

(Supporting information)

Nano-TiO₂ immobilized Polyvinylidene fluoride based spongy-spheres: Ciprofloxacin photocatalytic degradation with antibacterial activity removal, mechanism, UVA LED irradiation and easy recovery

Text S1: CIP concentration was analysed by high-performance liquid chromatography (HPLC Shimadzu LC-20A). The column used for HPLC was Phenomenex Kinetex EVO C18 2.6µm, 4.6X100mm. An Isocratic method with mobile phase of 0.1 % Formic acid in Water: Acetonitrile (85:15) at 0.8 mL/min flowrate was used.

Text S2. The degradation by-products were analysed by UPLC coupled with a Q-ToF mass spectrometer (Agilent G6546A, MS Q-ToF, Dual AJS ESI) with Poroshell-C18 column (2.1 X 50 mm, 2.7 µm). The mobile phase was 0.1% Formic acid in water (A) and Acetonitrile (B). The gradient method was used with compositions 95 % A and 5 % B for 0.5 min. 5 % A and 95 % B from 2.3 min and 0.9 min hold. 95 % A and 5 % B from 3.5 min till 4.0 min. The flow rate was 0.6 mL/min. The Q-ToF-MS system was equipped with an electrospray ionization interface (ESI) source. Positive Electrospray ionization (ESI) mode was employed for MS/MS analysis. The injection volume was 2 µL. The operations parameters for ESI were set up as follow: fragmentor voltage = 175 V, Gas temperature 320 °C,

Text S3: Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos\theta}$$

D is the crystallite size, K is the Scherrer constant (0.98), λ is the wavelength (1.54), β is the full width at half maxima (FWHM) of the peak

Text S4: Electrical energy

The electrical energy consumption is calculated by calculating the electrical energy per order [EE₀] kWh/m³/Order,

$$EE_0 = \frac{38.4 \times P}{V \times K}$$

Where, P is the power of the light source (kW), V is the treated volume (L), K is the pseudo first order rate constant ($k_{\text{obs}} = \text{min}^{-1}$).

Table S1. Real tap water (TW) characteristics.

Sr. NO.	Parameter	Tap water
1	Biological Oxygen Demand	< 2 mg/L
2	Chemical Oxygen Demand	< 4.0 mg/L
3	Total Suspended Solids (TSS)	18 mg/L
4	Total Dissolved Solids (TDS)	49.3 mg/L
5	Nitrate	0.052 mg/L
6	Phosphates	0.036 mg/L
7	Chlorides	13.91 mg/L
8	Sulphides	< 0.05 mg/L
9	Carbonate	3.94 mg/L
10	Bicarbonate	23.61 mg/L
11	Sodium	4 mg/L
12	Magnesium	1.46 mg/L
13	Iron	0.102 mg/L
14	pH	7.75
15	Temperature	26.4 °C
16	conductivity	69.5 μS
17	Salinity	38.6 mg/L

Table S2: BET analysis and porosity of T-PVDF beads

Sr. No	Sample name	Average surface area (m ² /g)	Total pore volume (cc/g)	Average pore radius (Å)	Porosity (ε) (%)
1.	PVDF	2.7550	0.0074	92.652	90.98
2.	PP	4.1065	0.0114	92.766	88.46
3.	TP	8.6374	0.0399	170.078	88.30
4.	TiO ₂	77.4609	0.3371	163.815	N.A.

Table S3: Pseudo first order rate constant for different initial concentration of CIP

Sr. No.	CIP concentration (ppm)	k_{obs} (min^{-1})
1	1	0.0761
2	2	0.0415
3	3	0.0339
4	4	0.0317
5	5	0.0282

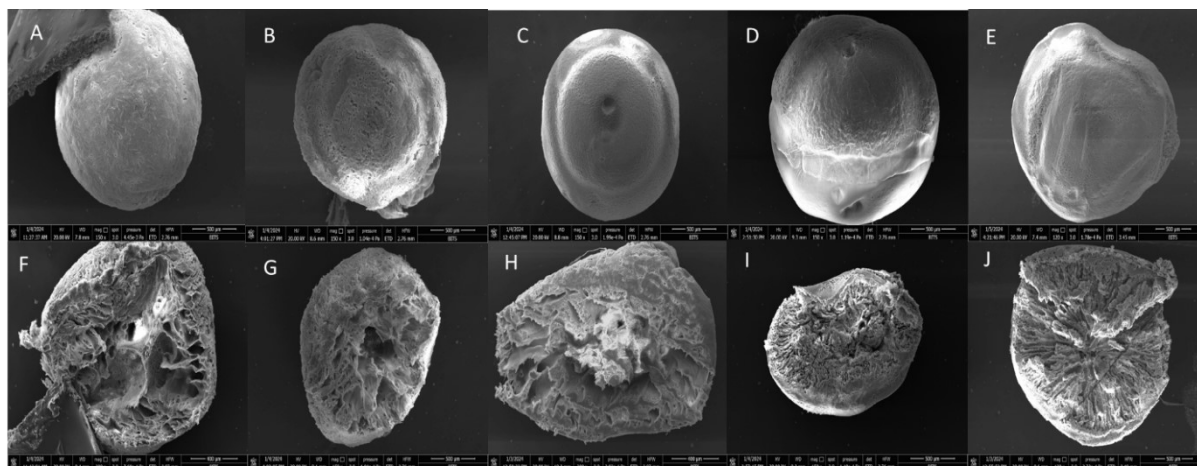


Figure S1: SEM image for different loading of TiO₂ in PVDF beads for whole bead (A-E) and corresponding cross-section (F-J) for 0.7% PVP loaded TP; A,F) 0 %, B,G) 1 % C,H) 5 %, D,I) 10 % , E,J) 15%

