

Supplementary information for

Construction of a multipurpose photochemical reactor with on-line
spectrophotometric detection

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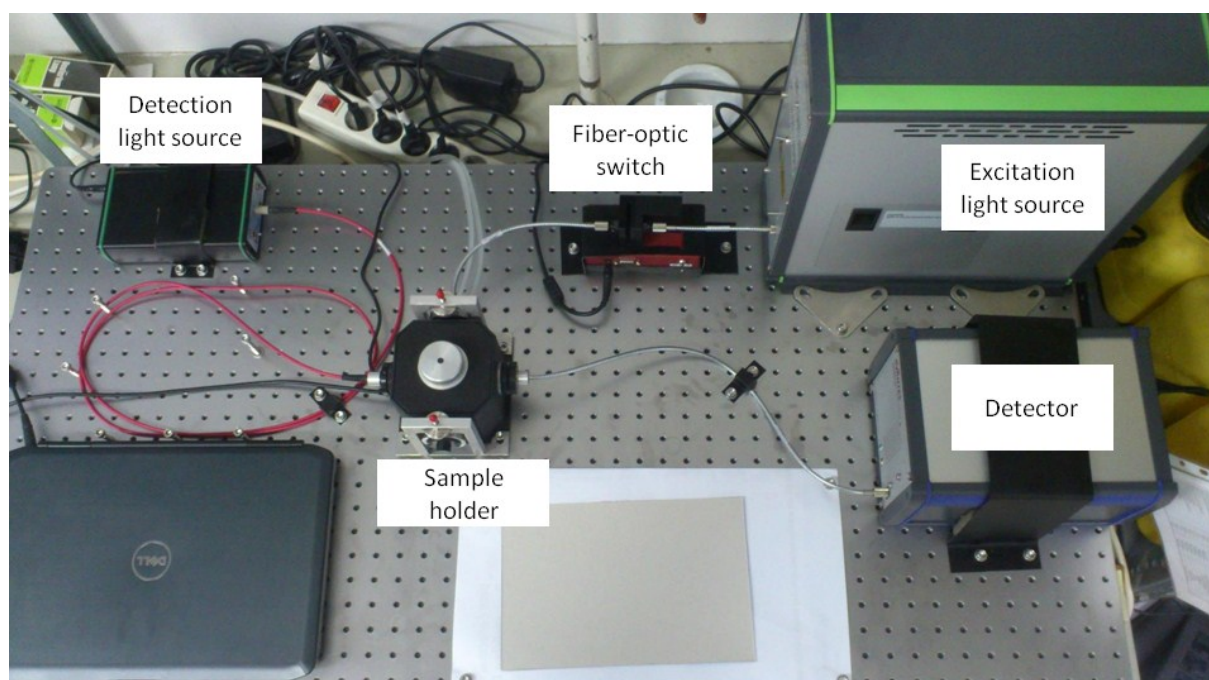


Fig. S1 Photograph of the photoreactor.
Note: the attenuator is not present in this setup.

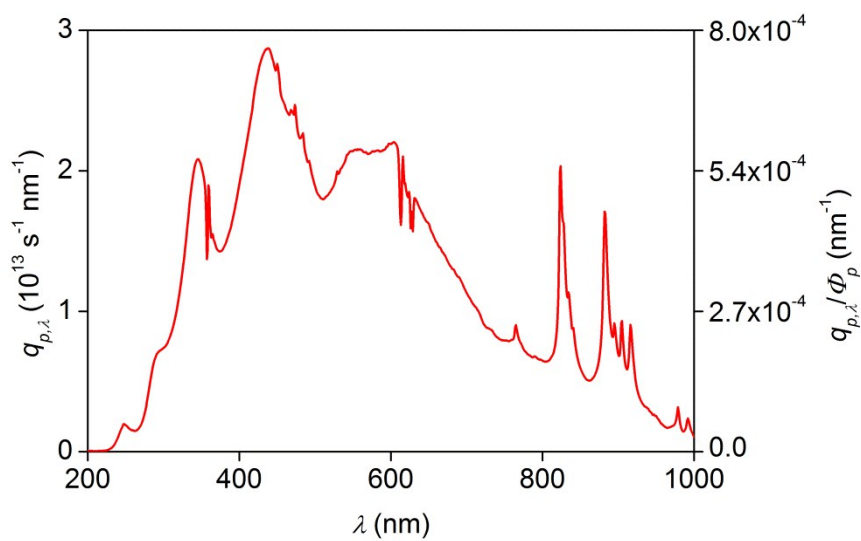


Fig. S2 Spectral photon flux of the excitation lamp as a function of wavelength as determined by relative energy measurements and actinometry (Φ_p : total photon flux of the lamp).

