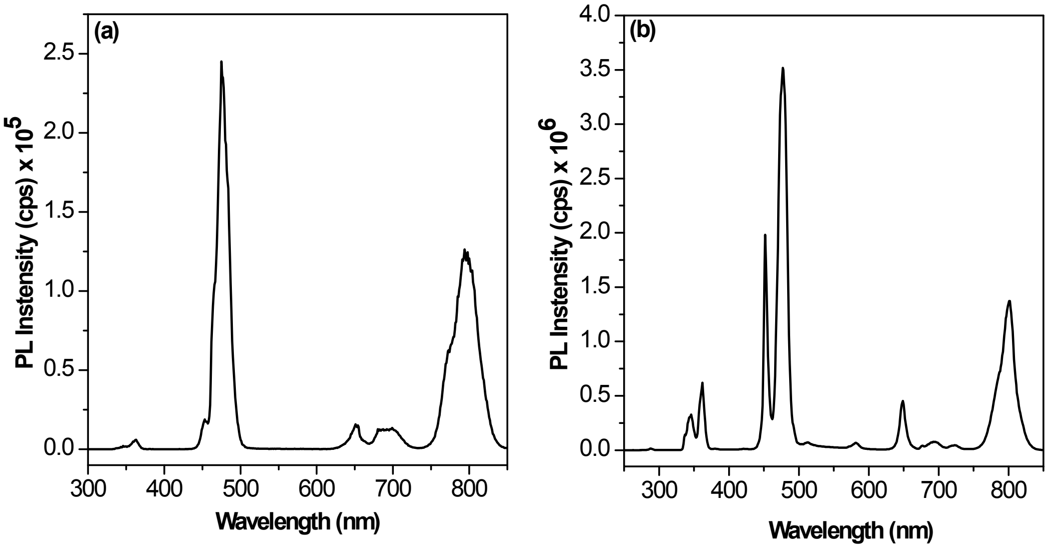


Figure S5: UC PL spectra of NaYF$_4$:Yb^{3+}/Tm^{3+} UCPs (a) after the co-precipitation step and (b) after both co-precipitation and MW-assisted hydrothermal step under otherwise identical experimental conditions. Not only the peaks become clearly defined but the PL intensity also increases after MW-assisted hydrothermal treatment.

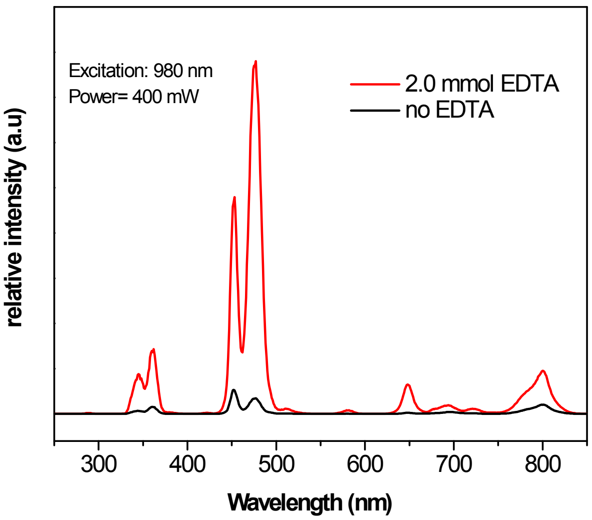


Figure S6: UC spectra of $NaYF_4$:Yb^{3+}/Tm^{3+} UCPs prepared using no EDTA (see Fig 2a) and 2 mmol EDTA (see Fig. 2d) under otherwise identical experimental conditions.