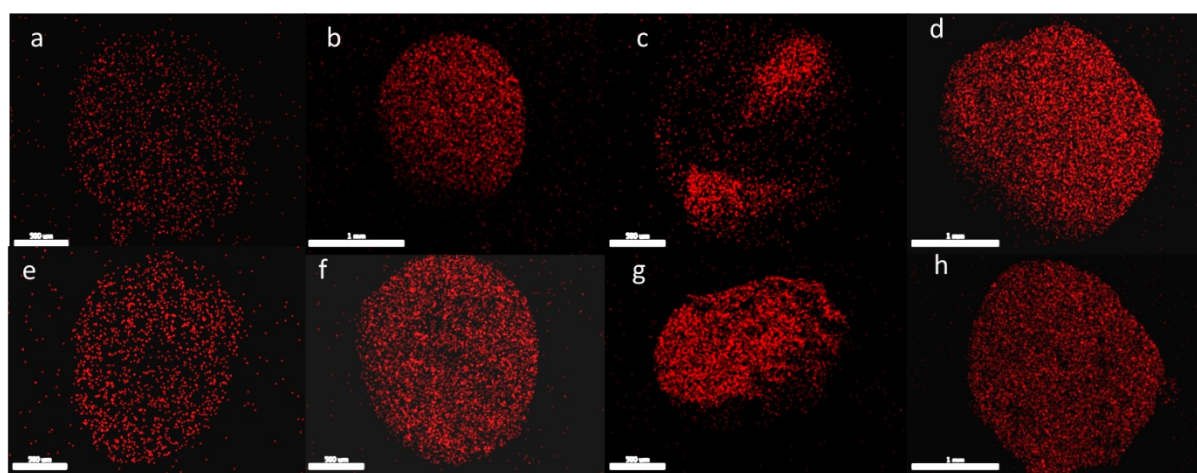


Figure S2: EDX elemental mapping for Ti, for different loading of TiO₂ in PVDF beads for whole bead (a-d) and corresponding cross-section (e-h) for 0.7% PVP loaded TP; a,e) 1 %, b,f) 5 % c,g) 10 %, d,h) 15 %

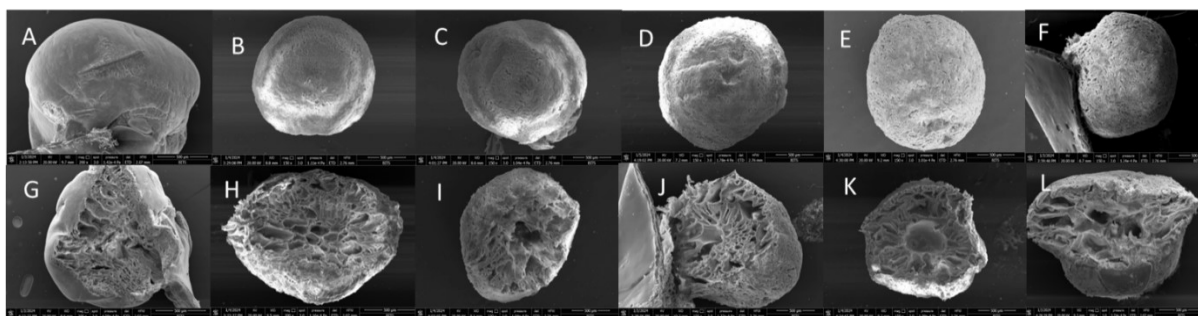


Figure S3: SEM images of whole TP bead with 1 % TiO_2 (A-F) and corresponding cross-sectional image (G-L) with different loading of PVP. A, G) 0%, B, H) 0.35 %, C, I) 0.7%, D, J) 1.4%, E, K) 2.1% and F, L) 2.8% of PVP

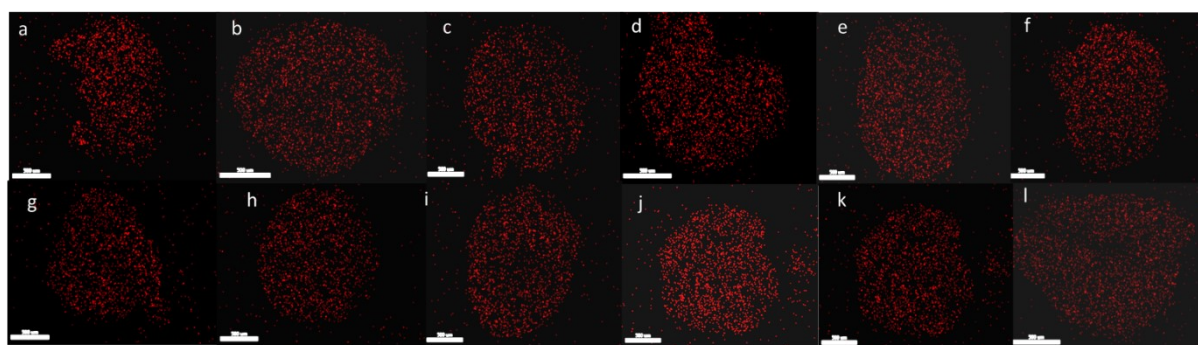


Figure S4: EDX elemental mapping for Ti, for different loading of PVP in PVDF beads for whole bead (a-f) and corresponding cross-section (g-l) for 1% TiO_2 loaded TP; a,g) 0, b,h) 0.35 c,i) 0.70, d,j) 1.4, e,k) 2.1 and f,l) 2.8

