

Electronic Supplementary Information

Photodegradation of Organic Dyes Based on Anatase and Rutile TiO₂ Nano-Particles

Ashish Gautam ^a, Anuraj Kshirsagar^a, Rahul Biswas ^a, Shaibal Banerjee ^a and Pawan K Khanna ^{*a}

^aNanochemistry Laboratory, Dept. of Applied chemistry,

Defence Institute of Advanced Technology (DIAT-DU),

DRDO, Govt. of India, Pune-411025

Corresponding author:

Email : pawankhanna2002@yahoo.co.in

Table S 1 Wt. loss of TiO₂ nanoparticles upon sintering at various temperatures.

(MA – myristic acid, PS – potato starch, PVP –Polyvinyl pyrrolidone)

Capping Agent	Initial Wt. (g)	Final Wt. (g)	Wt. Loss (g)	% Wt. loss
100°C sintered				
MA	1.0	0.8490	0.1510	15.10
PS	1.0	0.8501	0.1499	14.99
PVP	1.0	0.9001	0.0999	9.99
200°C sintered				
MA	1.0	0.7821	0.2179	21.79
PS	1.0	0.5041	0.4959	49.59
PVP	1.0	0.8402	0.1598	15.98
400°C sintered				
MA	1.0	0.5211	0.4789	47.89
PS	1.0	0.4913	0.5087	50.87
PVP	1.0	0.7732	0.2268	22.68
800°C sintered				
MA	1.0	0.4901	0.5099	50.99
PS	1.0	0.3800	0.6200	62.00
PVP	1.0	0.6981	0.3019	30.19

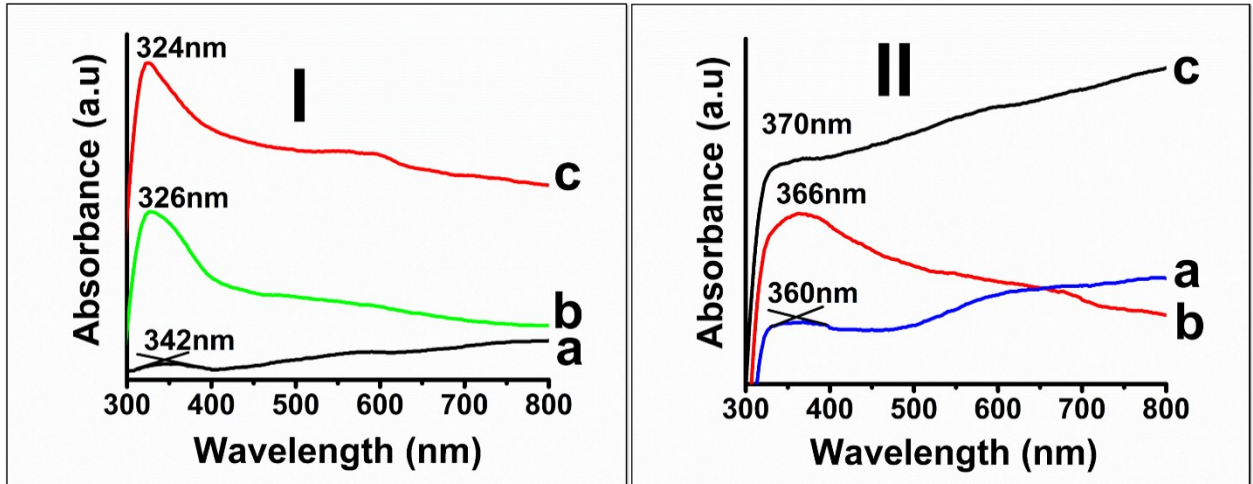


Fig. S1 UV absorbance spectra (I) anatase phase titania nanoparticles and (II) rutile phase titania nanoparticles where (a) PVP (b) Myristic (c) Potato starch coated

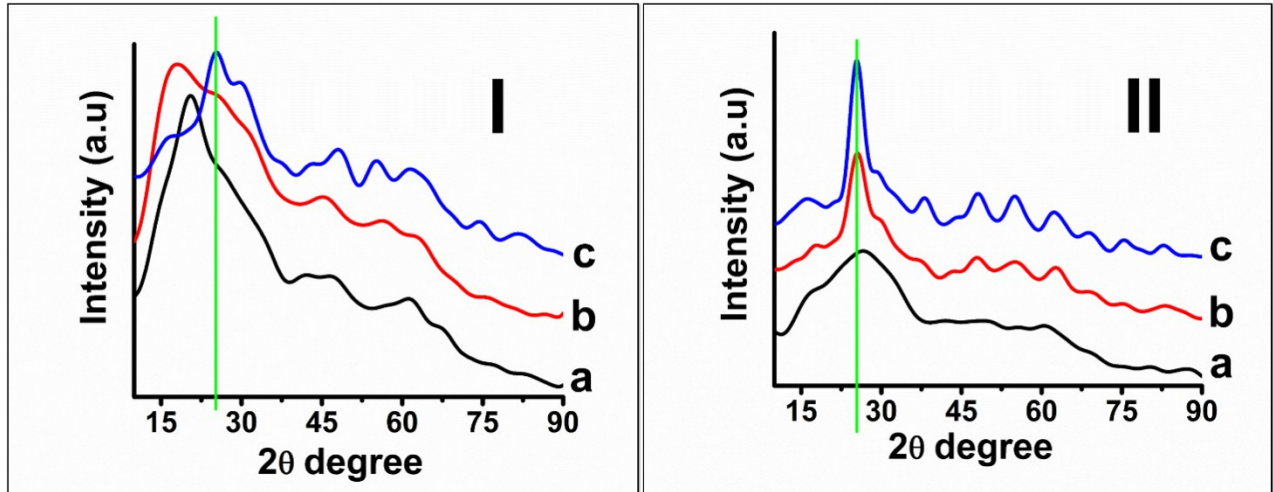


Fig. S2 XRD of TiO_2 nanoparticles sintered at 100°C (I), 200°C (II) with a) PVP coated, b) Myristic acid coated, c) Potato Starch Coated