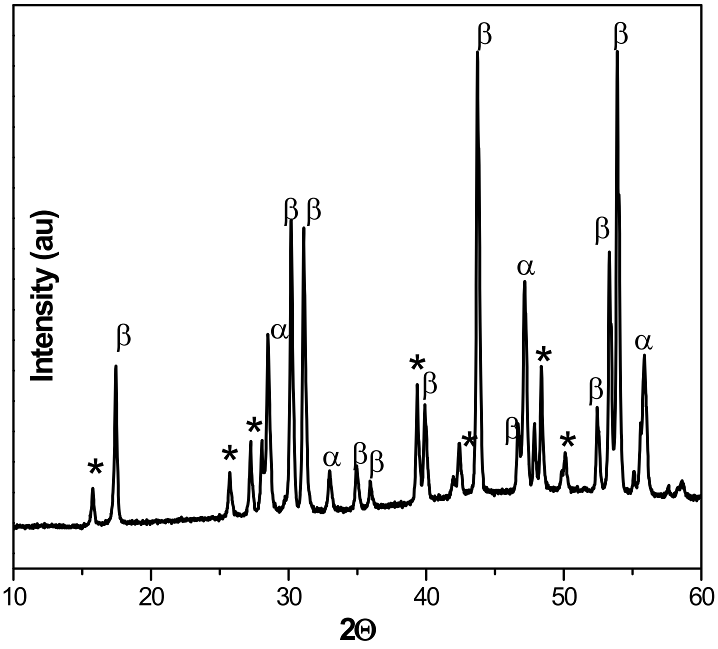


Figure S7: X-ray diffractogram of the UCPs (see Fig. 2a in main text) prepared without any EDTA in the reaction mixture. In addition to diffraction peaks characteristics of the cubic phase, α-$NaYF_4$, (PDF no. 6-342) and hexagonal phase, β-$NaYF_4$, (PDF no. 16-334), the diffractorgram also shows some additional diffraction peaks (marked with asterisk (*) ascribed to phase impurities.

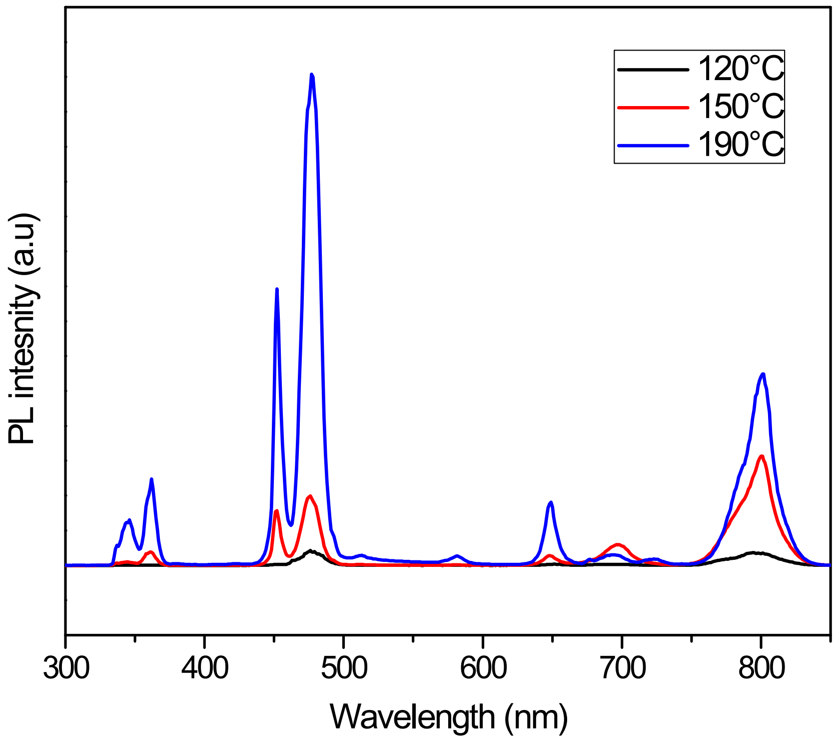


Figure S8: PL UC spectra of $NaYF_4:Yb^{3+}/Tm^{3+}$ UCPs obtained by co-precipitation/MW-assisted hydrothermal treatment at different temperatures showing the effect of hydrothermal temperature on the PL intensity

