Supplementary Information

Biomimetic Photocatalytic Reactor with a Hydrogel-Embedded Microfluidic Network

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Description of the simulation for the reagent transport in the hydrogel microfluidic device. The time-dependent distribution profiles of reagent concentration in the top-viewed device (2D geometry) were calculated by using the common equation

$$\frac{\delta c}{\delta t} = -v\nabla c + D\nabla \bullet \nabla c$$

where c is the concentration of reagent, D is the diffusion coefficient of the reagent (1×10^{-10} m^2/s, which of the order of magnitude of the values for large dye molecules in the literature[1] and v is the velocity of fluid. The velocity of fluid through the porous media and in the nonporous media was obtained from the preceding simulation by using the Brinkman equation and the Navier-Stokes equations for incompressible fluid

$$\frac{\eta}{k}\vec{v} = \nabla\cdot\left\{-\vec{p} + \frac{\eta}{\varepsilon_p}(\nabla\vec{v} + (\nabla\vec{v})^T)\right\} \quad \text{(in porous media)}$$

$$\rho\vec{v}\cdot\nabla\vec{v} = \nabla\cdot\left\{-\vec{p} + \eta(\nabla\vec{v} + (\nabla\vec{v})^T)\right\} \quad \text{(in nonporous media)}$$

$$\nabla\cdot\vec{v} = 0 \quad \text{(in all media)}$$

where η is the viscosity of the solutions (1×10^{-3} Pa·s), ρ is the density of the solvent (1×10^{3} kg/m^3 for water), k is the permeability of the agarose gel (5.82×10^{-16} m^2)[2] and ε_p is the porosity of the gel (0.98). The volume fraction of the agarose in the hydrated gel is almost the same as its mass fraction.[3] The inlet boundary conditions are a constant pressure of 3×10^3 Pa and a concentration of 0.4 mol/m^3. The outlet boundary conditions are zero pressure and conserved convective flux. The time-lapse results from the COMSOL™ numerical simulation of the dye transport in the gel reactor are illustrated in **Movie 1** and compared to the experimental results in **Fig. S2**.

Supporting Figures

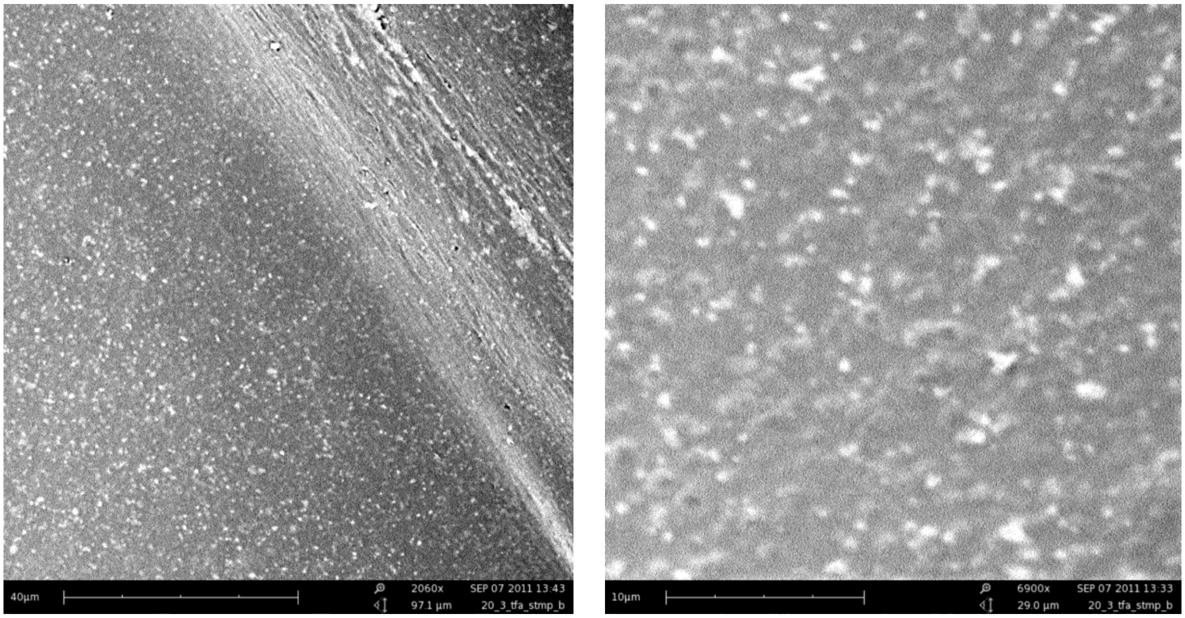

Fig. S1 SEM images of the dried agarose gel with the embedded TiO_2 particles. Note that the sub-micron clusters of the TiO_2 catalyst are uniformly dispersed throughout the gel matrix.