Table S 2 XRD studies of TiO₂ nano-particles sintered at 400°C

Crystal planes	B (FWHM)	2θ	θ	Particle Size (nm)	d-spacing (nm)	Avg. Size (nm)
PVP coated TiO₂ Nanoparticles						
101	0.70	25.39	12.83	15.3	0.35	37.71
004/112	0.39	38.02	19.12	14.3	0.24	
200	0.23	48.14	24.15	17.6	0.19	
105	0.07	54.69	27.10	97.15	0.17	
204	0.03	62.79	31.49	44.2	0.15	
Myristic Acid coated TiO₂ Nanoparticles						
101	0.56	25.43	12.69	11.8	0.35	8.36
004/112	0.52	37.99	19.01	5.8	0.24	
200	0.52	48.17	24.07	9.9	0.19	
105	0.23	54.25	27.15	5.4	0.17	
204	0.05	62.76	31.39	8.9	0.15	
Potato Starch coated TiO₂ Nanoparticles						
101	0.68	25.50	12.75	8.3	0.35	5.0
004/112	0.60	38.24	19.03	5.5	0.24	
200	0.19	47.99	24.16	6.8	0.19	
105	0.39	54.80	27.12	5.1	0.17	
204	0.11	63.15	31.37	7.1	0.15	

Table S 3 XRD studies of TiO₂ nano-particles sintered at 800°C

Crystal planes	B (FWHM)	2θ	θ	Particle Size(nm)	d-spacing (nm)	Avg. Size (nm)
PVP coated TiO₂ Nanoparticles						
110	0.13	27.47	13.73	68.9	0.32	74.13
101	0.15	36.11	18.04	61.2	0.25	
200	0.18	39.24	19.72	52.2	0.23	
111	0.15	41.26	20.66	61.5	0.22	
210	0.05	44.07	22.32	195.3	0.20	
211	0.15	54.35	27.17	67.2	0.17	
220	0.20	56.67	28.32	52.3	0.15	
002	0.26	62.76	31.37	40.2	0.15	
310	0.11	64.10	32.27	95.4	0.14	
Myristic Acid coated TiO₂ Nanoparticles						
110	0.16	27.47	13.75	58.1	0.32	50.93
101	0.15	36.09	18.04	63.5	0.25	
200	0.20	39.29	19.84	48.1	0.23	
111	0.20	41.26	20.77	48.6	0.21	
210	0.14	44.14	22.39	67.2	0.20	
211	0.17	54.34	27.48	58.1	0.17	
220	0.23	56.67	28.42	43.0	0.16	
002	0.36	62.75	31.39	28.9	0.15	
310	0.24	64.06	32.37	43.9	0.14	
Potato Starch coated TiO₂ Nanoparticles						
110	0.13	27.27	13.78	69.4	0.32	75.94
101	0.15	36.10	18.38	59.7	0.25	
200	0.08	39.24	19.82	121.5	0.23	
111	0.14	41.26	0.86	68.3	0.21	
210	0.14	44.09	22.37	67.2	0.20	
211	0.09	54.35	27.37	107.4	0.17	
220	0.14	56.65	28.44	69.1	0.16	
002	0.20	62.76	31.40	57.0	0.15	
310	0.16	64.08	32.40	63.9	0.14	

Table S4 XPS data analysis of anatase and rutile titania

Elements \longrightarrow	Ti ($2p_{1/2}$, $2p_{3/2}$)	O (1s)	C (1s)
Anatase			
Peak Position (eV)	462.04	533.52	283.70
	467.58	535.21	288.19
	--	536.66	--
FWHM (eV)	1.853	2.669	1.771
	2.400	1.80	2.927
	--	7.556	--
Area	22350.87	43687.86	22700.660
	10728.17	5963.92	14589.800
	--	2392.476	--
Rutile			
Peak Position (eV)	462.18	533.579	283.158
	467.779	--	288.200
FWHM (eV)	1.385	1.792	1.777
	2.112	--	2.094
Area	32000.00	51192.640	5481.678
	16589.65	--	18062.200
Deviation in peak position (eV) with respect to anatase titania	0.14	0.059	0.542
	0.199	--	0.01