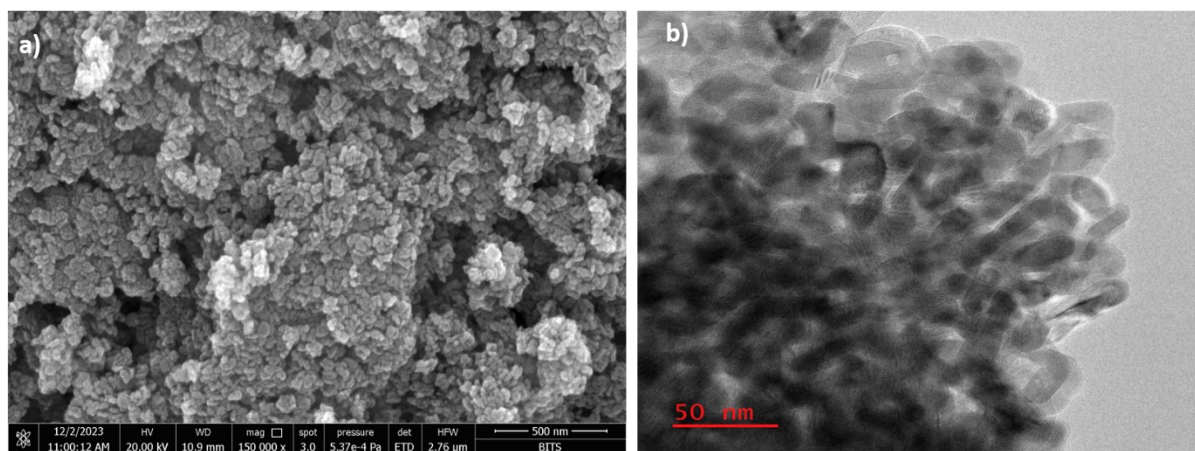


Figure S5: a) SEM image and b) TEM image of TiO_2 nanoparticles.

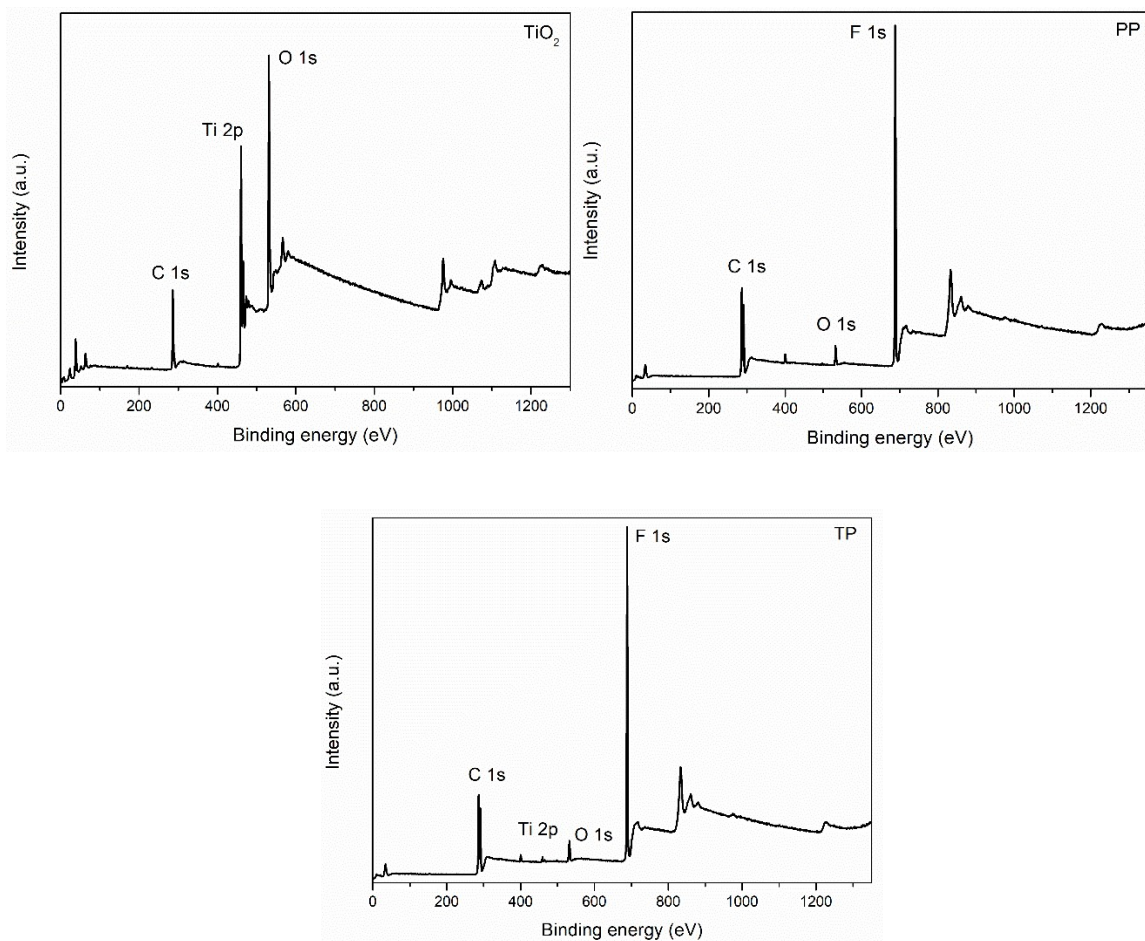


Figure S6: XPS survey spectra for a) TiO_2 , b) PP and c) TP, TP = 1% TiO_2 with PVDF having 0.7 % PVP, PP = PVDF having 0.7 % PVP

