Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Self-Assembled Nanoparticle-Stabilized Photocatalytic Reactors

Thomas Burdyny[1], Jason Riordon[1], Cao-Thang Dinh[2], Edward H. Sargent[2] and David Sinton[*,1]

[1] Department of Mechanical and Industrial Engineering and Institute for Sustainable Energy, University of Toronto, 5 King's College Road, Toronto, ON, Canada, M5S 3G8.

[2] Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario, Canada, M5S 3G4.

[*] Corresponding author: DS sinton@mie.utoronto.ca.

Fluorescent microscopy of Nile red and fluorescein

Photocatalytic degradation of Nile red and fluorescein dyes was observed fluorescently using an inverted fluorescent microscope (DMI 6000B, Leica Microsystems Inc.) while images were captured with a CCD camera (Orca AG, Hamamatsu). Ultraviolet irradiation of the photocatalyst and imaging of the dye degradation was performed using two different filter cubes. The fluorescent images were then adjusted for spatial differences in intensity due to shading using dark and reference images. As dye concentration has been shown to be proportional to the fluorescence intensity, the corrected fluorescent intensities were used to determine the exponential decay of the dyes over time (Fig. S3a). The degradation rate was then found by taking the slope of the logarithmic normalized intensity over time as seen in Fig. S3b.

As a control the same procedures for forming the emulsions were performed without amphiphiles. For the oil-in-water case the emulsions in the control scenario were on the order of 100 μm instead of the 10 - 20 μm in the Pickering emulsions and were seen to coalesce over time. Furthermore, large agglomerates of nanoparticles were witnessed; application of UV light showed that dye degradation occurs preferentially on the portion of the surface where the agglomerations were visible and negligibly on the other surfaces, unlike the diluted Pickering emulsions where degradation occurred uniformly.

Spectrometer measurements of methylene blue

Methylene blue concentration was determined by measuring the absorbance of samples at 664 nm using a spectrometer (BRC112E-USB-VIS/NIR, Edmund Optics Inc.), coupled with a light source (SLS201, Thorlabs Inc.) and deionized water as a reference. Each measurement used a reference curve taken at the same time to remove any variability in the spectrometer measurement over time.

The Beer-Lambert law was then used to convert absorbance into methylene blue dye concentration using a cuvette path length of 1 cm and a molar extinction coefficient of 74028 cm^{-1} M^{-1} at 664 nm. Prior to measuring the absorbance spectrum the samples were centrifuged and run through a 0.22 μm filter to remove any nanoparticles present in the fluid. An example of a typical absorbance spectrum and accompanying concentration change over time is found in Fig. S6 for the case of an aqueous suspension batch reactor with mild agitation.

Fig. S1: Picture of nanoparticle-stabilized photocatalytic emulsions sitting at the top of a 250 mL beaker. The amount produced is directly scalable to the quantity of materials.

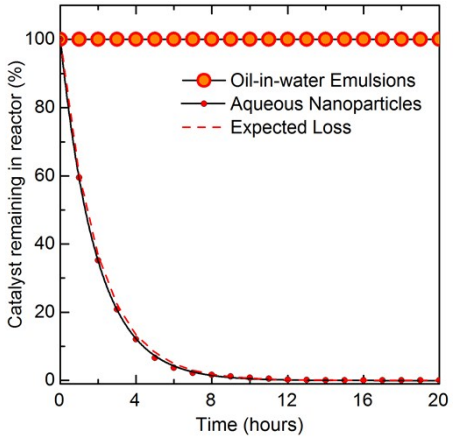

Fig. S2: Comparison of total nanoparticle retention for the SNPR and aqueous suspension in the continuous reactor process over time.

