Electronic Supplementary Material (ESI) for Nanoscale.

# Combining photocatalytic collection and degradation of microplastics using self-asymmetric Pac-Man $TiO_2$

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## Supporting Information

**List of Videos:**

**Video S1**: Propulsion of Pac-Men $TiO_2$ microparticles in different concentration of $H_2O_2$.

**Video S2**: Interaction of Pac-Men and $SiO_2$ microparticles in presence and absence of UV light in 10 % $H_2O_2$ concentration.

## Characterization of Pac-Man $TiO_2$ particles

The Pac-Man microparticles are further characterized, inherently-asymmetric microparticles are formed in bulk amount with uniform size dispersity (Figure S1A). The FTIR analysis of the photocatalyst is performed, the spectrum of Pac-Man shows the formation of a broad band below $800\,\mathrm{cm}^{-1}$ attributed to the stretching vibration of Ti-O-Ti band, typical for $TiO_2$ microparticles (Figure S1B).[1] The formed Pac-Man particles consist of rutile phase $TiO_2$ (Figure S1C) with a bandgap of 2.92 eV (Figure S1D), and thus having an absorbance in the UV region and in the violet part of the visible light spectrum

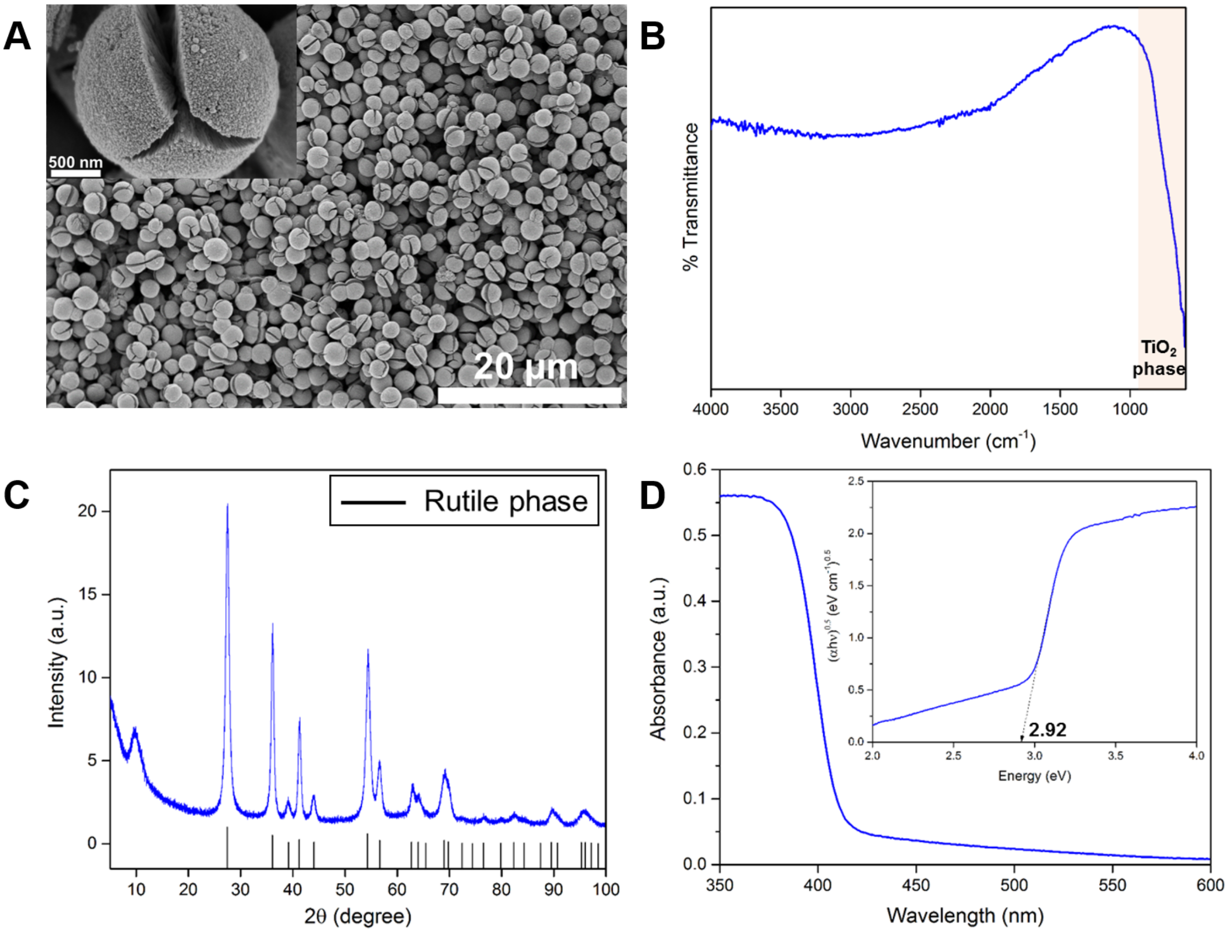


Figure S1: (A) SEM image (B) FTIR spectra, (C) XRD pattern, & (D) UV-vis DRS analysis of Pac-Man $TiO_2$ particles.

