

# Supplementary Content

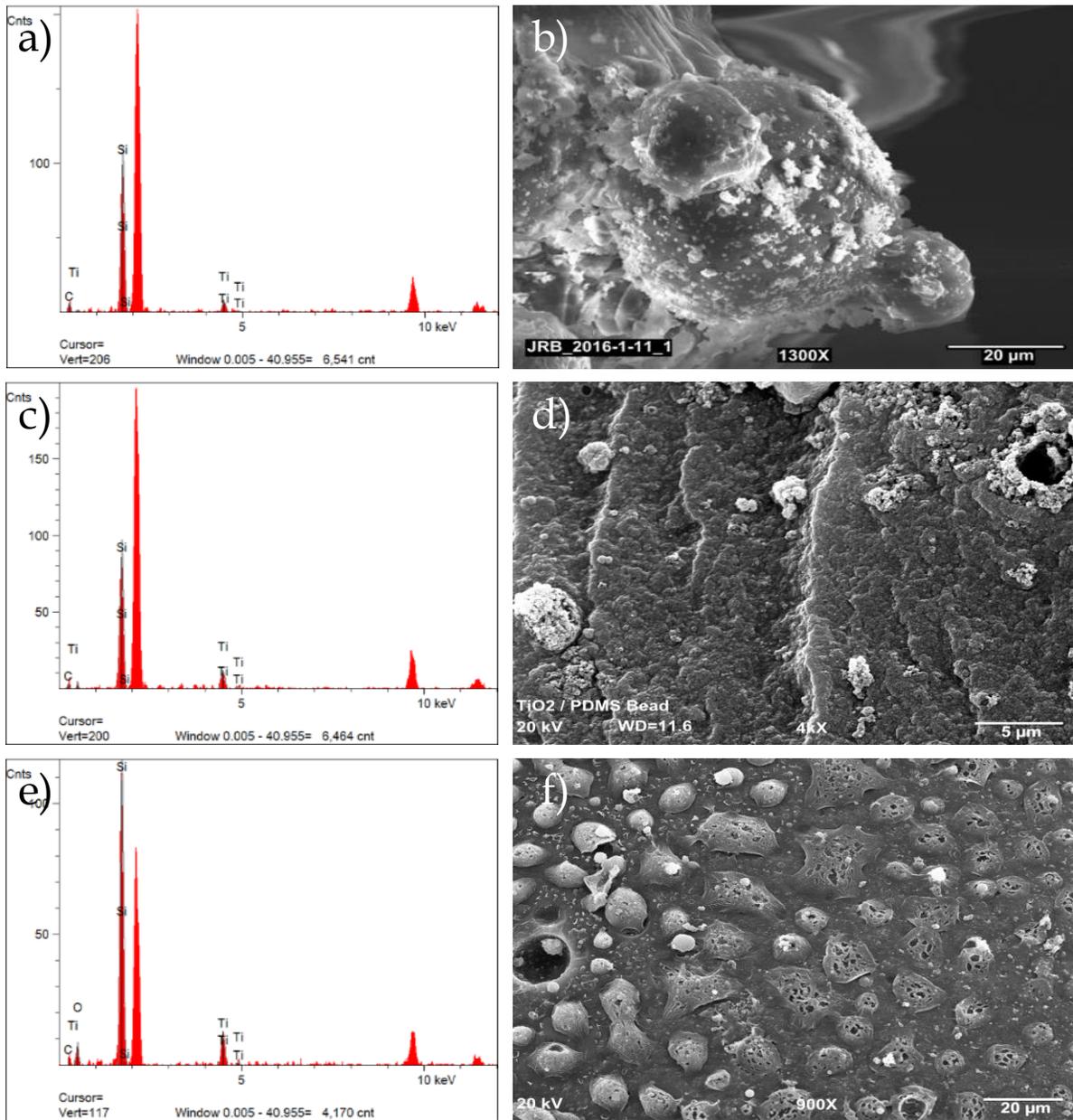
## A Buoyant, Microstructured Polymer Substrate for Photocatalytic Degradation Applications