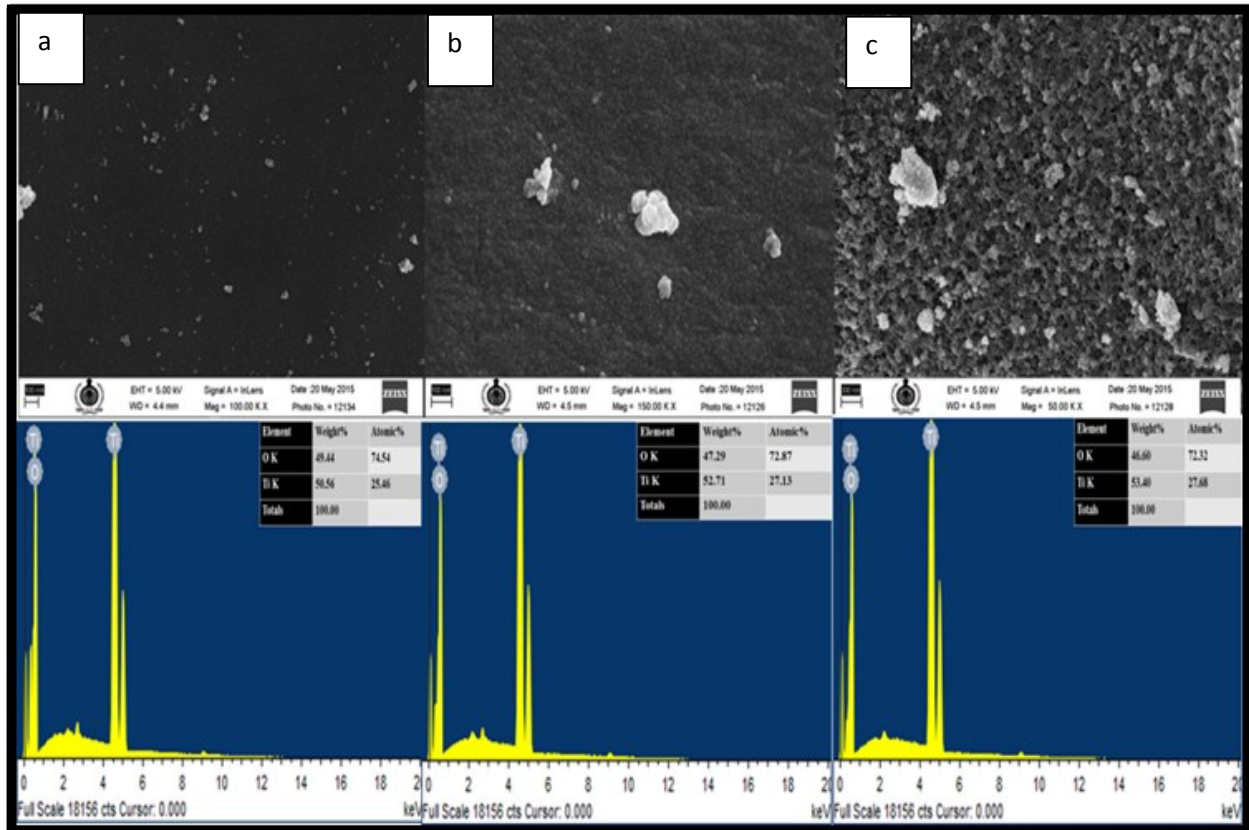


Fig. S3 SEM/EDS of anatase TiO₂ NPs coated with a) PVP b) Myristic acid c) Potato Starch after 400°C sintering

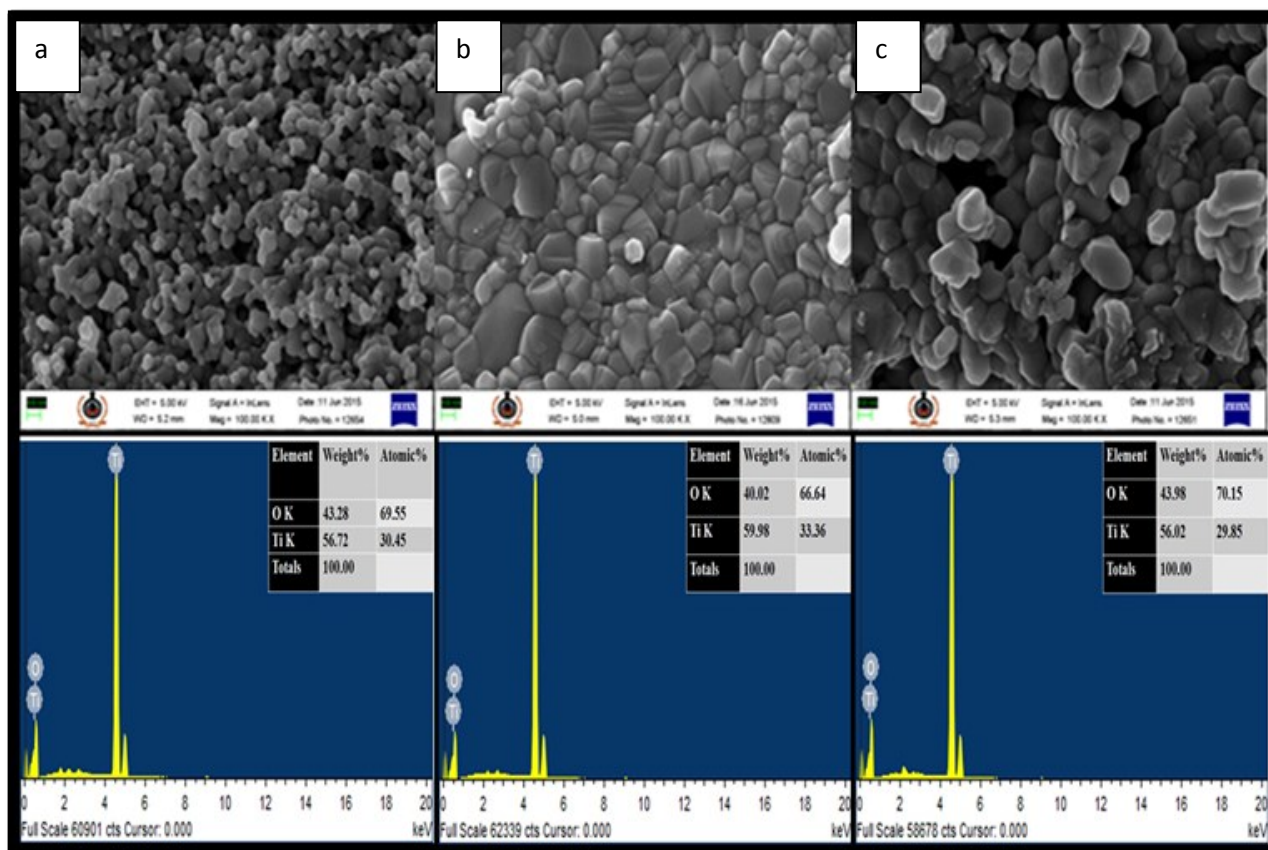


Fig. S4 SEM/EDS of rutile TiO₂ NPs coated with a) PVP b) Myristic acid c) Potato Starch after 800°C sintering