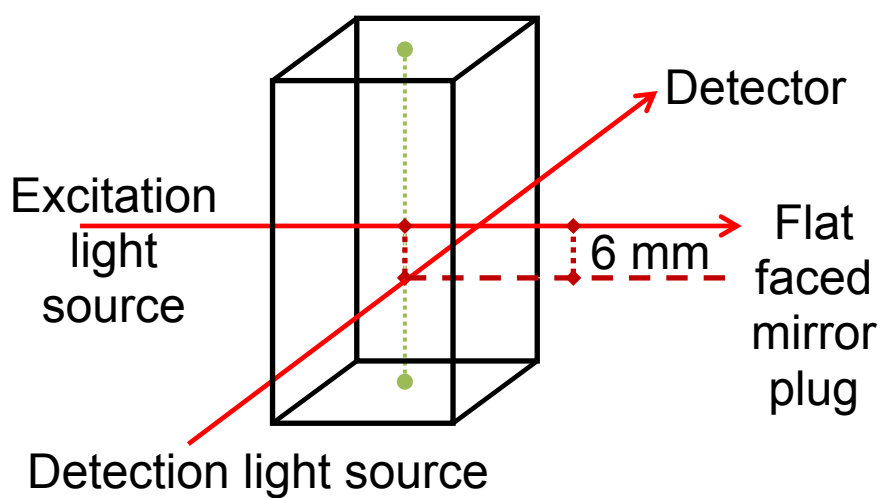


Fig. S3 Separation of the detection and excitation planes inside the cuvette.

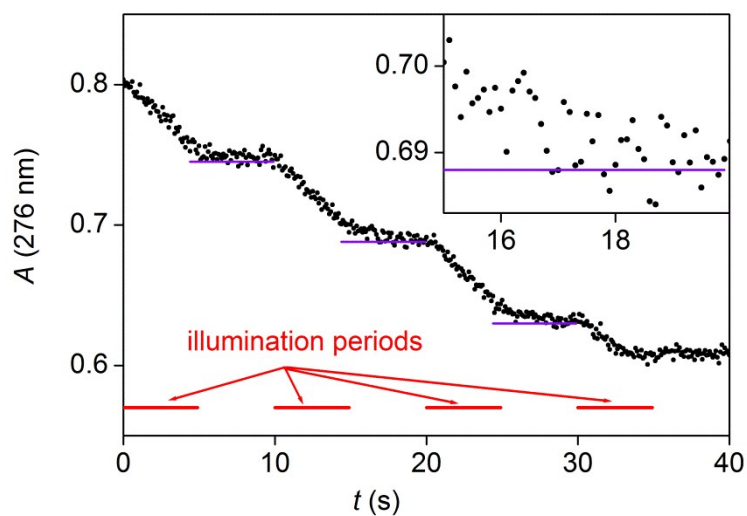


Fig. S4 Disappearance of aqueous sulfur(IV) in the photoinitiated and cerium(III)-catalyzed autoxidation of $\text{H}_2\text{O} \cdot \text{SO}_2$ detected at 276 nm. $[\text{Ce(III)}] = 1.0 \text{ mM}$; $[\text{S(IV)}] = 2.0 \text{ mM}$; $[\text{H}_2\text{SO}_4] = 0.10 \text{ M}$; $[\text{O}_2] = 0.20 \text{ mM}$; path length: 1.00 cm ; $V = 3.00 \text{ cm}^3$; $T = 25.0 \text{ }^\circ\text{C}$; stirring: 800 rpm . Illumination pattern: 5 s periods of illumination (marked with red line) followed by 5 s of dark periods. (Inset: a closer view of the dark period between 15 and 20 s).