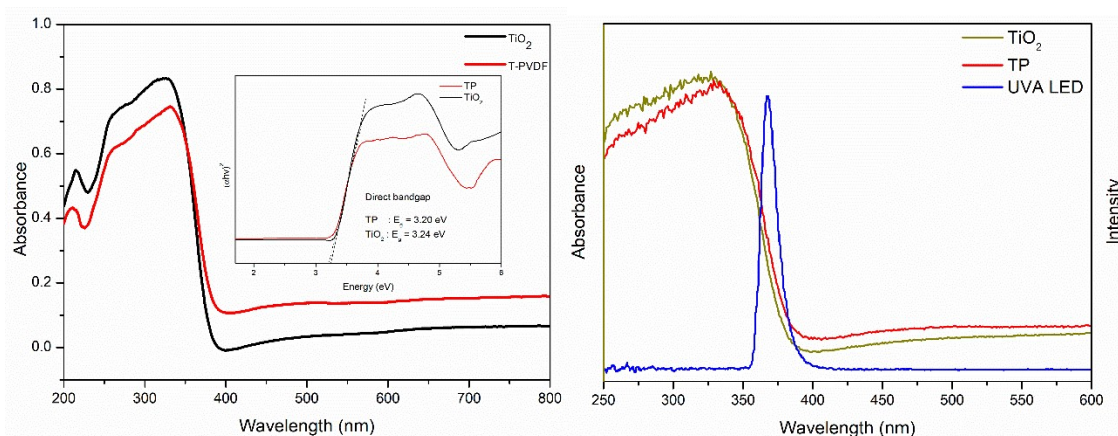


Figure S7: a) UVDRS graph and the band gap energy (E_g) of TiO_2 and TP beads, b) UVDRS spectra of TiO_2 and TP, and UVA LED emission spectra, TP = 1% TiO_2 with PVDF having 0.7 % PVP.

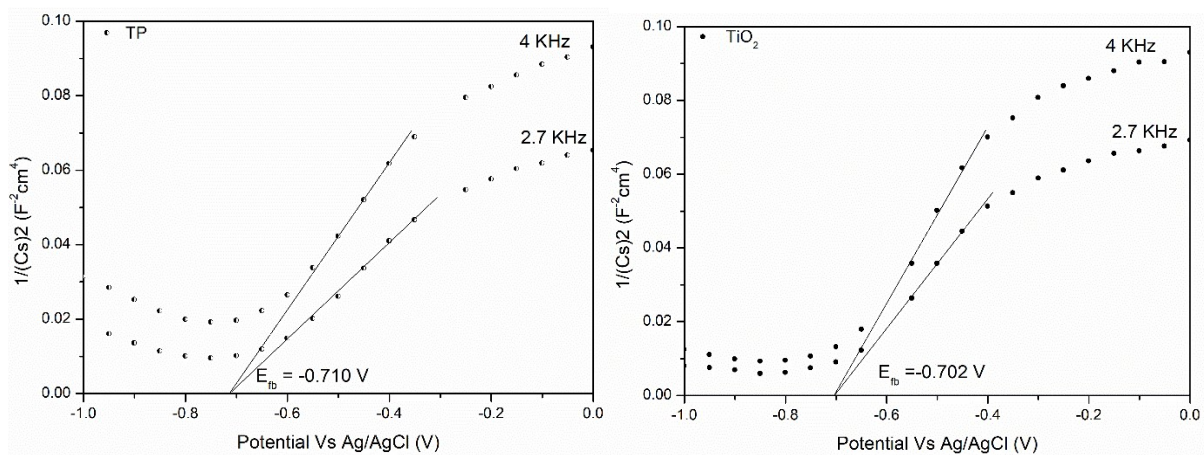


Figure S8: Mott-Schottky plot for a) TP and b) TiO_2 at frequency range of 10 kHz to 10 Hz, from -1.0 V to 0 V against Ag/AgCl, TP = 1% TiO_2 with PVDF having 0.7 % PVP.

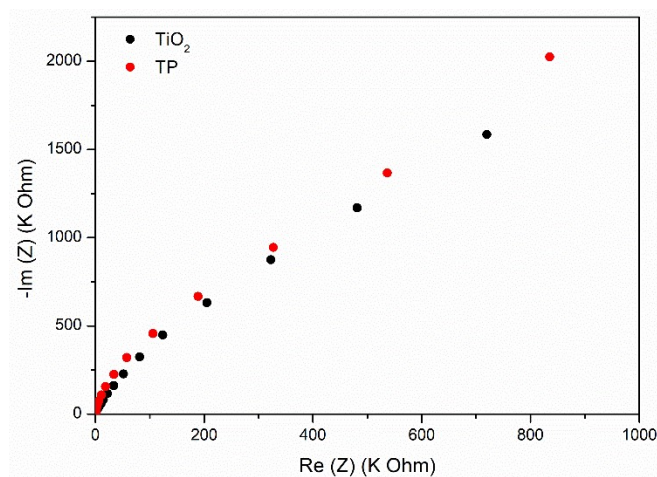


Figure S9: Nyquist plot for TP and TiO_2 at frequency range of 100 kHz to 0.1 Hz, at 0.7 V against Ag/AgCl, TP = 1% TiO_2 with PVDF having 0.7 % PVP.

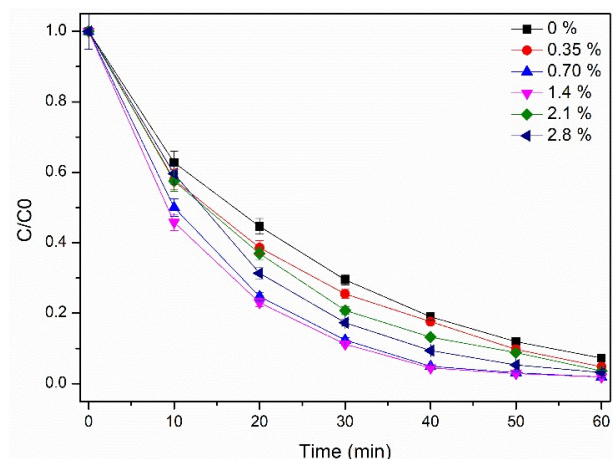


Figure S10. Effect of PVP loading over degradation of CIP by TP under UVA LED irradiation. Experimental conditions: [CIP] =1 ppm, Number of TP beads = 100, TP = 1 % TiO₂ with PVDF, Reaction volume = 50mL