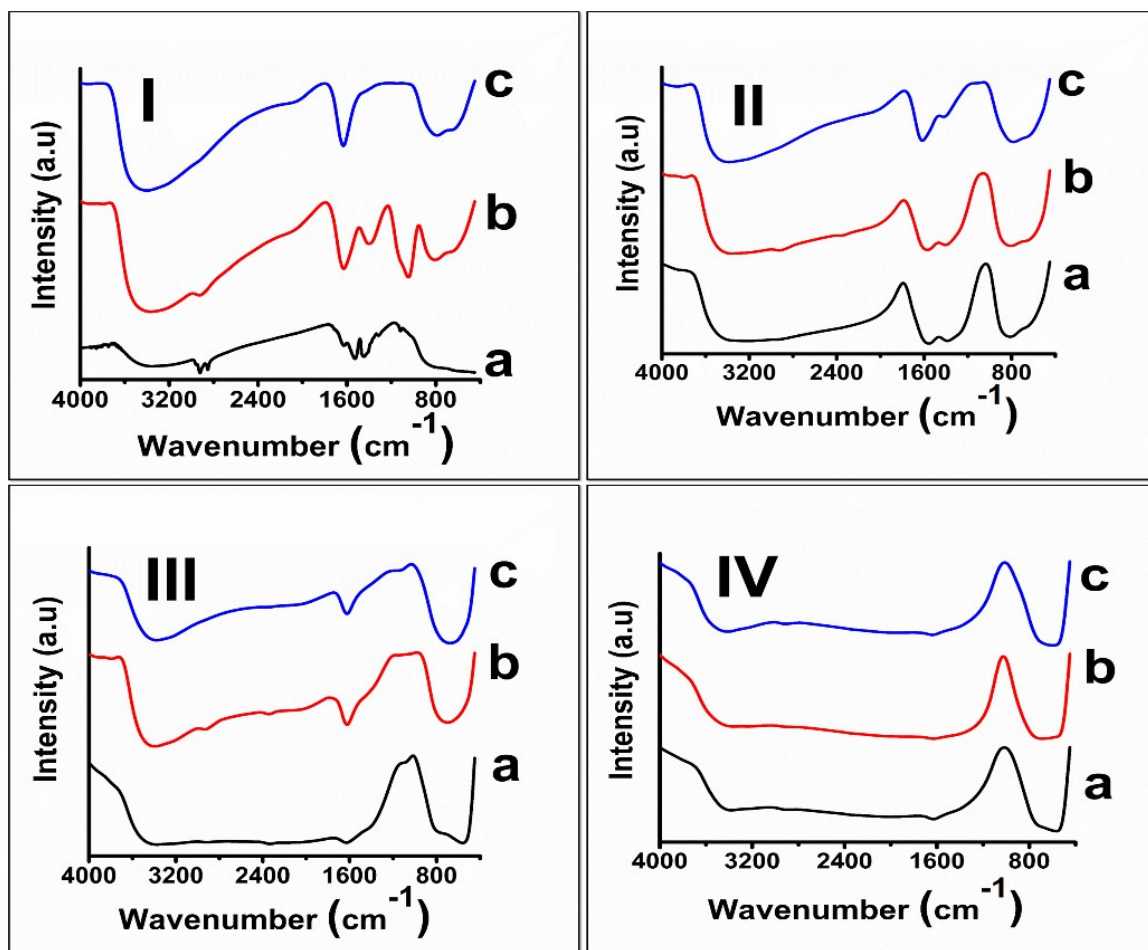


Fig. S5 FTIR spectra of TiO₂ sintered at (I) 100°C, (II) 200°C, (III) 400°C and (IV) 800°C: a) PVP b) Myristic acid c) Potato Starch coated TiO₂

Table S 5 FTIR frequencies for the various functionalities

Functional groups	PVP capped TiO₂NPs (cm⁻¹)	MA capped TiO₂ NPs (cm⁻¹)	PS capped TiO₂ NPs (cm⁻¹)
C-H symm. and antisymm. stretching	2923 & 2852	2900	-
C=O stretching*	1639 (<i>w</i>)	1626 (<i>s</i>)	1638 (<i>s</i>)
C-O stretching	1121	1049	-
N-C stretching	1519	-	-
C-H bend	1442	1403	-
Ti-O stretch	895	812	813