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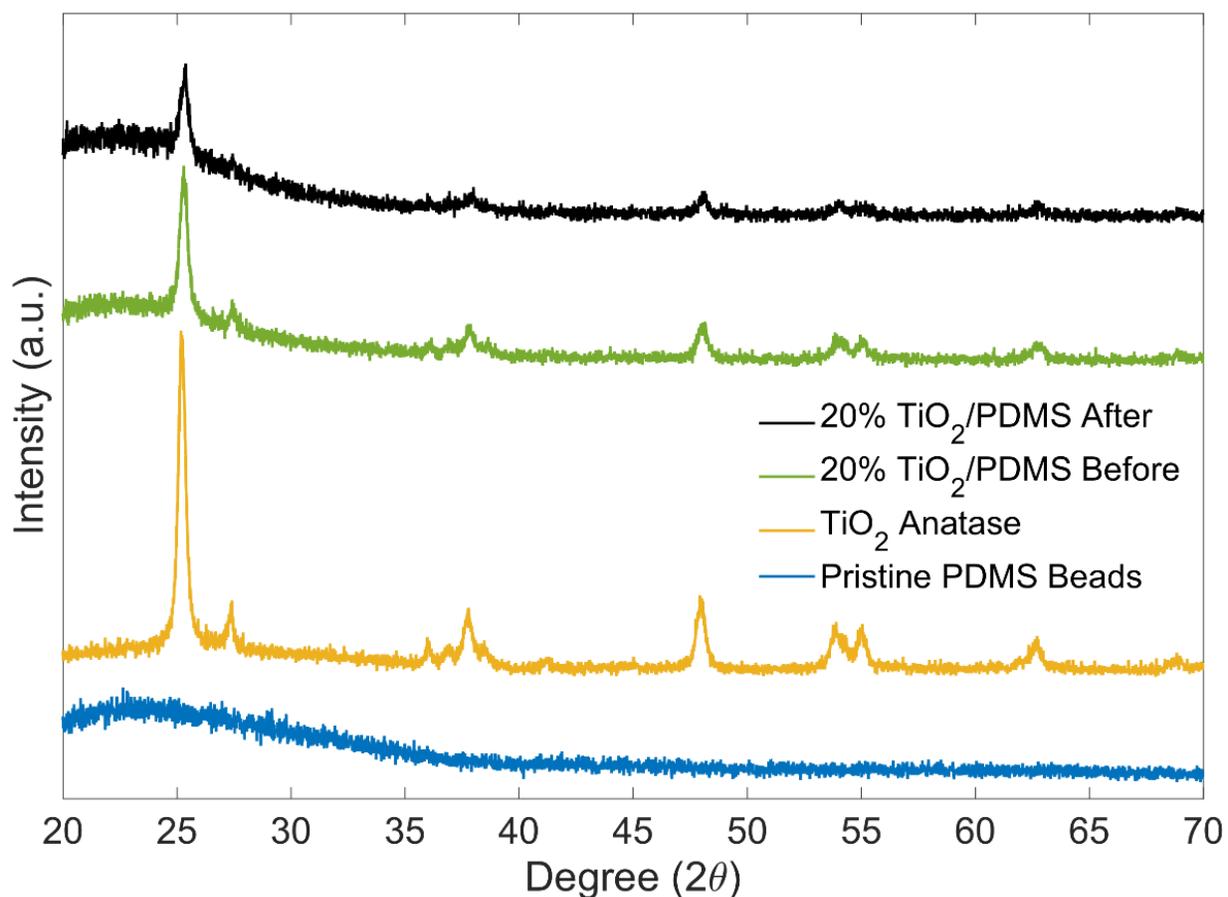
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Presented in this supplemental information are the representative energy dispersive spectra (EDS) along with SEM images of the surface regions analyzed for PDMS beads inoculated with a varying TiO<sub>2</sub> load. Figure S-1 depicts the SEM images and resulting spectra of the buoyant photocatalyst materials in a TiO<sub>2</sub>/PDMS 5% (a, b), 10% (c, d), and 20% (e, f) mass ratio. The mass percent of Ti relative to Si (whose presence is attributed to PDMS) was recorded and reported in Table 1 of the main text. Because site-to-site variance was greater than the instrumental error, uncertainties listed in Table 1 for the Ti/Si ratio are based on standard deviations of values at three different sites. The unlabeled peaks observed at 2.1 keV, 9.7 keV, and 11.3 keV originate from the Au coating applied to the TiO<sub>2</sub>/PDMS beads prior to SEM-EDS analysis.