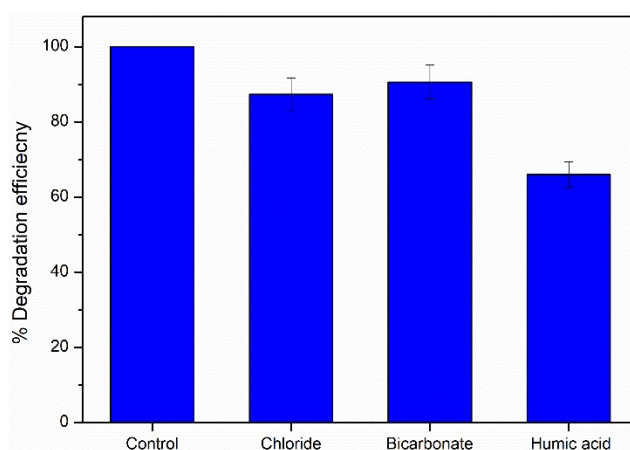


Figure S11. Effect of inorganic anions and NOM, Chloride (Cl⁻), Bicarbonate (HCO_3^-), Humic acid (HA) over degradation of CIP by TP under UVA LED irradiation. Experimental conditions: [CIP] =1 ppm, inorganic anion and NOM = 10 mg/L (ppm), TP = 1 % TiO₂ with PVDF, Reaction volume = 50mL, Reaction time = 60 min.

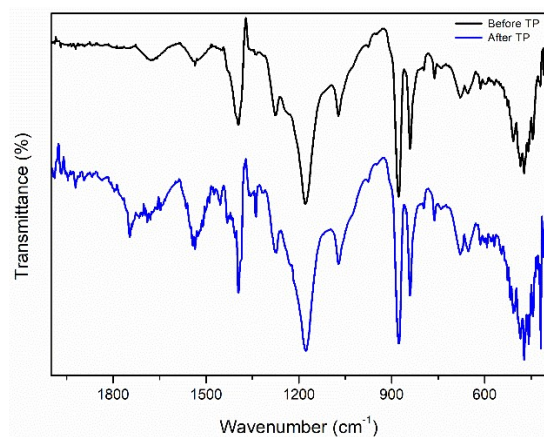


Figure S12: IR spectra of the TP beads before and after 30 cycles of photocatalysis, TP = 1% TiO₂ with PVDF having 0.7 % PVP.



Figure S13: SEM images of the full and cross-section TP beads reused after 30 cycles of photocatalysis, TP = 1% TiO₂ with PVDF having 0.7 % PVP.