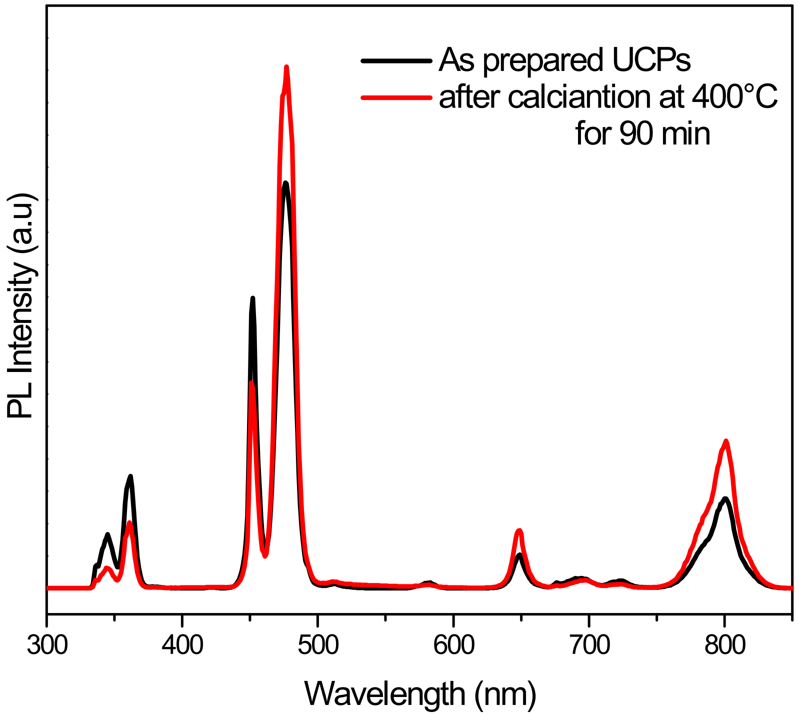


Figure S9: PL UC spectra of $NaYF_4$:Yb^{3+}/Tm^{3+} UCPs obtained by co-precipitation/MW-assisted hydrothermal treatment before and after calcination at 400°C for 90 min in air. The slight increase in PL intensity after calcination may be attributed to a small increase in crystallinity and crystallite size, decrease of crystal defects and decomposition of the organic molecules on the surface of the particles.[1,2]