**w* and *s* corresponding to the weak and strong peaks in the spectrum

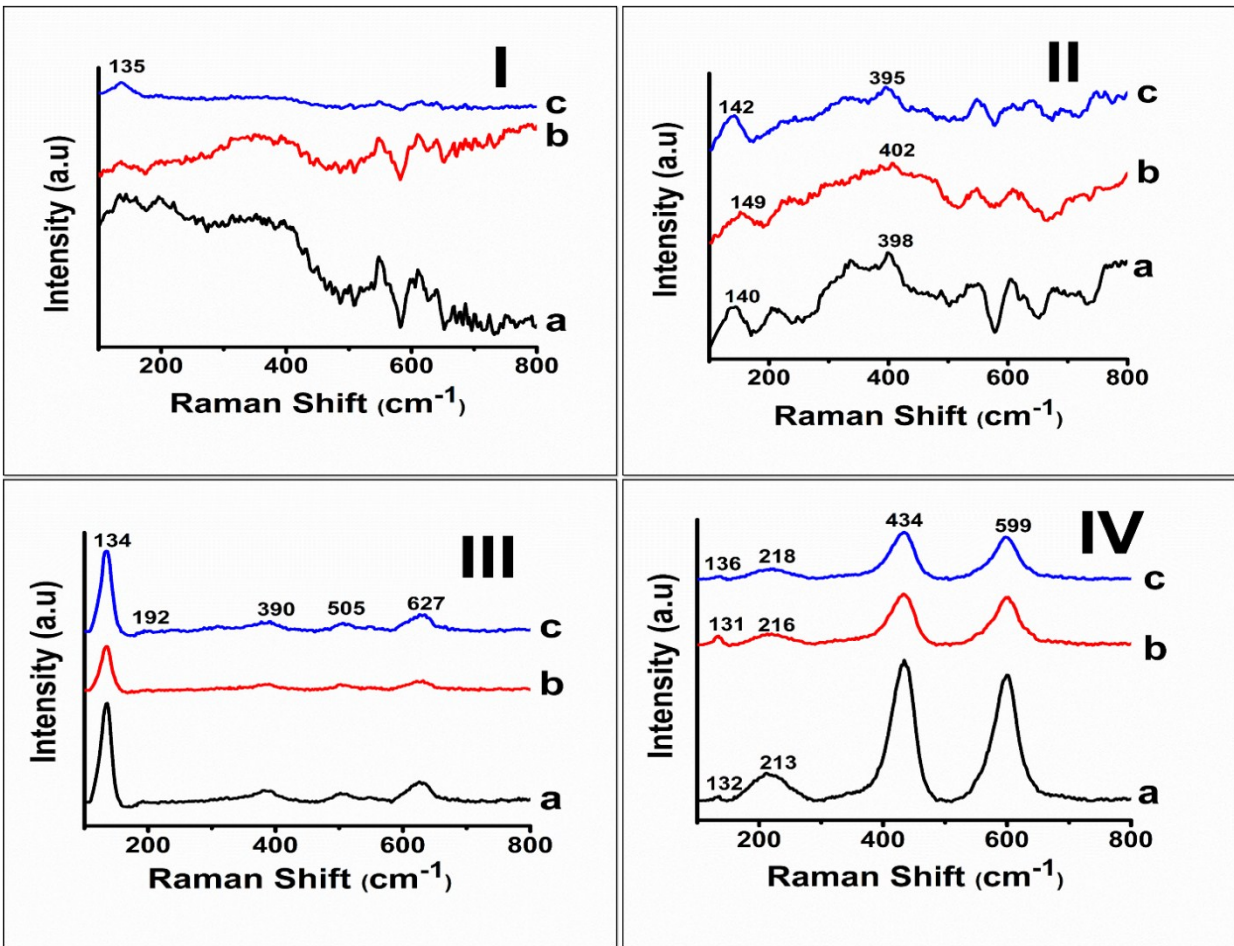


Fig. S6 Raman spectra of TiO₂ sintered at (I) 100°C, (II) 200°C, (III) 400°C and (IV) 800°C: a) PVP b) Myristic acid and c) Potato Starch coated TiO₂

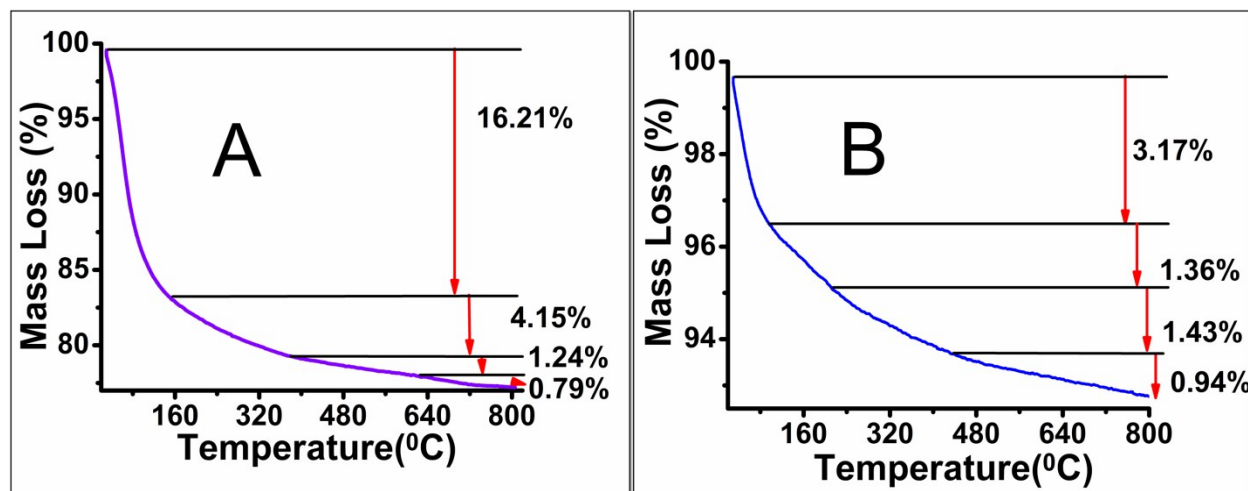


Fig. S7 TGA analysis of starch coated TiO₂ nanoparticles

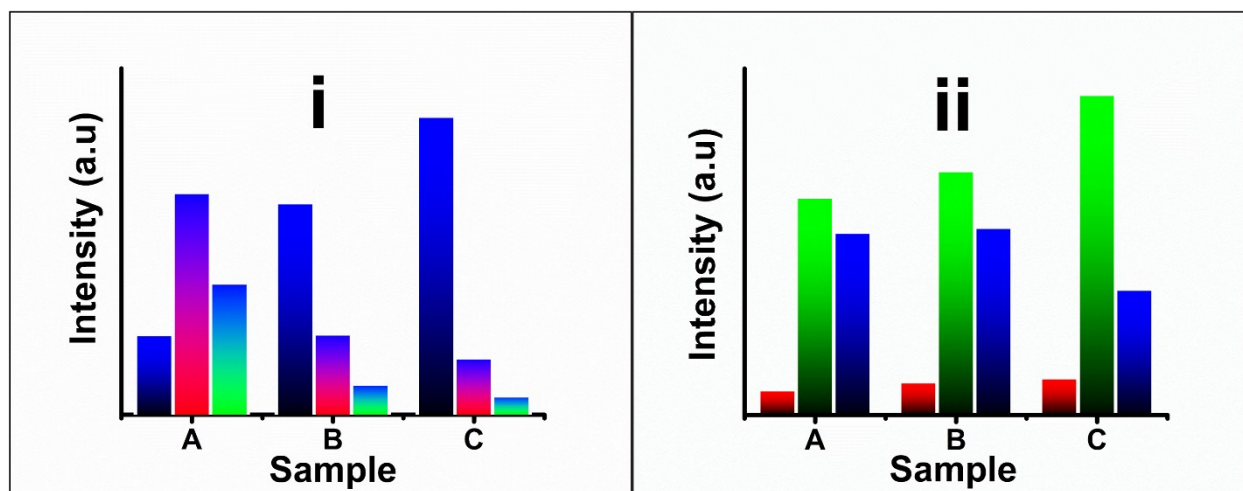
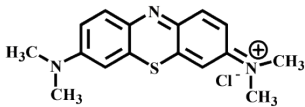
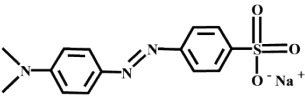
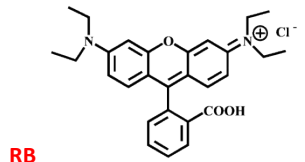
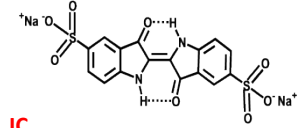
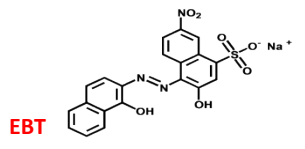