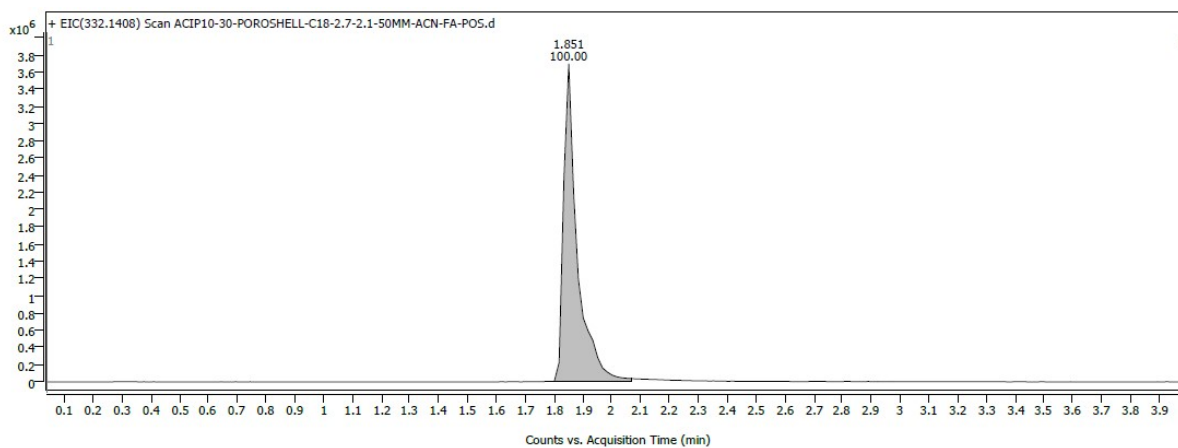


Figure S14: Extracted ion chromatogram (EIC) for $m/z = 332$

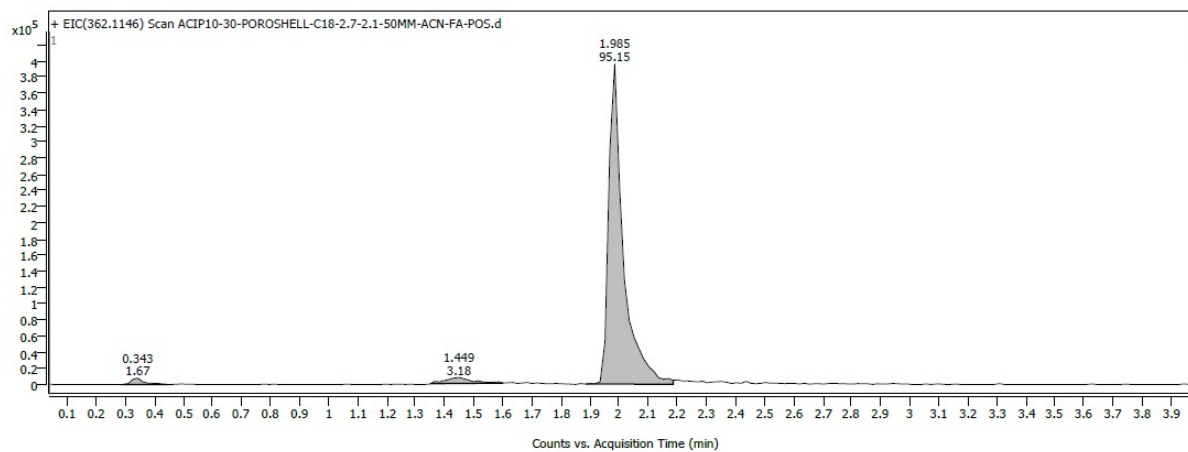


Figure S15: Extracted ion chromatogram (EIC) for $m/z = 362$

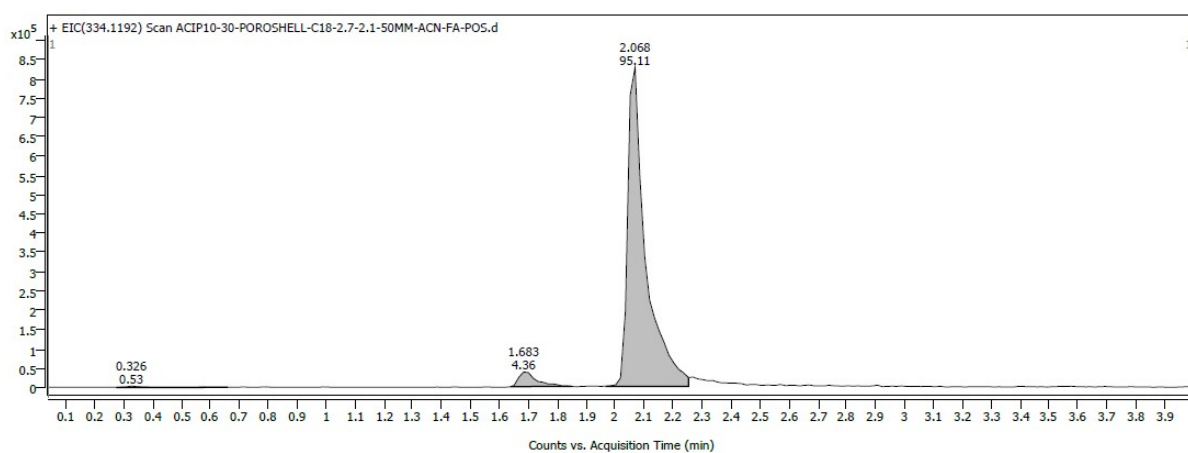


Figure S16: Extracted ion chromatogram (EIC) for $m/z = 334$

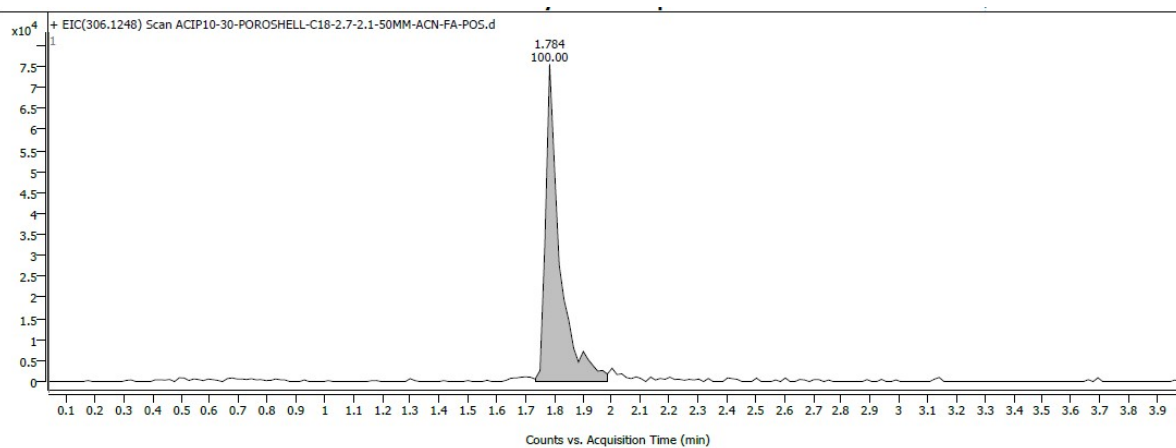