## Mean-square displacement (MSD) of Pac-Man particles in water and in different $H_2O_2$ concentrations

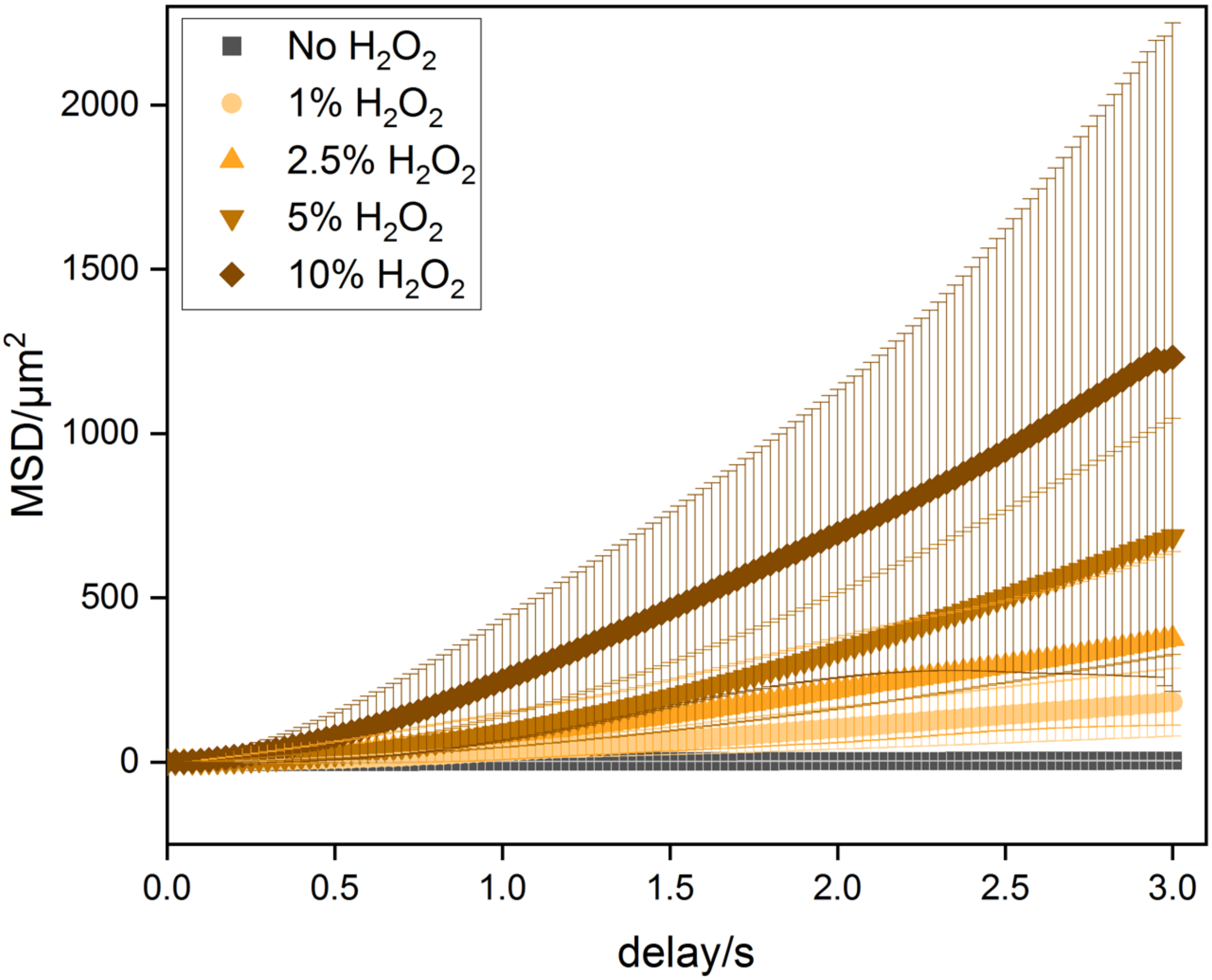


Figure S2: Comparative mean square displacement of Pac-Man particle in water (no UV and $H_2O_2$) and in different concentrations of $H_2O_2$ over a time interval of 3s. In water the particles show Brownian motion and propels ballistically in presence of $H_2O_2$. A UV light of intensity 19.08 W cm$^{-2}$ and wavelength 385 nm is used.

## $O_2$ evolution experiment

The setup used in the oxygen evolution study is shown in Figure S3A, it was a custom-made setup, where a mixture of photocatalysts is prepared in different concentrations of $H_2O_2$ and placed in a quartz GC vial, the vial is fixed at the center of the aluminum core containing 8

LEDs (0.25 W/cm$^2$intensityeach uniformly located throughout the aluminum core for evenly and radially illuminating the catalyst solution. The evolved oxygen is collected by using an inverted gas syringe tightly connected to the GC vial by a vial adapter. The main reason for using a Quartz GC vial is due to its absorption properties, UV light of 385 nm and lower is used for the gas evolution studies, now if we compare the UV-vis absorbance of these a standard GC vial with quartz vial and quartz cuvette (Figure S3B), we find that, unlike the quartz vials, the glass/standard vial absorb light of wavelength lower than 363 nm and thus will not allow the catalyst to utilize the whole UV spectrum.