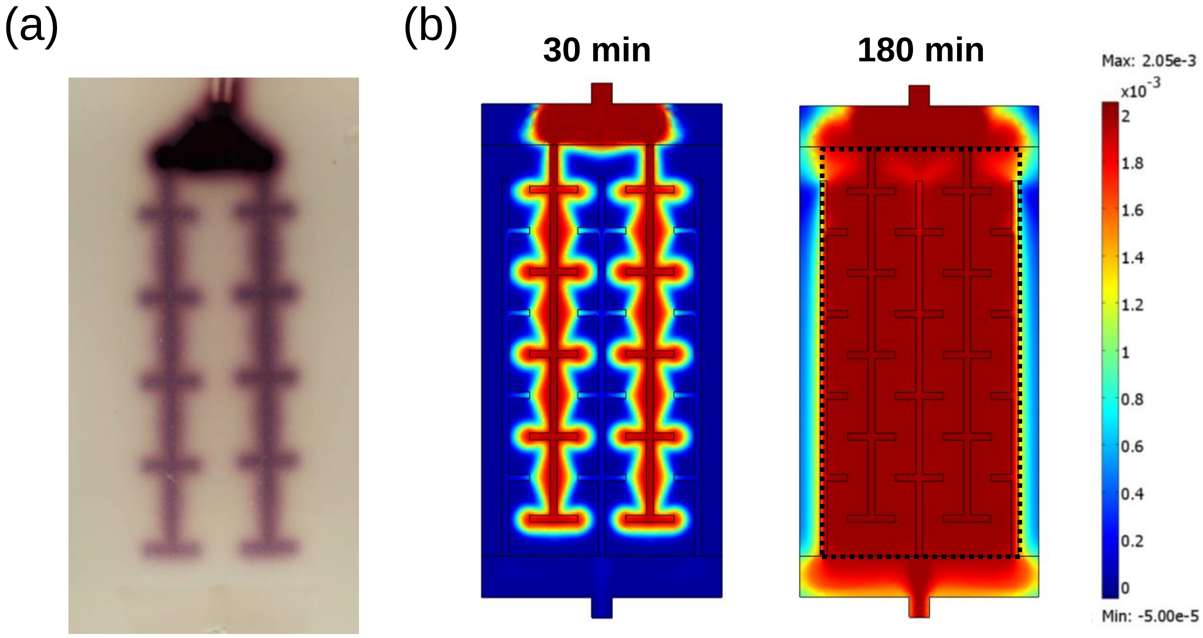

Fig. S2 (a) Experimental image of the dye distribution after injection for 30 min. (b) Simulation result for the dye penetration through the gel-microvascular network after dye injection for 30 min and 180 min. The unit of the dye concentration is mol/m^3. The dotted rectangle in (b) surrounds the “reaction area” through which most of the dye solution flows under illumination.

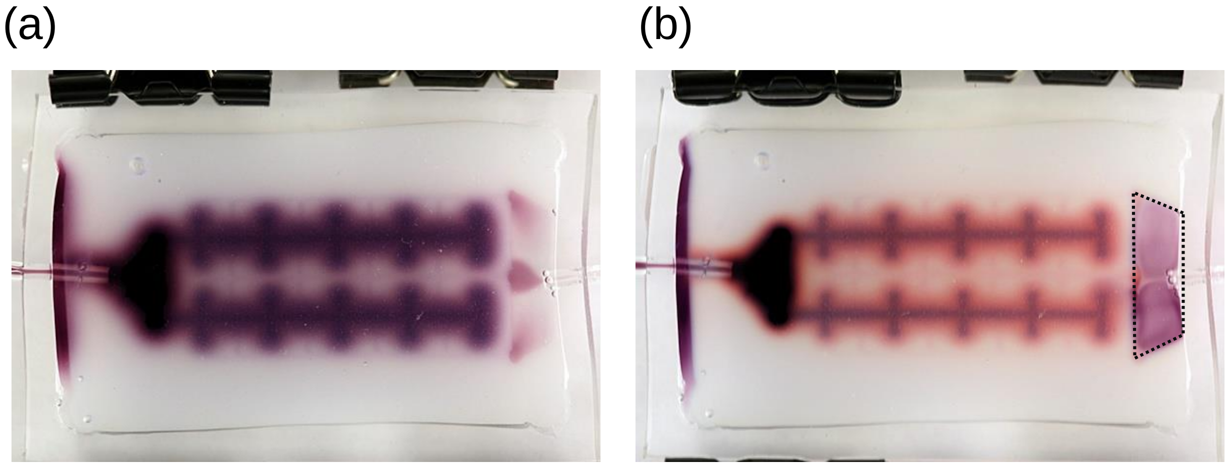

Fig. S3 Partial degradation of the Methylene Blue and Allura Red dye in the light-driven gel reactor (a) before and (b) after UV illumination for 3 min. The dye solutions were continuously supplied during the UV illumination. The concentration of both dyes in the mixed solution is 1 mM. The area surrounded by the dotted line is a non-reactive region, where the photocatalytic reaction does not take place because of the absence of TiO_2 catalyst.