Figure S17: Extracted ion chromatogram (EIC) for $m/z = 306$

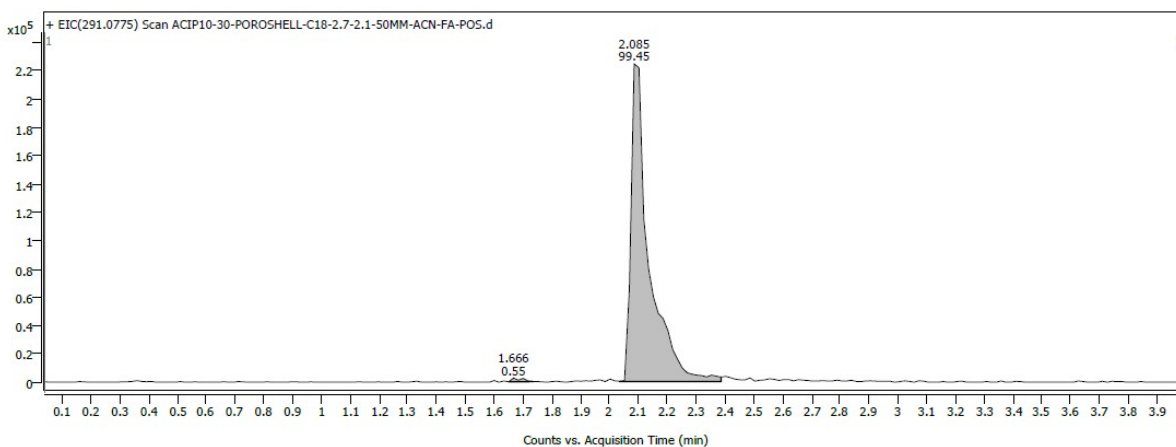


Figure S18: Extracted ion chromatogram (EIC) for $m/z = 291$

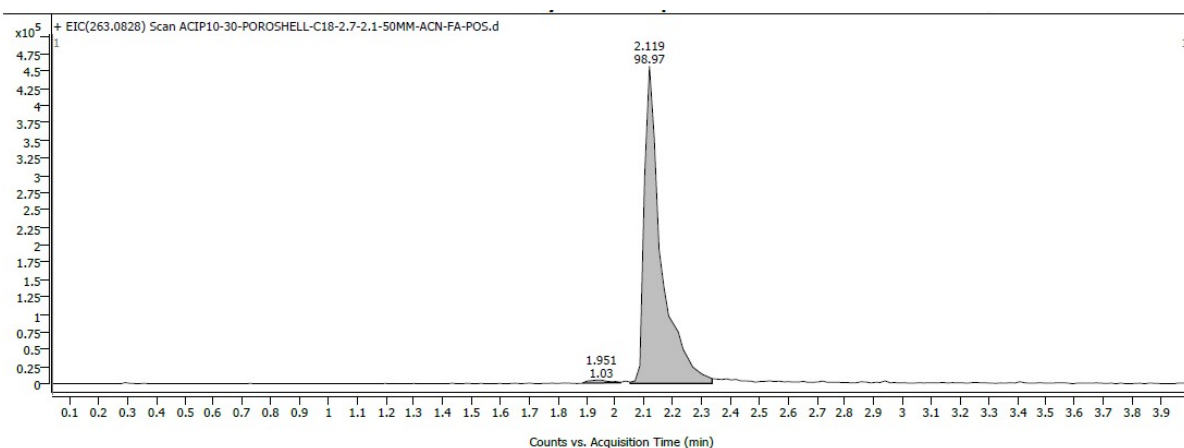


Figure S19: Extracted ion chromatogram (EIC) for $m/z = 263$

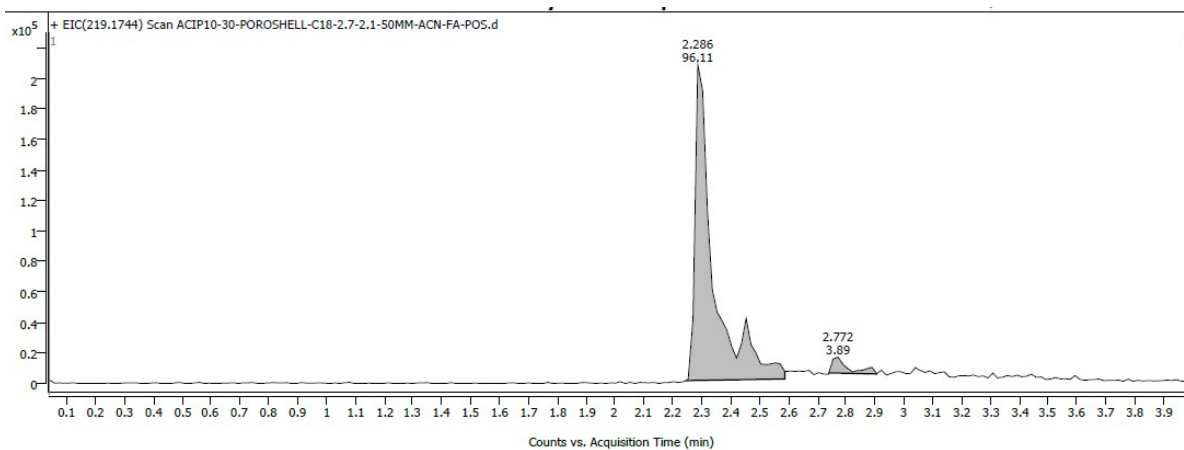


Figure S20: Extracted ion chromatogram (EIC) for $m/z = 219$

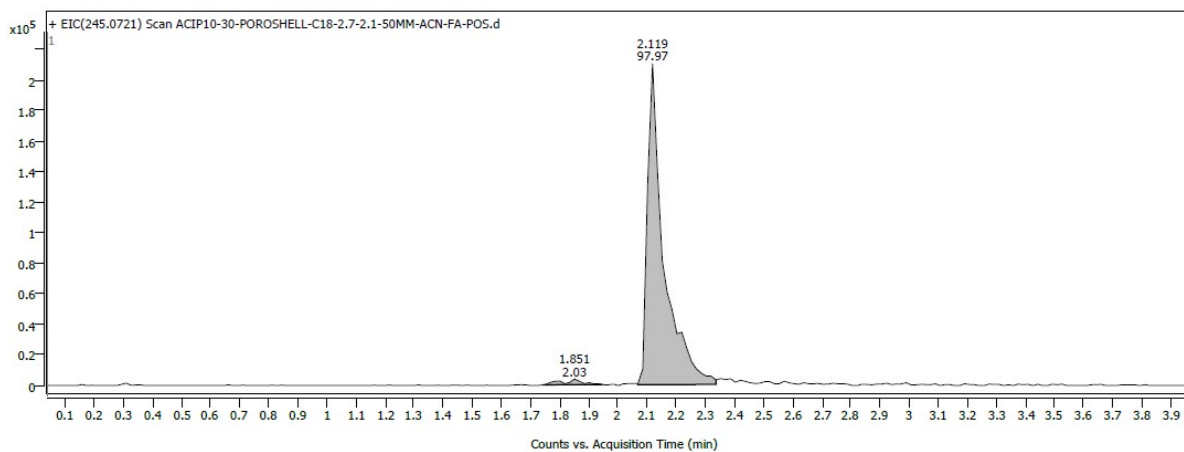