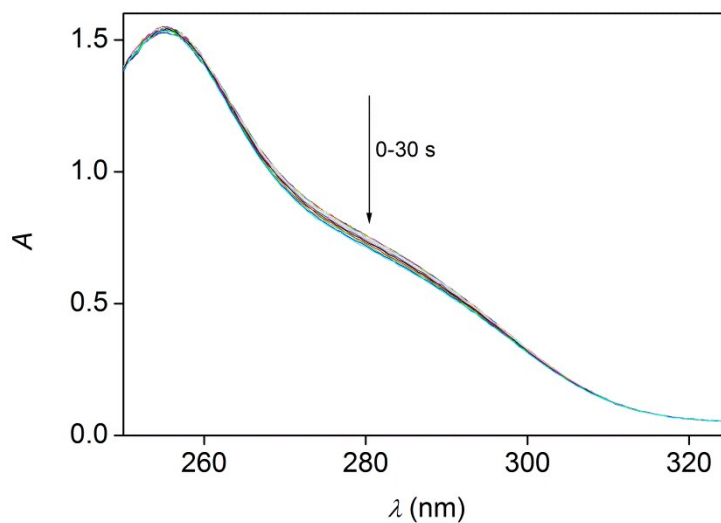


Fig. S5 Spectral changes observed during photoinitiated and cerium(III)-catalyzed autoxidation of $\text{H}_2\text{O} \cdot \text{SO}_2$. $[\text{Ce(III)}] = 1.0 \text{ mM}$; $[\text{S(IV)}] = 2.0 \text{ mM}$; $[\text{H}_2\text{SO}_4] = 0.10 \text{ M}$; $[\text{O}_2] = 0.20 \text{ mM}$; path length: 1.00 cm ; $V = 3.00 \text{ cm}^3$; $T = 25.0 \text{ }^\circ\text{C}$; stirring: 800 rpm .

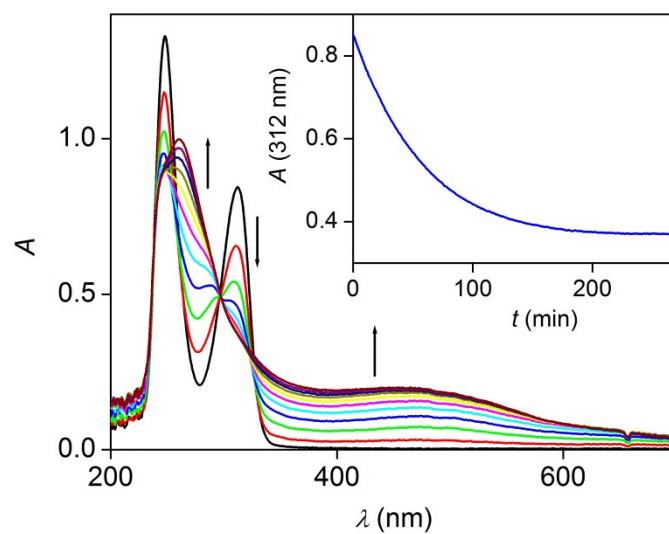


Fig. S6 Direct photochemical degradation of 2,4,6-trichlorophenol (TCP) in aqueous solution. [TCP] = 0.20 mM; [phosphate buffer] = 10.0 mM; path length: 1.00 cm; $V = 3.00 \text{ cm}^3$; $T = 25.0 \text{ }^\circ\text{C}$; stirring: 800 rpm. Inset: kinetic trace measured at 312 nm.