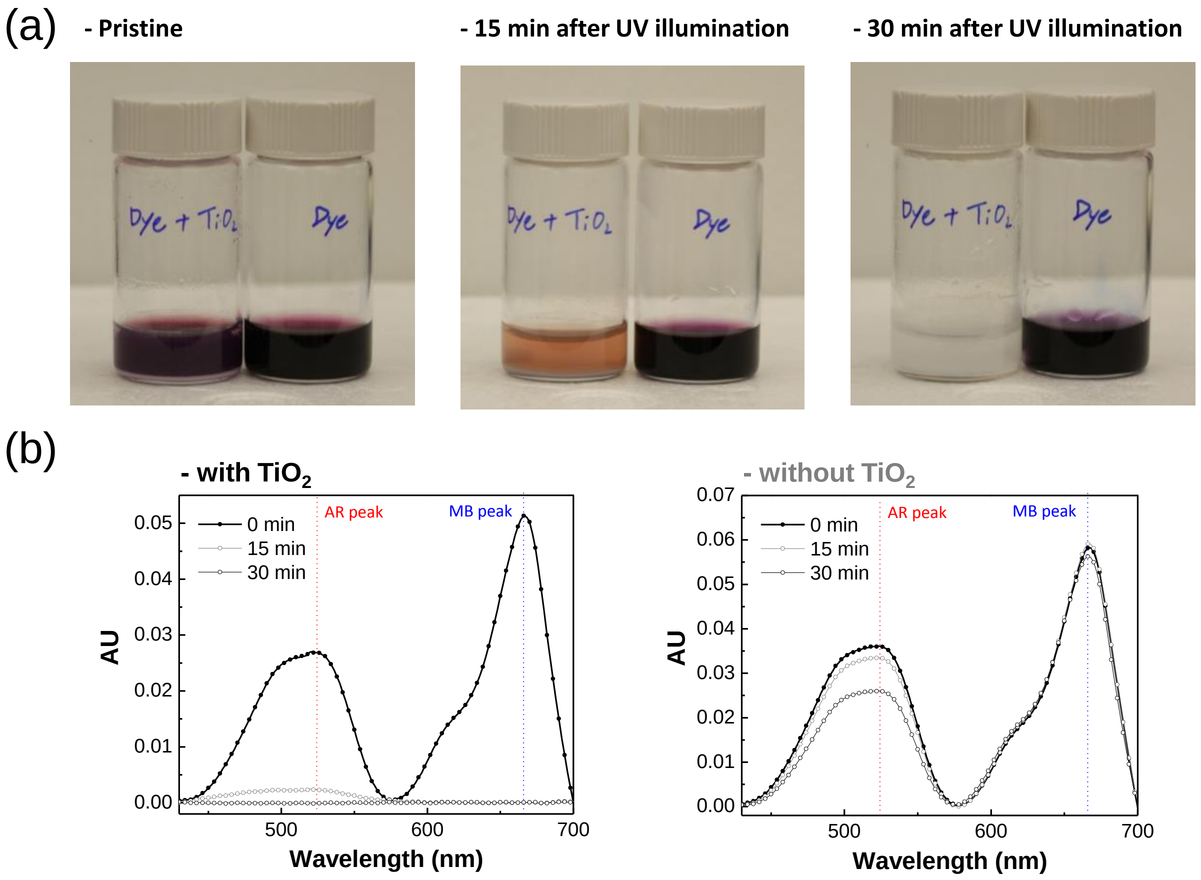

Fig. S4 (a) Effect of the presence of TiO_2 particles on the color change of the solution of Allura Red and Methylene Blue dye mixture under UV illumination. (b) UV-vis absorption spectra of the dye solutions in (a). The absorbance of both dyes with TiO_2 catalysts drastically decreases under UV illumination. Thus, TiO_2 particles facilitate the degradation of the dyes even though a slight degradation of the Allura Red in the dye solution without TiO_2 catalyst was observed. The Allura Red dye may be more susceptible to UV degradation.