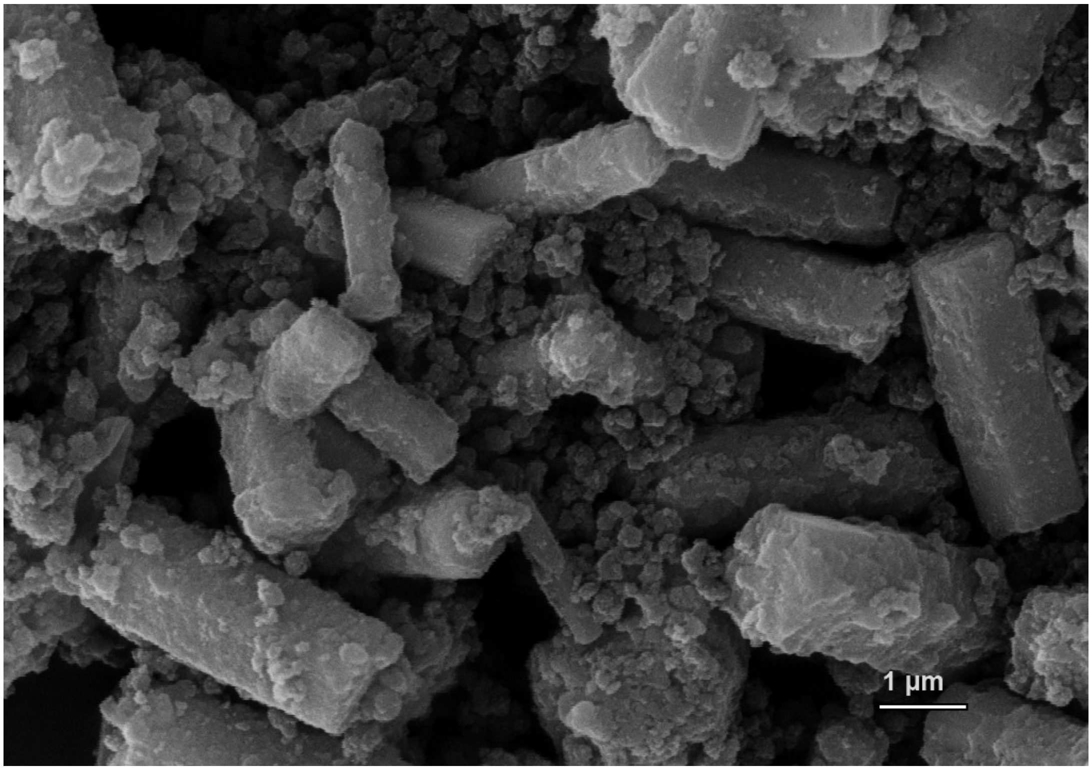


Figure S10: SEM image of UCPs@TiO_2 sample prepared in the absence of PVP. Free coreless TiO_2 particles are also formed in addition to the core@shell UCPs@TiO_2 particles.

SEM/TEM-EDX analysis

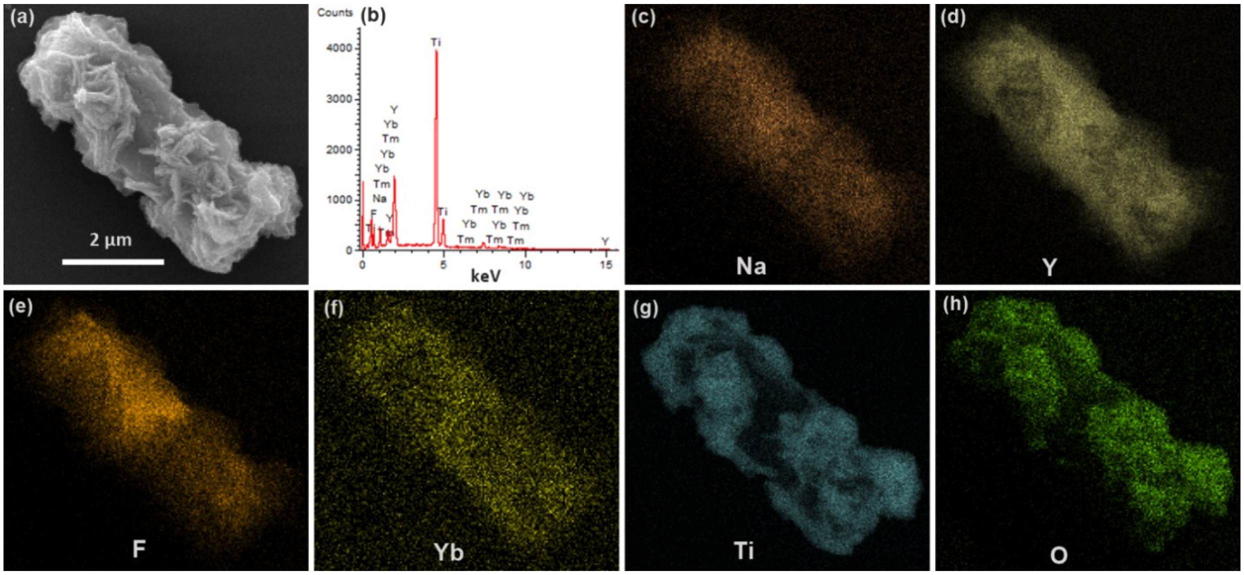


Fig. S11: (a) SEM image (b) EDX spectrum and (c-h) elemental mapping of Na, Y, F, Yb, Ti and O of UCPs@TiO_2 sample.