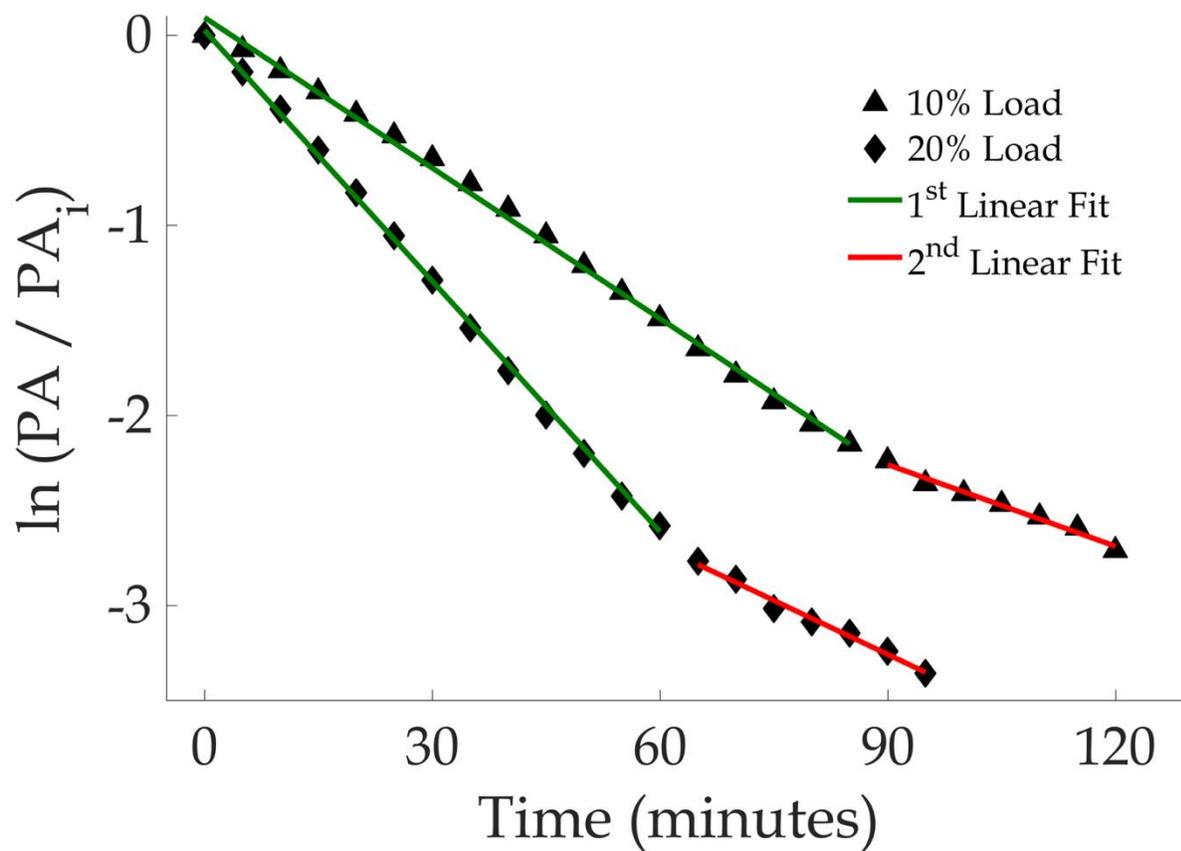
**Figure S-1.** Energy dispersive spectra and corresponding surface SEM images for 5% (a, b) 10% (c, d) and 20% (e, f) TiO<sub>2</sub>/PDMS loads used to assess the extent of photocatalyst load onto the buoyant substrate.

Figure S-2 shows x-ray diffraction data as a function of scattering angle ( $2\theta$ ) for the PDMS beads and anatase  $\text{TiO}_2$ . The somewhat broader peaks are consistent with previous work on nanoscale powders such as the material used for these syntheses. As expected, the PDMS beads do not show any evidence of crystalline structures, but the  $\text{TiO}_2$  peaks are clearly seen in the diffraction from 20%- $\text{TiO}_2$ /PDMS beads, providing clear evidence that the crystallinity is preserved in the synthesis process, and that it is minimally altered by degradation of MB solution under UV irradiation.



**Figure S-2.** XRD data for (bottom to top) pure PDMS beads, pure anatase nanopowder, and 20%  $\text{TiO}_2$  loaded PDMS beads, before and after three cycles of MB degradation.

Figure S-3 shows the multiple linear fits applied to the natural log of the peak area ratio of methylene blue (MB) absorbance found in Figure 3. The first linear fit for each set of data represents the rate constant ( $k_{TOT}$ , Table 1), during which, three phenomena responsible for MB removal are taking place: adsorption, photolysis, and photooxidation. As the reaction proceeds, the adsorption of MB reaches equilibrium and ceases to contribute to its removal. Thus, the second linear region represents a depreciated rate constant consisting of removal by photolysis and photooxidation only ( $k_{TOTeq}$ , Table 1). Based on the kinetic model presented in Eq. 1, when adsorption of MB onto  $TiO_2$  has reached equilibrium, the value of the second slope (red in Figure S-2) should correspond to the sum of  $k'_{PO}$  and  $k'_{hv}$ , which, as is clear in Table 1, it does. The decrease in the removal rate observed relative to the initial linear region was attributed to an established equilibrium between species of MB adsorbed onto the  $TiO_2$  surface and those remaining in solution. Thus,  $k_{TOTeq}$  represents the removal of MB by photolysis and photooxidative species only. Indeed, the sum of  $k'_{PO}$  and  $k'_{hv}$  for 20% and 10% in Table 1 agrees with this kinetic model with  $k_{TOTeq}$  values, lying well within the reported uncertainties of the sum. Assuming that  $[TiO_2]$  and  $[hv]$  are constant for all of our experiments (for a given set of beads, we use the same amount of beads for each trial, and the lamp power is maintained at 300 W for all experiments), we are able to use control experiments to assess the first two terms in Eq. 2, thereby determining  $k_{PO}[Ox]$  by subtraction based on the experimental values. These rate constants, which are the best indicator of absolute photocatalytic degradation activity, are included in Table 1.



**Figure S-3.** First and second linear fits of natural log of the peak area ratio for MB absorption. The negative slope of the first linear fit represents the rate constant  $k_{TOT}$ , while the second represents the rate constant  $k_+$ .