Evaluation of the rate of the photocatalytic degradation of the dye molecules in the TiO_2-hydrogel reactor

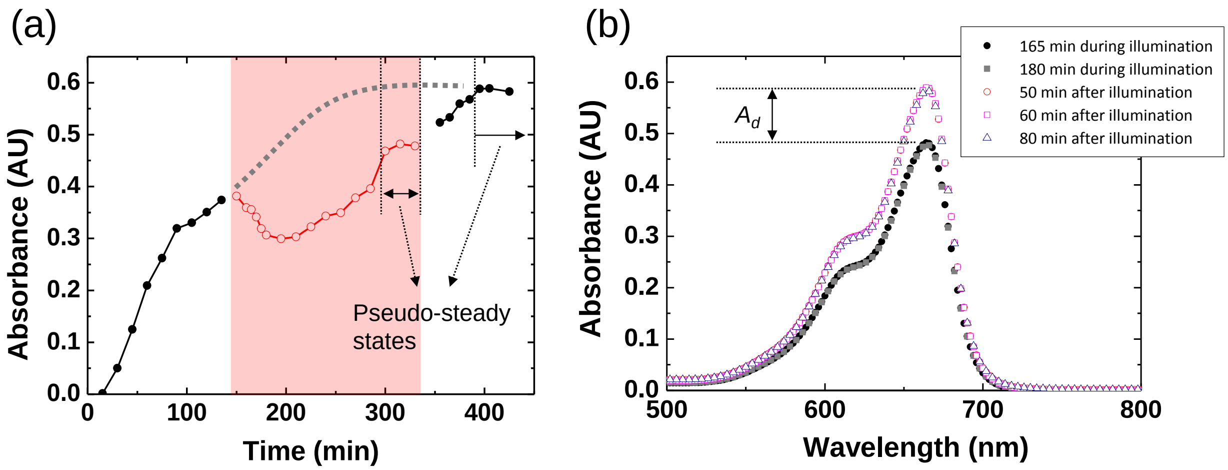

Fig. S5 UV-vis absorbance of the solution exiting the TiO_2-hydrogel reactor as a function of (a) time and (b) UV-vis spectra at the “Pseudo-steady states”. The device was illuminated from 145 min to 330 min indicated by the red-colored box. The light was incident from the channel side of the microfluidic device. The collected solution was diluted before UV-vis absorption measurement at 640 nm. It was confirmed that the absorbance intensity is linearly proportional to the concentration of the dye solution in the concentration regime used for the measurement.

The number of the degraded molecules was calculated from the difference of the UV-vis absorbance intensity of the solutions exiting the TiO_2-hydrogel reactor between in dark and under illumination. We continuously injected a solution of 5 mM Methylene Blue dye into the gel reactor, which was illuminated with a solar simulator. The position of the absorbance peak intensity of the Methylene Blue coming out of the gel reactor is shown in Figure S5(a). The peak intensity decreases with the light illumination starting at 145 min due to photocatalytic degradation. The absorbance peak intensity is stabilized after 300 min, when a “pseudo-steady state” is established. When the illumination stops at 330 min, the absorbance peak intensity increases again, because of the termination of the photocatalytic reaction. The rate of the photocatalytic degradation of the dye molecules in the TiO_2-hydrogel reactor can be calculated by the expression

$$Rate\ of\ the\ photocatalytic\ degradation\ of\ the\ dye = Rate\ of\ the\ supply\ of\ the\ dye\ \times \frac{A_d}{A_0}$$

where A_0 is the UV-vis absorbance of the pristine stock dye solution and A_d is the difference between the absorbance of the UV-degraded dye solutions and the non-degraded dye solutions under pseudo-steady state, as shown in Figure S5(b). A_0 and A_d were 0.786 and 0.111, respectively. Since the rate of the supply of the Methylene Blue dye molecules at 10 μL/min injection rate is 5.02×10^{14} molecules/s, the evaluated rate of the dye degradation in the gel reactor is 7.09×10^{13} molecules/s. Since the number of the incident photons from the solar simulator to activate the TiO_2 particles ($\lambda \leq 387.5$ nm) is 2.85×10^{16} s^{-1}, the apparent quantum efficiency is

$$\frac{7.09\times10^{13}\,molecules/s}{2.85\times10^{16}\,photons/s}\times100\cong0.25\%$$

Two reactions may lead to the photobleaching of Methylene Blue by the illuminated TiO_2 catalysts.[4]

$$\text{Methylene Blue} + 25.5\ O_2 \rightarrow HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \qquad (1)$$

$$\text{Methylene Blue} + \text{SED (sacrificial electron donor)}$$
$$\leftrightarrow \text{Leuco-Methylene Blue (colorless)} + SED^{2+} \qquad (2)$$

Reaction (1) is an irreversible reaction for the complete mineralization of Methylene Blue and Reaction (2) is a reversible transformation between colored and leuco form of Methylene Blue. Reaction (1) requires 102 oxidizing equivalents to totally mineralize one Methylene Blue molecule.[4] When only the reaction (1) is taken into account, the maximum possible quantum efficiency is 25%. It should be noted that this value could be slightly overestimated if the reaction (2) occurred in the reactor and partially contributed to the photobleaching of Methylene Blue. Water or Methylene Blue might act as SED for the reaction (2).

References

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