Fig. S11a and S11b show the SEM image and EDX spectrum of an isolated TiO_2-coated $NaYF_4:Yb^{3+}/Tm^{3+}$ microrod, respectively. The presence of TiO_2 in the sample is confirmed by the presence of clear emission peaks of Ti at 4.5 keV (Ti Kα) and 4.9 keV (Ti Kβ) (Fig. S11b). A clear picture of TiO_2 coating on the microrod is manifested in the elemental mapping for Na, Y, F, Yb, Ti and O (Figs. S11c-h). The Ti and O distribution resembles closely indicating that the layered coating on the surface of UCPs consists of TiO_2.

Similarly, the EDX line scan performed across the diameter of the UCPs@TiO_2 particle shows prominent Ti signal at distances corresponding to the borders of the UCPs@TiO_2 particle while signals for Na, Y and F are more prominent in the middle part of the particles and these signals closely resemble/overlap each other (Fig. S12). The EDX line scan thus further confirms the formation of a core@shell structure in the UCPs@TiO_2 particles

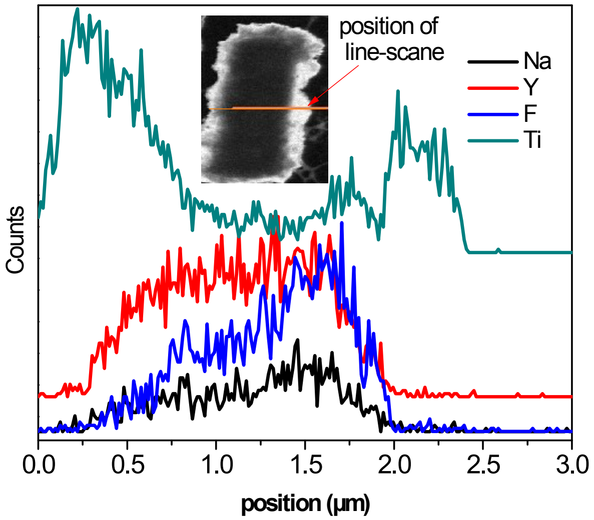


Figure S12: EDX line scan across the border of UCPs@TiO_2 particle (shown as inset). The Na, Y, and F signals closely resembles in form and position while the Ti signal is stronger at the border of the particles.