Fig. S8 BET analysis A- PVP, B- MA, C- PS coated nanoparticles corresponding to SSA, Particle Size and Crystallite size (L to R) where (i) anatase (ii) rutile phase.

Table S6 The molecular structure and chemical properties of organic dyes

Molecular Structure	Chemical properties ⁴⁵⁻⁴⁹
 <p>MB</p>	Chemical formula; C₁₆H₁₈N₃SCl Absorption maximum; 668nm
 <p>MO</p>	Chemical formula; C₁₄H₁₄N₃NaO₃S Absorption maximum; 507 nm
 <p>RB</p>	Chemical formula; C₂₈H₃₁ClN₂O₃ Absorption maximum; 554nm
 <p>IC</p>	Chemical formula; C₁₆H₈N₂Na₂O₈S₂ Absorption Maximum; 608 nm
 <p>EBT</p>	Chemical formula; C₂₀H₁₂N₃O₇SNa Absorption maximum; 503 nm

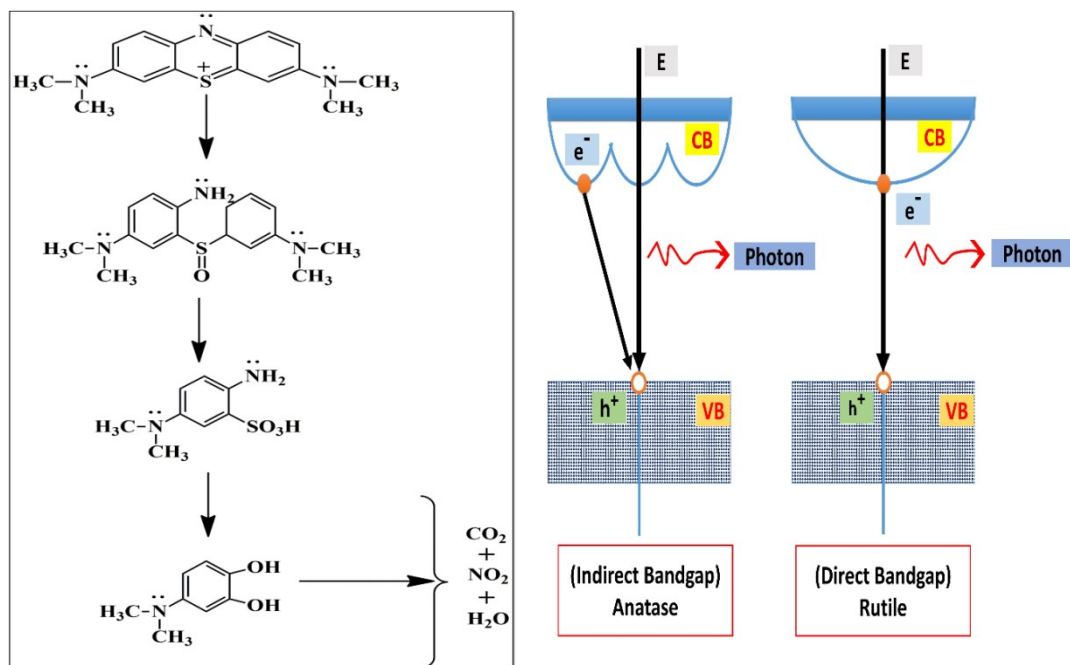


Fig. S9 Possible pathway of oxidative degradation for MB under UV irradiation using titania catalyst⁵⁰ and interaction of the photons in direct and indirect bandgap semiconductor⁵¹