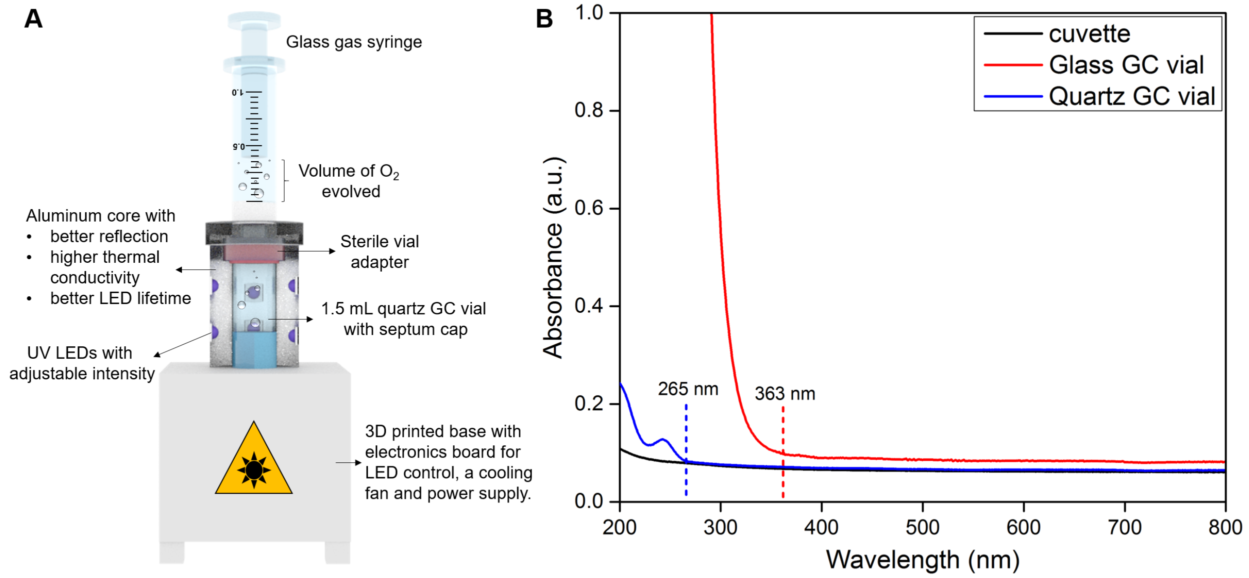


Figure S3: (A) Schematic representation of the setup used for determining the amount of O$_2$ evolved (B) UV-vis spetra comparing the absorbance properties of a quartz cuvette, glass GC vial and quartz GC vial.

## Active-passive interactions

Collective behavior of Pac-Men particles (active) with non-catalytic (passive) particles arises due to the self-propulsion and attractive phoretic interactions. The forces guiding these interactive assemblies are not charged-based (Figure S4) and the assemblies are only observed only when the light is turned on (Video S2). These interactions are also short-ranged and non-selective i.e. independent of the nature and size of passive particles.[2]

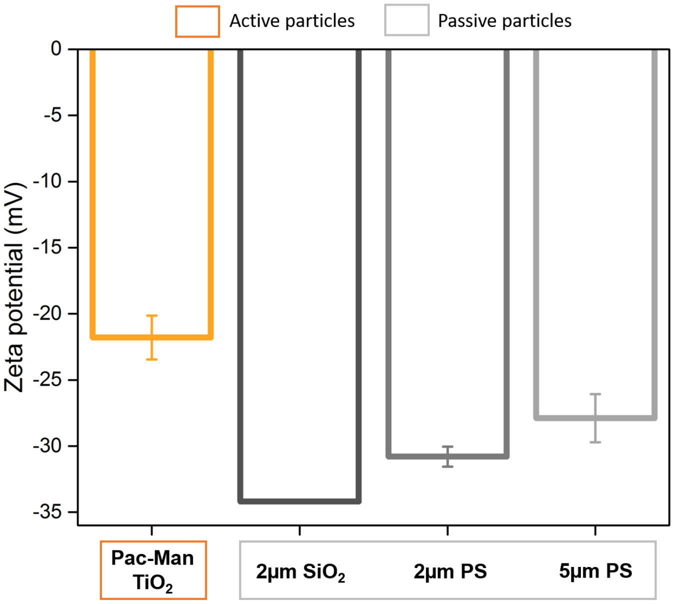


Figure S4: Average zeta pottential values of used active and passive particles measured using Malvern Zetasizer Nano ZSP device.

As seen in Figure S5, the active particles interact with passive particles of different types (PS and SiO$_2$) and of different sizes (2 & 5 µm PS) under the same experimental conditions. Although the assembly in the case of PS particles is not in a single plane and the 3-dimensional rafts are formed due to the lower density of PS spheres.

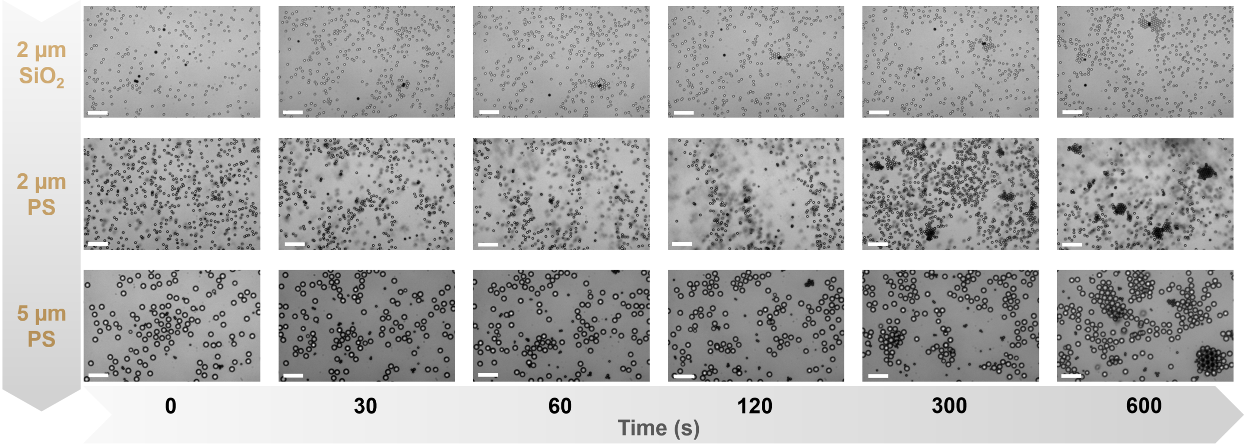


Figure S5: Collective assembly of active Pac-Man colloids with passive particles (2µm SiO$_2$ or 2µm or 5µm polystyrene particles) in 2.5 % (w/w) $H_2O_2$ solution. Images are taken with microscope at definite time interval of 30s, 60s, 120s, 300s and 600s. Scale bar: 20 µm. A UV light of intensity 19.08 W cm$^{-2}$ and wavelength 385 nm is used.