Figure S21: Extracted ion chromatogram (EIC) for $m/z = 245$

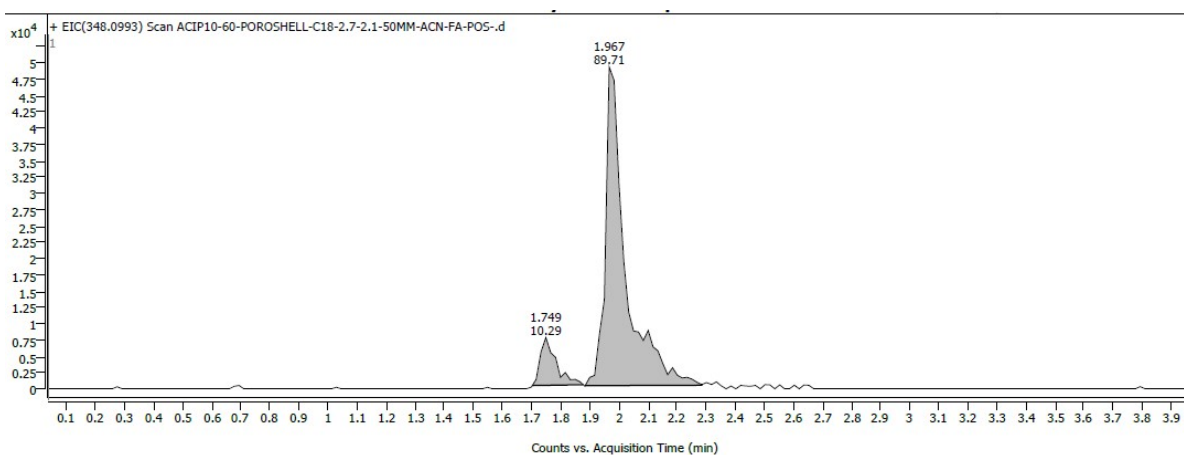


Figure S22: Extracted ion chromatogram (EIC) for $m/z = 348$

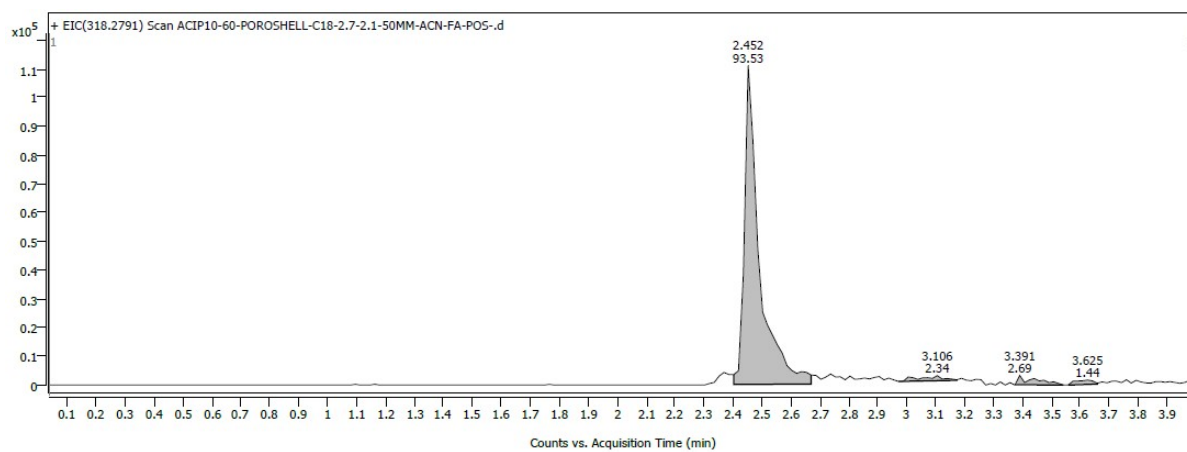


Figure S23: Extracted ion chromatogram (EIC) for $m/z = 318$

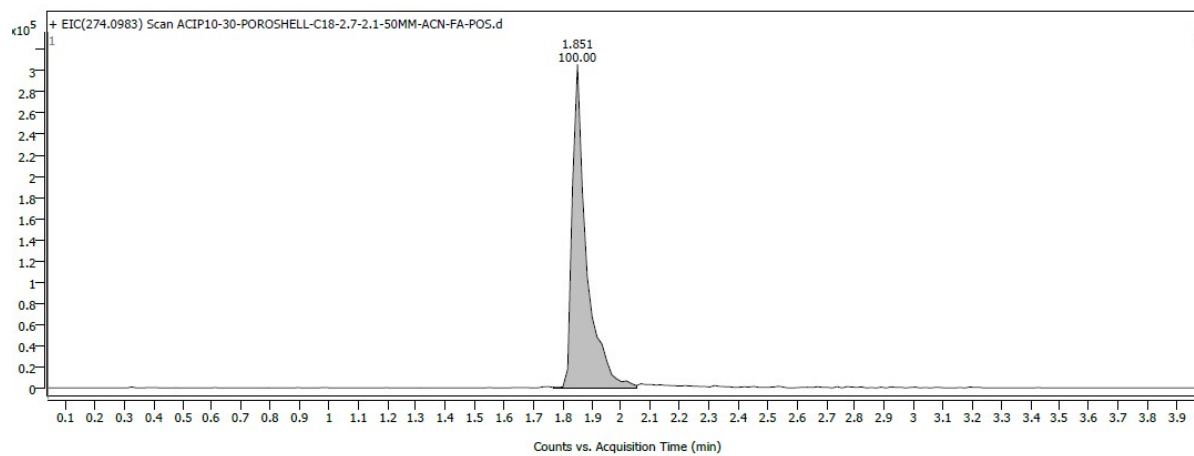


Figure S24: Extracted ion chromatogram (EIC) for $m/z = 274$