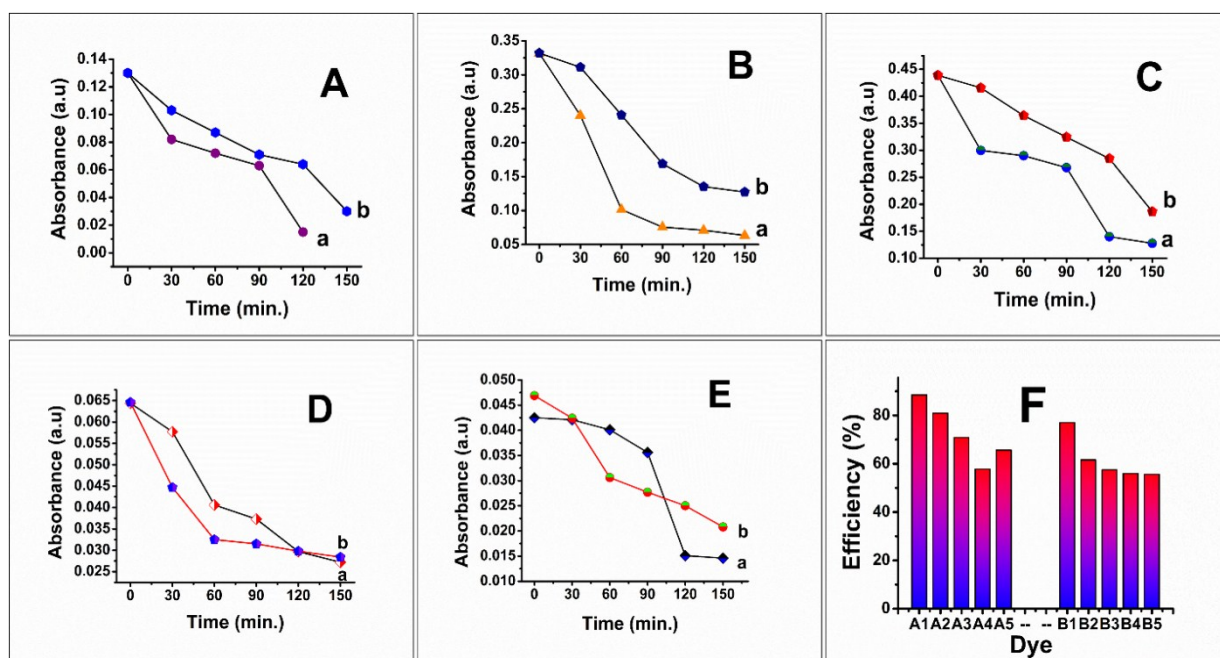


Fig. S10 Evaluation of photocatalytic activity of dye decomposition using absorbance peak value Vs time plots for (A) Methylene Blue, (B) Methyl Orange, (C) Rhodamine B, (D) Carmine Indigo and (E) Eriochrome Black T) with anatase TiO₂ (a), rutile TiO₂ (b) and (F) degradation efficiency of the nanoparticles, with reference to Methylene Blue, Methyl Orange, Rhodamine B, indigo carmine and Eriochrome Black T (A1, A2, A3, A4, A5) for anatase and (B1, B2, B3, B4, B5) for rutileTiO₂ nano-particles (for short UV intensity 122lux)

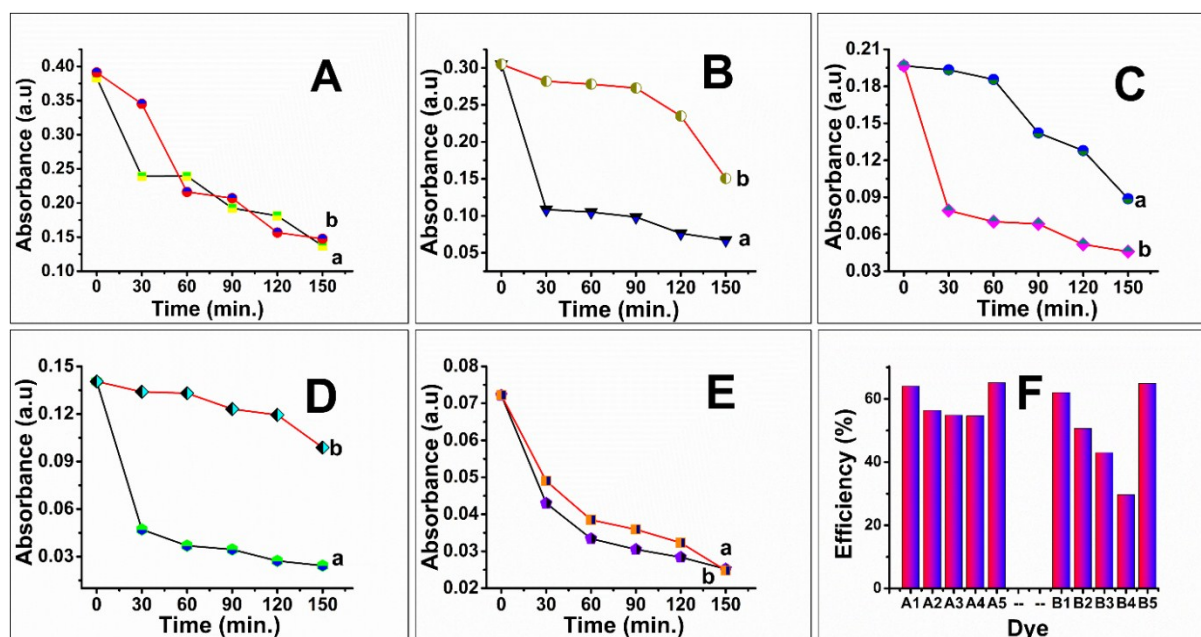


Fig. S11 Evaluation of the photocatalytic activities of anatase and rutile titania using absorbance peak value Vs time plots against (A) Methylene Blue, (B) Methyl Orange, (C) Rhodamine B, (D) Carmine Indigo and (E) Eriochrome Black T) with anatase TiO₂ (a), rutile TiO₂ (b) and (F) degradation efficiency of the nanoparticles, with reference to Methylene Blue, Methyl Orange, Rhodamine B, indigo carmine and Eriochrome Black T (A1, A2, A3, A4, A5) for anatase and (B1, B2, B3, B4, B5) for rutile TiO₂ nano-particles (long UV intensity 28lux).