## Dye Degradation

The absorbance of the control sample (without photocatalyst) do not change when irradiated with UV light for 30 minutes (Figure S6A). Figure S6B display the residual concentration of the dye degraded in presence and absence of photocatalyst. The dye was kept in dark condition to reach the absorption-desorption equilibrium with the catalyst.

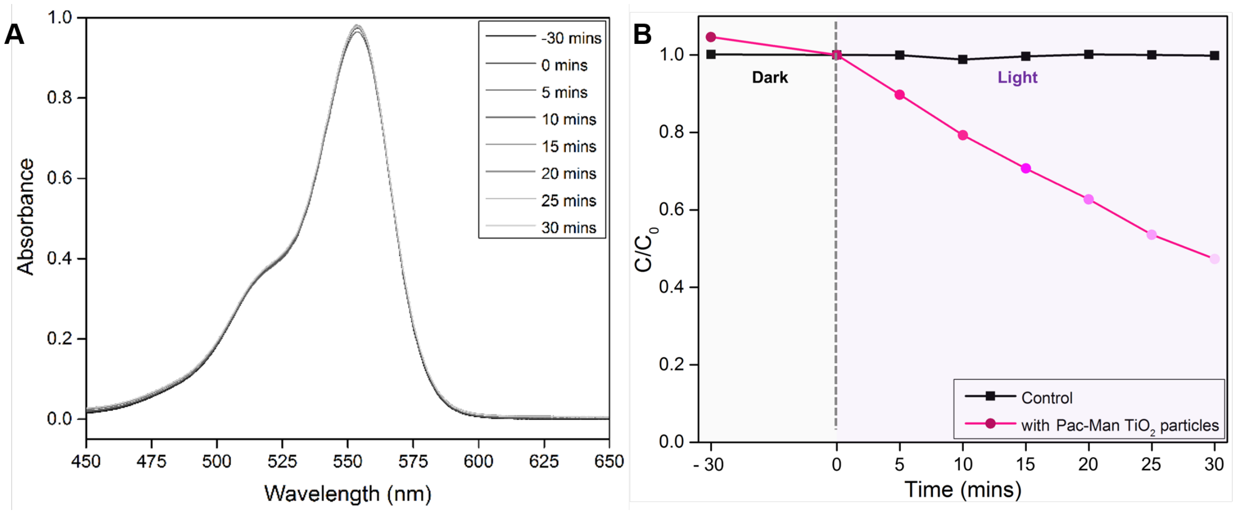


Figure S6: (A) UV-visible spectra of RhB showing the degradation of control sample in UV light, studied over a time period of 30 minutes at each 5 minutes interval. (B) Comparison of residual concentration of the dye in presence and absence of photocatalyst.
For the experiment, a UV lamp of intensity $950\,\mu W\,cm^{-2}$ with a wavelength of 365 nm was used. Concentration of $TiO_2$ and RhB is $1\,mg\,mL^{-1}$ and 0.01 mM respectively.