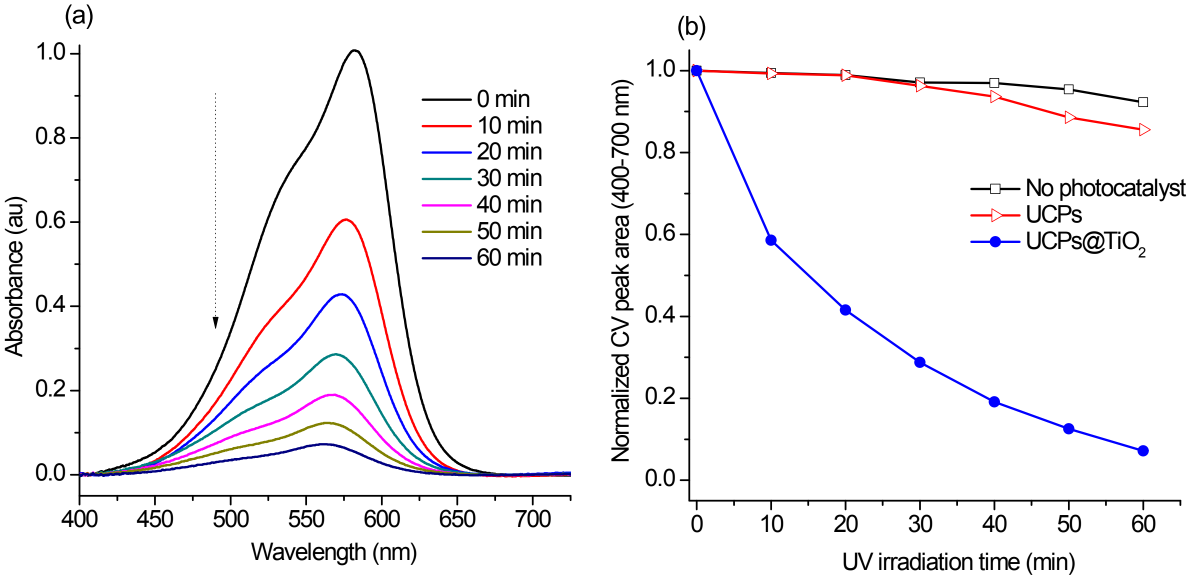


Figure S13: (a) Visible absorption spectra of CV dye solution and (b) decrease in area of CV peak (400-700 nm) as function of UV irradiation time (min) in the presence of UCPs and UCPs@TiO_2 photocatalysts. The direct photolysis in the absence of any photocatalyst is also shown for comparison.

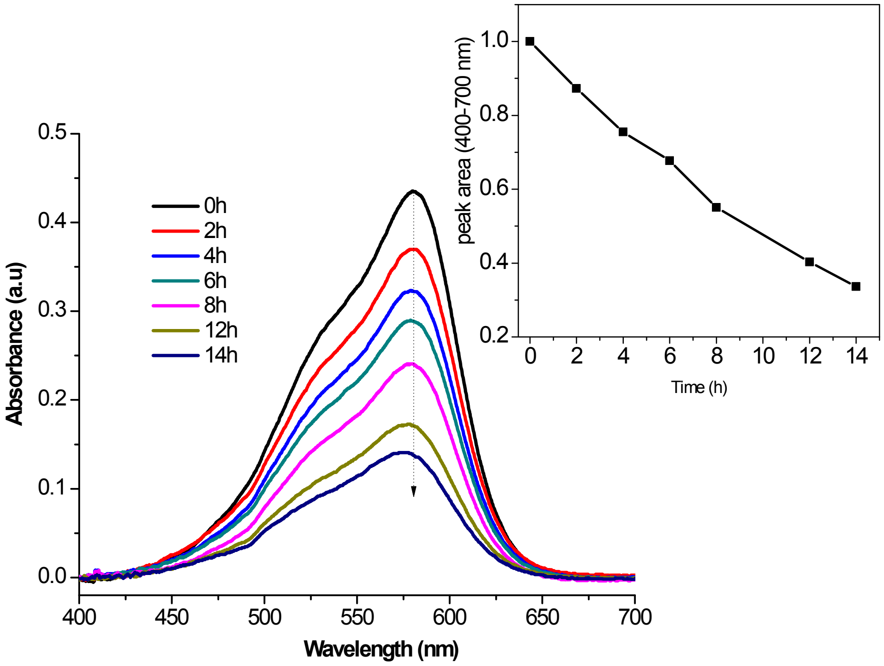


Figure S14: (a) Change in the UV-visible spectra of CV dye solution in the presence of UCPs@TiO_2 photocatalysts under NIR (980 nm) irradiation. The inset shows the decrease in area of CV peak (400-700 nm) as function of UV irradiation time (h).

References:

1 R. H. Krishna, B. M. Nagabhushana, H. Nagabhushana, N. S. Murthy, S. C. Sharma, C. Shivakumara and R. P. S. Chakradhar, *J. Phys. Chem. C*, 2013, **117**, 1915–1924.

2 D. Yang, D. Chen, H. He, Q. Pan, Q. Xiao and J. Qiu, *Sci. Rep.*, 2016, **6**, 29871.