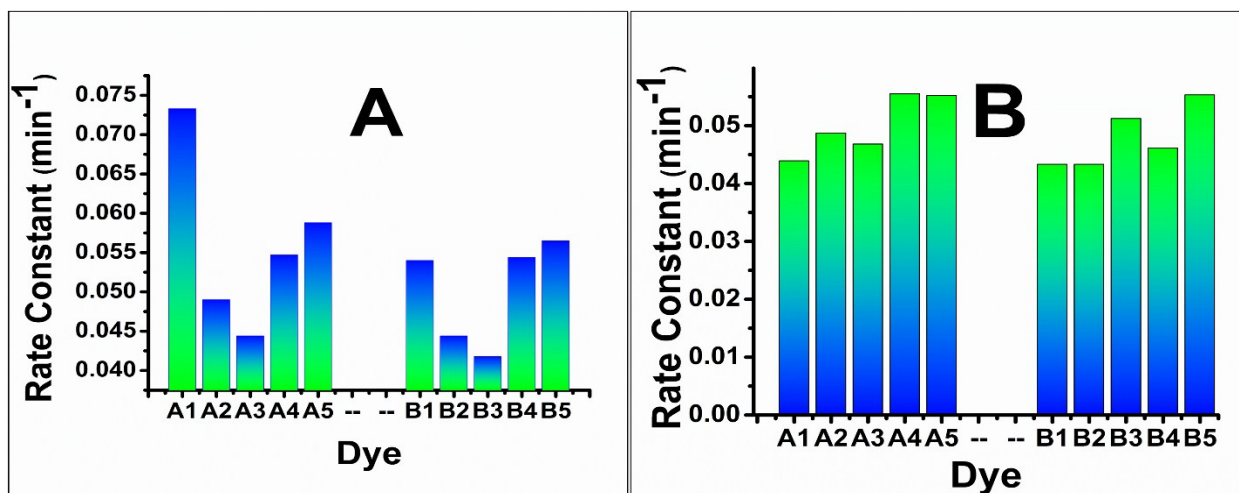


Fig. S12 Rate constant of the degradation, with reference to Methylene Blue, Methyl Orange, Rhodamine B, indigo carmine and Eriochrome Black T (A1, A2, A3, A4, A5) for anatase and (B1, B2, B3, B4, B5) under 254 nm (short) UV irradiation - A and under 365nm (long) UV irradiation - B.

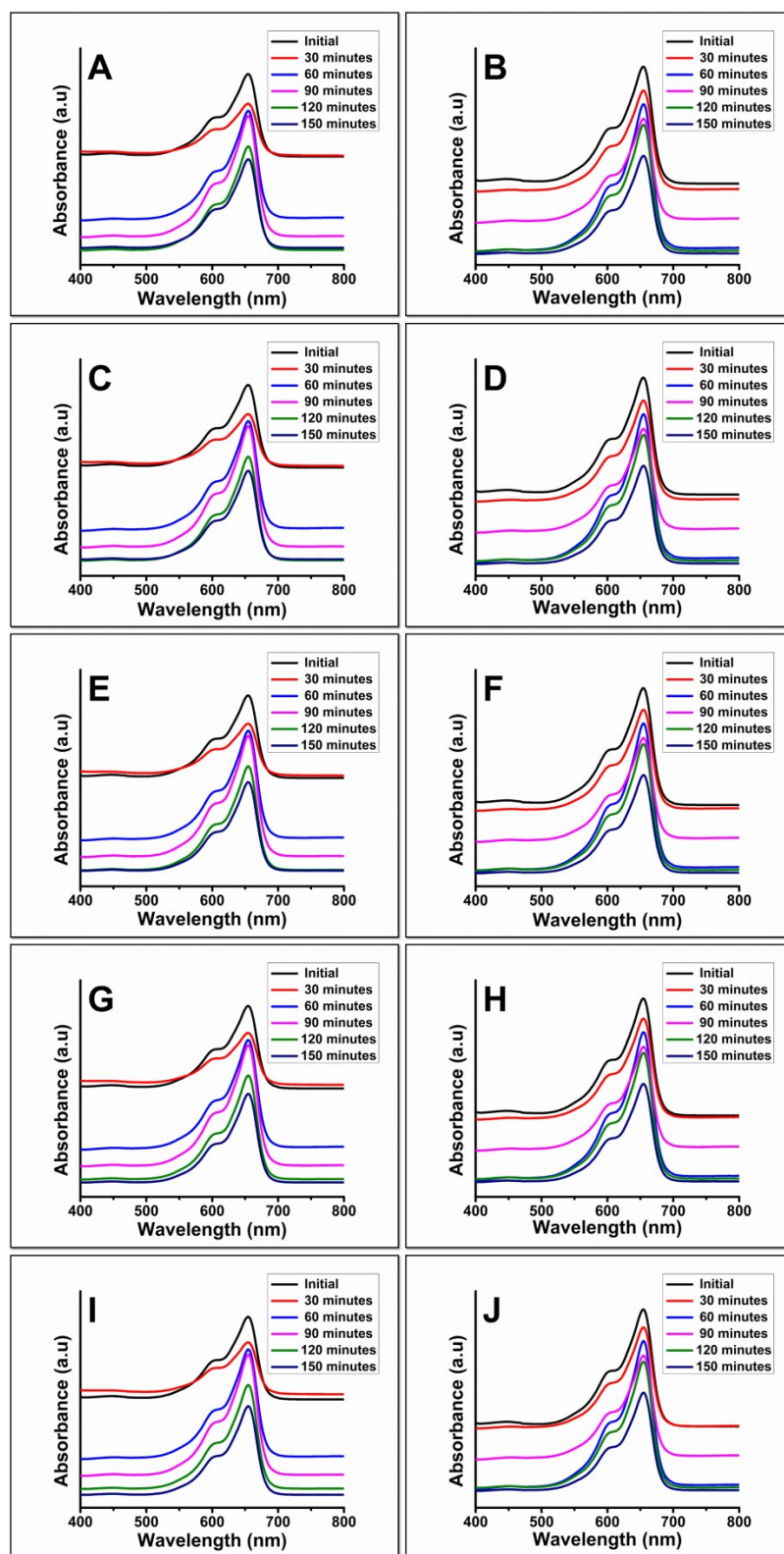


Fig. S13 Photocatalytic activities of recovered anatase (A, C, E, G, I) and rutile (B, D, F, H, J) titania against Methylene Blue under short UV irradiation.