## Standard curves of RhB dye at different degradation times

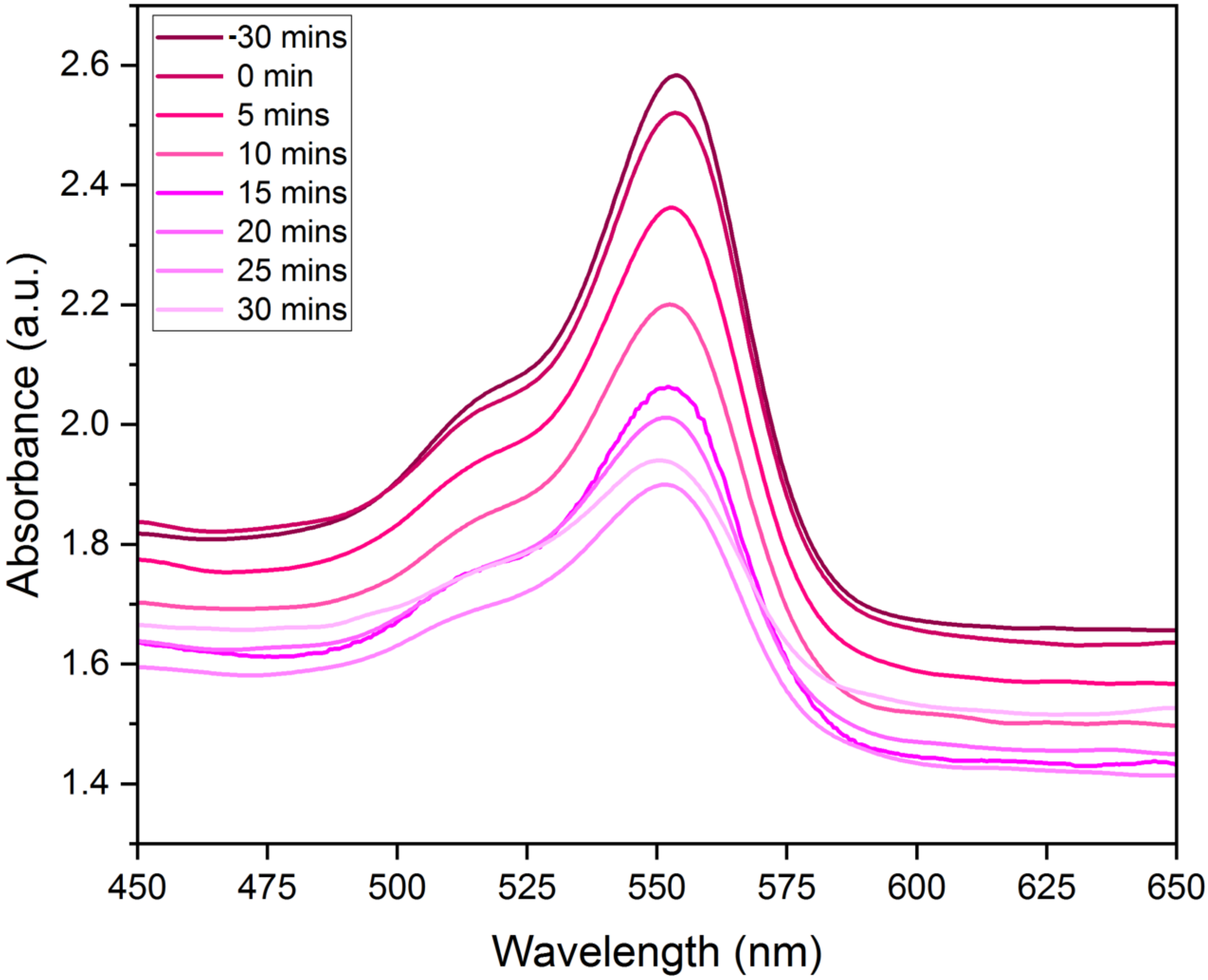


Figure S7: UV-visible spectra of RhB showing the degradation of in presence of Pac-Man $TiO_2$ in UV light, studied over a time period of 30 minutes at each 5 minutes interval. The graph shows the standard curve without any normalization.

## Microplastic Degradation

The setup used in microplastics degradation is shown in Figure S8, the petri dishes were placed 5 cm away from the UV source and irradiated for 70 h in a closed box without any addition mechanical agitation.

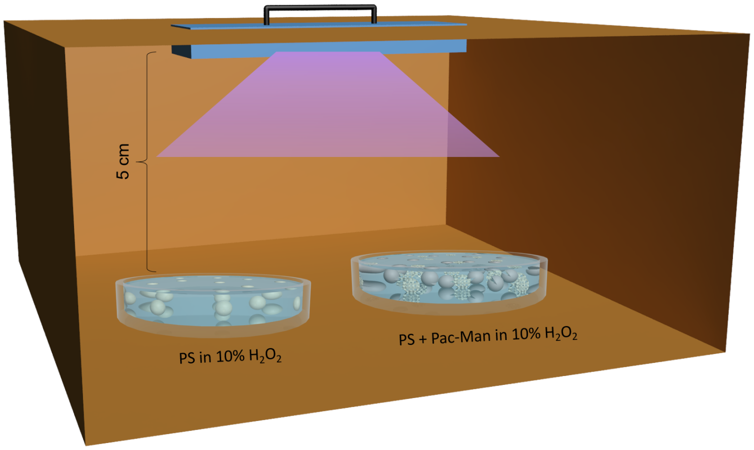
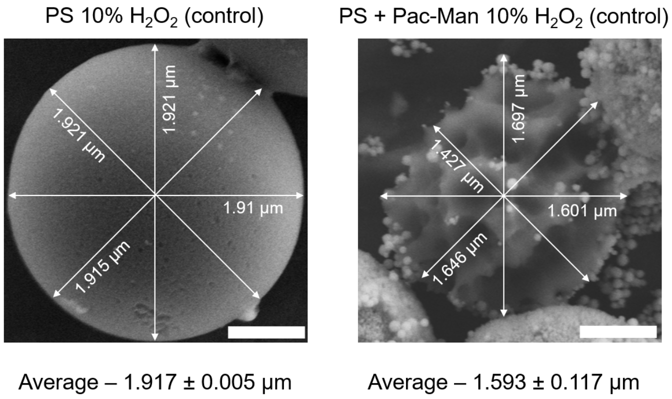


Figure S8: Microplastic degradation setup

Followed by the degradation, the PS samples are washed and imaged using SEM, and the diameter of the PS spheres is determined to evaluate the extent of degradation after photocatalysis. The diameter is measured from 4 sides, at an angle of 0°, 90°, 45°, −45° (Figure S9).


PS 10% $H_2O_2$ (control)

PS + Pac-Man 10% $H_2O_2$ (control)

Average – 1.917 ± 0.005 µm

Average – 1.593 ± 0.117 µm

Figure S9: Evaluation based on size change of polystyrene microparticles after photocatalytic degradation

### Motion of Pac-Man before and after the microplastic degradation reaction

Although the $H_2O_2$ is consumed over the course of the reaction, the Pac-Man particles continues to move during the irradiation time of 70 h, we studied the Pac-Man motion in $H_2O_2$ (at the lowest and highest concentration) before and after the microplastic degradation (Figure S10).