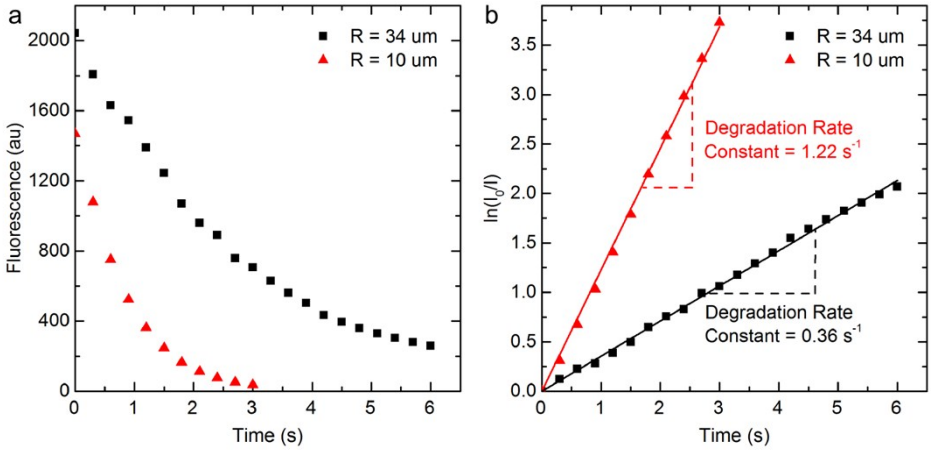

Fig. S3: Fluorescent degradation of Nile red dye in individual photocatalytic nanoparticle-stabilized oil-in-water droplets of radius 34 μm and 10 μm showing the a) change in fluorescence and b) normalized intensity giving first-order degradation rates.

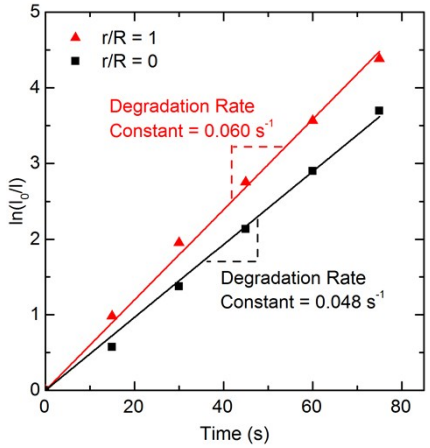

Fig. S4: Degradation rate of Nile red dye at the centre ($r/R = 0$) and edge ($r/R = 1$) of a photocatalytic nanoparticle-stabilized oil-in-water droplet.

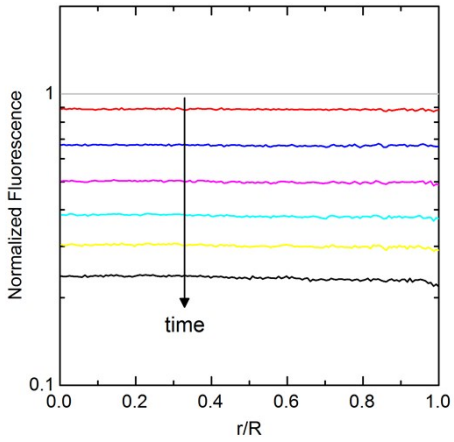

Fig. S5: Spatial photocatalytic degradation of fluorescein dye inside a photocatalytic nanoparticle-stabilized water-in-oil droplet.

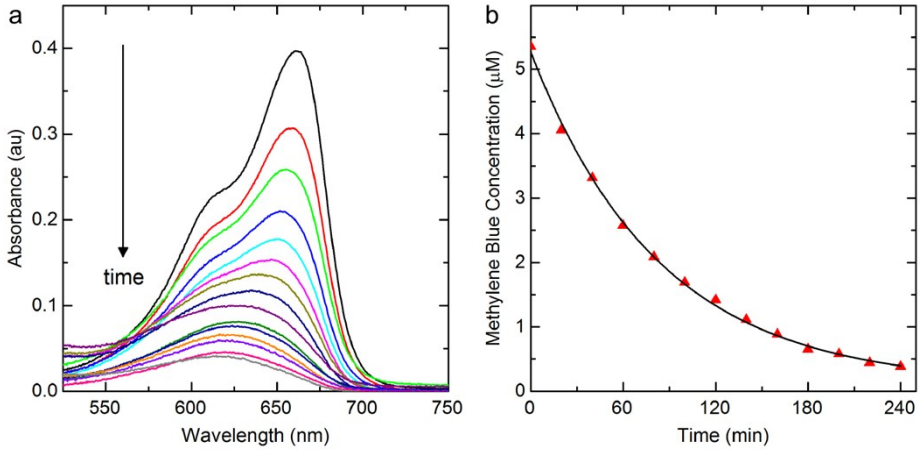

Fig. S6: The a) time dependent methylene blue absorbance spectrum and b) exponential decay curve at 664 nm for the photocatalytic degradation of methylene blue in a fixed-photocatalyst batch reactor of sedimented nanoparticles under mild agitation.