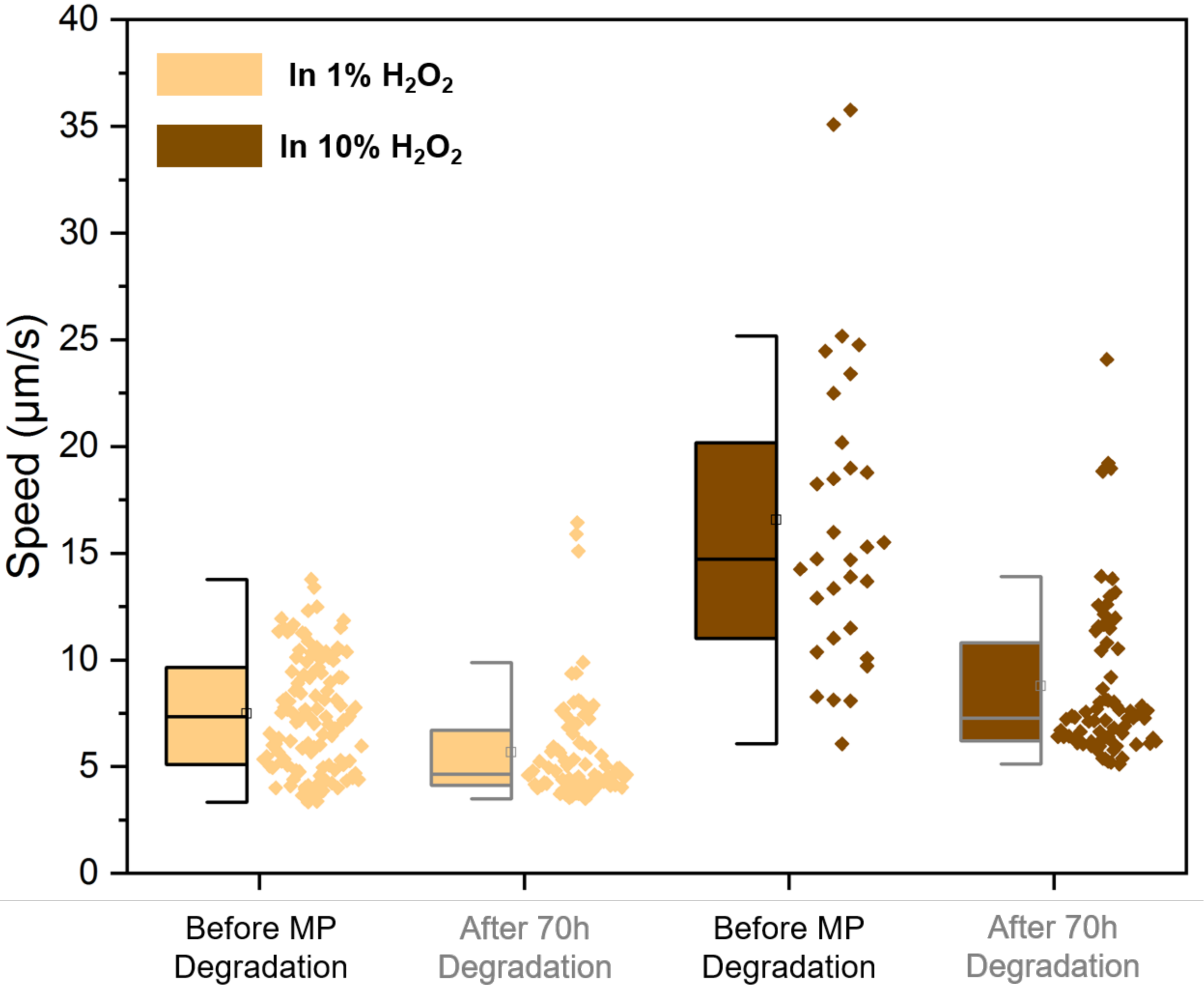


Figure S10: Box plots of speed values for at least 30 motile particles for the lowest (1 %) and highest (10 %) $H_2O_2$ concentration obtained before and after the MP degradation study.

The average speed decreased over the degradation time, as the Pac-Man particles start moving at lower speed, but they remain motile throughout the 70h time.

## Degradation of 5 µm PS particles

Photocatalytic and morphological degradation of microplastics is also observed with 5 µm PS particles, there is a reduction of particle size at higher concentrations of $H_2O_2$ (Figure S11), the degradation is very evidently observed from SEM images (Figure S11 (i -vi)), formation of pores, dents, cavities and wear off is indisputable at 5 & 10 % peroxide.

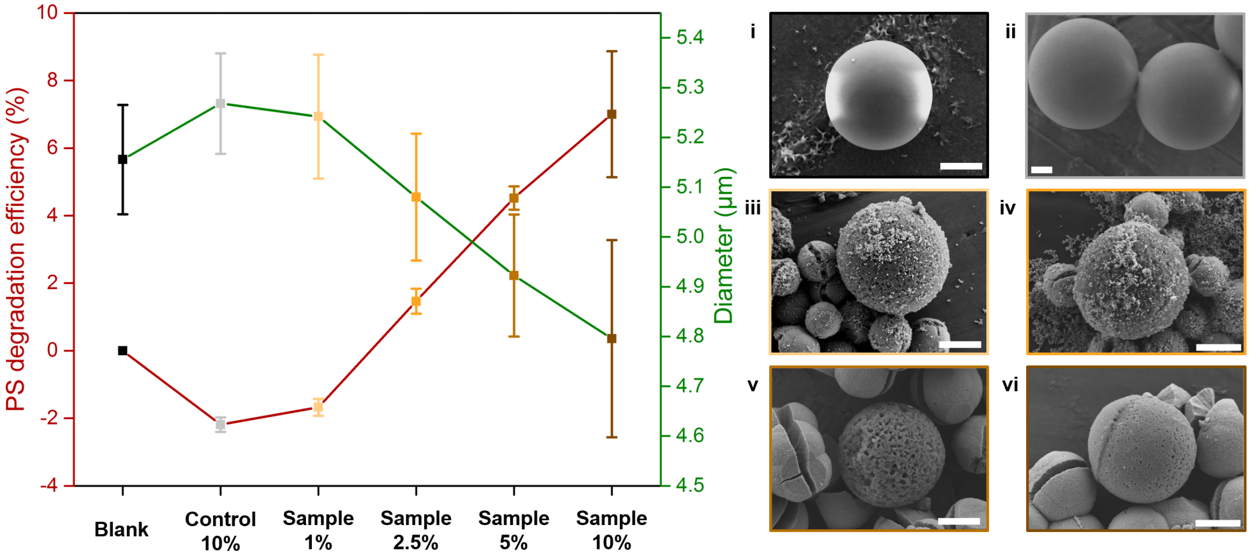


Figure S11: Degradation efficency (%) and corresponding diameter of 5 µm PS particles in different reaction conditions. A example image depicting the degradation is shown in the right side to see the morphological changes over different reaction conditions. i & ii being the blank and control sample (in 10 % (w/w) $H_2O_2$) respectively, iii to vi are PS with Pac-Man $TiO_2$ particles in increasing peroxide concentrations from 1 %, 2.5 %, 5 %, and 10 % (w/w) respectively. A UV lamp of intensity 950 µW cm$^{-2}$ with a wavelength of 365 nm was used, and the experiment was carried out for 70 h. Concentration of $TiO_2$ and microplastics is 50 mg mL$^{-1}$ and 0.2 wt.%. Scale bar: 2 µm.

## Morphological comparison of 2 µm and 5 µm PS particles at higher $H_2O_2$ concentrations

Morphology of 2 and 5 µm PS particles with their average size at 5 & 10 % peroxide concentrations compared with the control (at 10 % $H_2O_2$ concentration). It can be clearly observed that with an increase in $H_2O_2$ concentrations, a higher degradation is followed and the smaller PS particles are degraded at a much higher extent compared to the larger particles

(5 µm). The control particles remain unaffected in these critical experimental conditions in the absence of the photocatalyst (Figure S12).

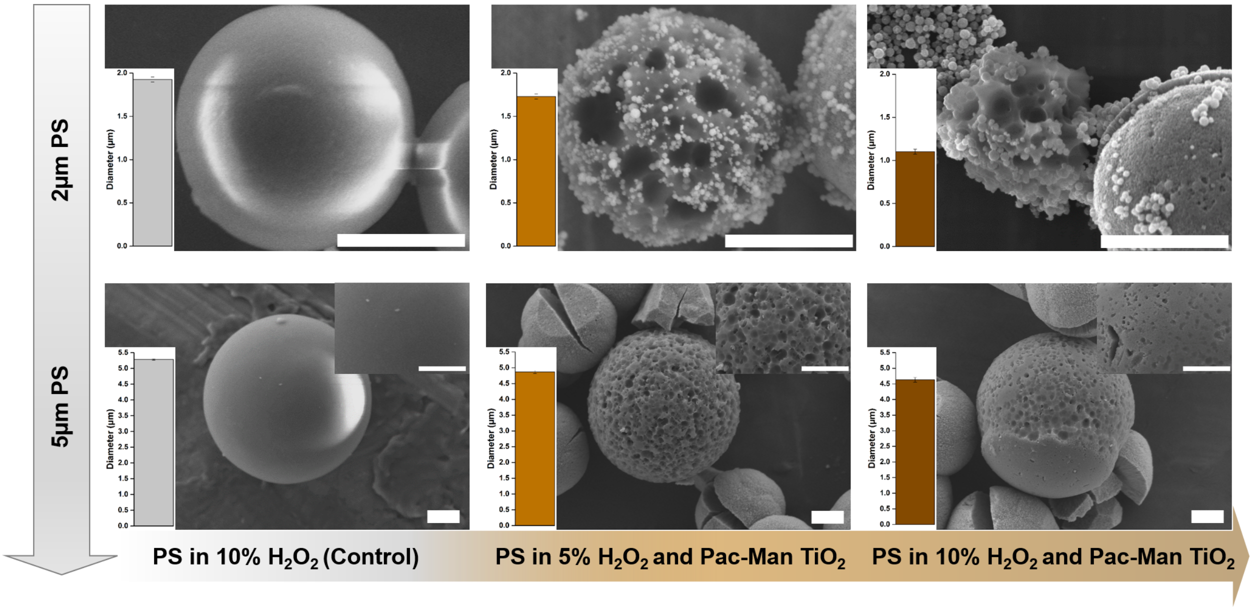


Figure S12: SEM images of 2 µm and 5 µm PS particles comparing the morphological changes in 5 %, and 10 % (w/w) $H_2O_2$ with respect to control in 10 % (w/w) $H_2O_2$. The measurement of average diameter of the PS is given on the left side of every images. The insets in case of 5µm PS particles are the enlarged view of the corresponding SEM images. Scale bar: 2 µm.

## Statistical significance of microplastic degradation experiment

For statistical analysis, the data were used without any pre-processing. The diameter change of PS particles (for at least 35 PS particles) in different condition is evaluated and the data is presented as the average with the standard deviation (avg ± SD).

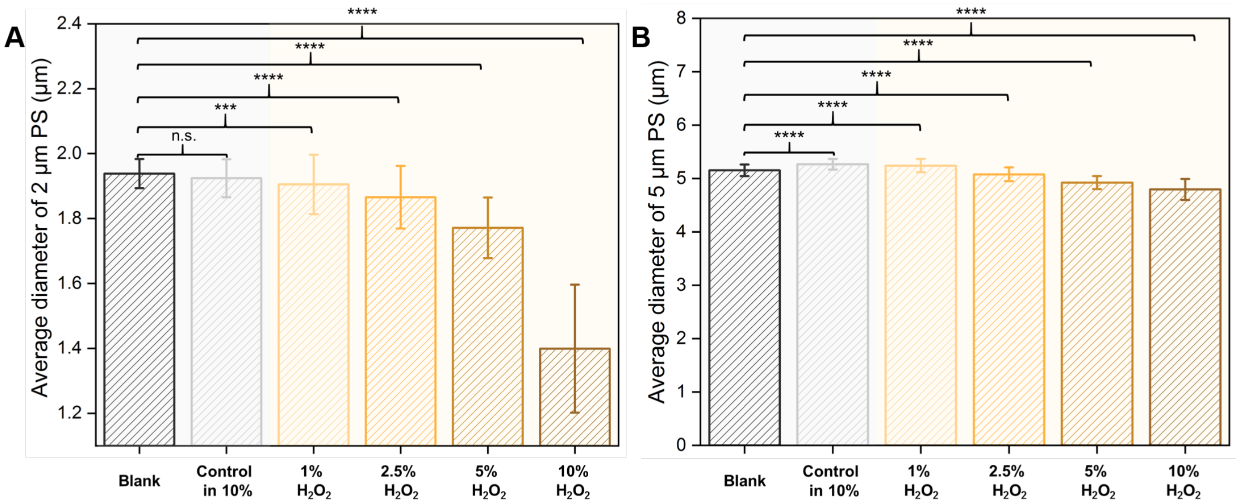


Figure S13: Average diameter change (imaged for 35 different PS samples in SEM) of (A) 2 µm and (B) 5 µm after treating with Pac-Man in different $H_2O_2$ concentrations. Degradation of a blank and control (at the highest $H_2O_2$ concentration of 10 % (w/w)) sample is also compared. A constant degradation time of 70 h is maintained for each case. Concentration of $TiO_2$ and microplastics is $50\,\mathrm{mg\,mL^{-1}}$ and 0.2 wt.%. Statistical treatment was performed with one-way ANOVA test in excel. Data presentation: Avg ± SD. The significance level was set at: **** ($P < 0.0001$); *** ($P < 0.001$); ** ($P < 0.01$); * ($P \leq 0.05$); n.s (statistically non-significant, $P > 0.05$)

## Evaluation based on carbonyl absorption band

The degradation of PS was also monitored by the carbonyl index (CI) study using FTIR measurements. As can be noted from Figure S14, there is a marked tendency between the CI and the peroxide concentration. In comparison to the blank samples, the concentration of PS treated with photocatalyst decreases with increasing peroxide concentration, achieving the highest reduction of $\sim$ 70 % at 10 % $H_2O_2$ in case of 2 µm PS particles (Figure S14A). The extent of reduction is lower in case of 2 µm PS particles reaching around 40 % at the highest peroxide concentration. A reduction of 9 % to 10 % is observed in the control sample at the highest $H_2O_2$ concentration for both sizes of PS. However, it is expected that the degradation of PS will lead to an increase in CI as has been reported before.[3,4] Nakatani *et al.* reported a similar phenomenon while investigating the degradation of PS in water.[5] They observed that the CI fluctuated during the degradation experiments and attributed it to the repetitive oxidation and separation process. Nonetheless, further experiments and tests would be needed to understand our degradation process and the decrease of CI.

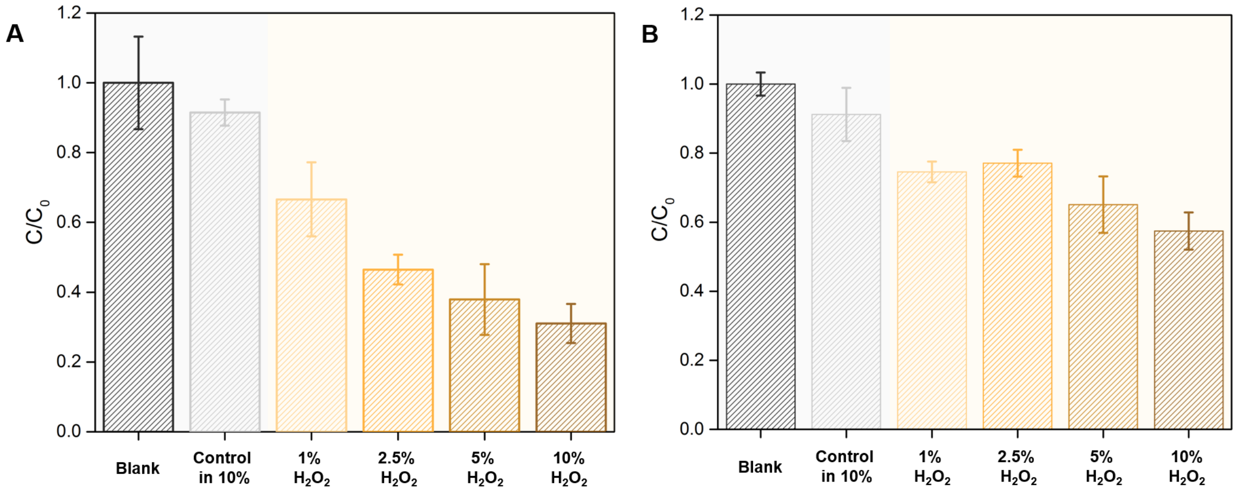


Figure S14: residual concentration obtained from CI study (measured using FTIR), of (A) 2 µm and (B) 5 µm PS particles after treating with Pac-Men $TiO_2$ in different $H_2O_2$ concentrations with respect to the blank PS sample. Degradation of a control sample is also compared at the highest $H_2O_2$ concentration of 10 % (w/w). A constant degradation time of 70 h is maintained for each case. Concentration of $TiO_2$ and microplastics is 50 mg mL$^{-1}$ and 0.2 wt.%. A UV hand lamp of intensity 950 µW cm$^{-2}$ intensity with a wavelength of 365 nm is used.

# References

(1) Othman, S. H.; Rashid, S. A.; Ghazi, T. I. M.; Abdullah, N. Dispersion and stabilization of photocatalytic TiO2 nanoparticles in aqueous suspension for coatings applications. *Journal of Nanomaterials* **2012**, *2012*, 2–2.

(2) Wang, L.; Simmchen, J. Interactions of active colloids with passive tracers. *Condensed Matter* **2019**, *4*, 78.

(3) Kemp, T. J.; McIntyre, R. A. Influence of transition metal-doped titanium (IV) dioxide on the photodegradation of polystyrene. *Polymer degradation and stability* **2006**, *91*, 3010–3019.

(4) Liu, X.; Sun, P.; Qu, G.; Jing, J.; Zhang, T.; Shi, H.; Zhao, Y. Insight into the characteristics and sorption behaviors of aged polystyrene microplastics through three type of accelerated oxidation processes. *Journal of Hazardous Materials* **2021**, *407*, 124836.

(5) Nakatani, H.; Ohshima, Y.; Uchiyama, T.; Motokucho, S. Degradation and fragmentation behavior of polypropylene and polystyrene in water. *Scientific Reports* **2022**, *12*, 18501.