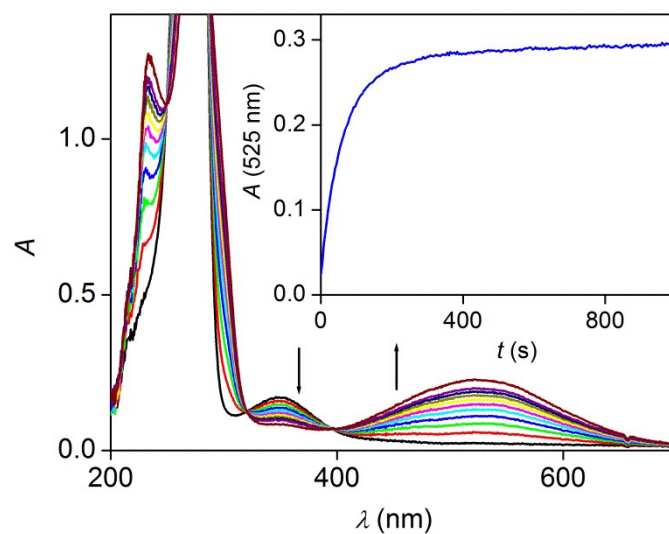


Fig. S7 Photochemical degradation of 2,6-dichloro-1,4-benzoquinone (DCQ) in aqueous solution. [DCQ] = 0.31 mM; path length: 1.00 cm; $V = 3.00 \text{ cm}^3$; $T = 25.0 \text{ }^\circ\text{C}$; stirring: 800 rpm. Inset: kinetic trace measured at 525 nm.

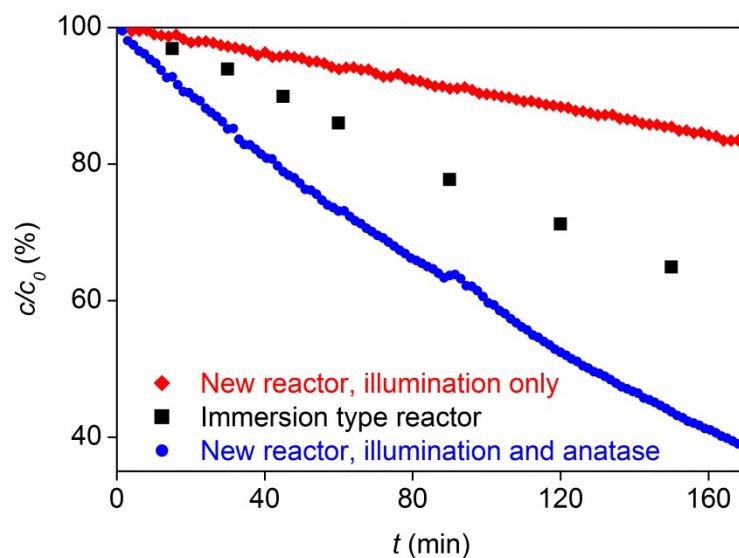


Fig. S8 Degradation of methylene blue under different conditions, 1.0 L of 50 μM MB irradiated by medium pressure mercury lamp (■), 2.00 cm^3 of 40 μM MB in the constructed photoreactor (●), 2.00 cm^3 of 30 μM MB with 114 μg anatase in the constructed reactor (▲). Path length: 1.00 cm; $V = 2.00 \text{ cm}^3$; $T = 25.0 \text{ }^\circ\text{C}$; stirring: 1000 rpm.

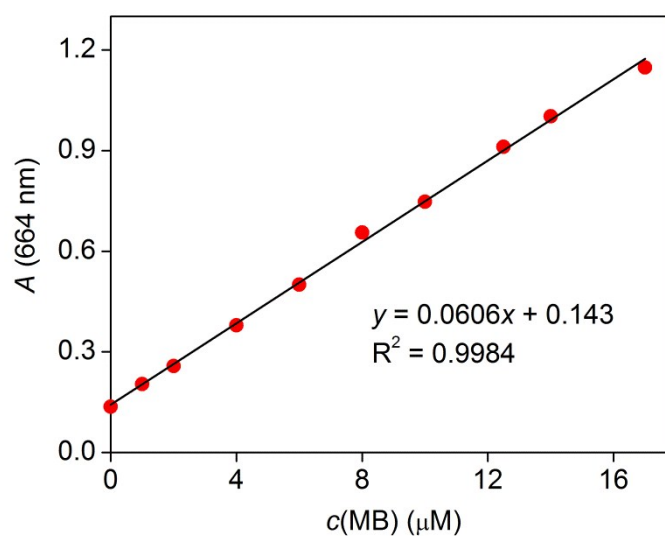


Fig. S9 Beer's plot for methylene blue in the presence of suspended anatase. $c(\text{TiO}_2) = 50.2 \mu\text{g/mL}$, pH 7.15 (10.0 mM phosphate buffer), $T = 25.0 \text{ }^\circ\text{C}$; stirring: 1000 rpm.

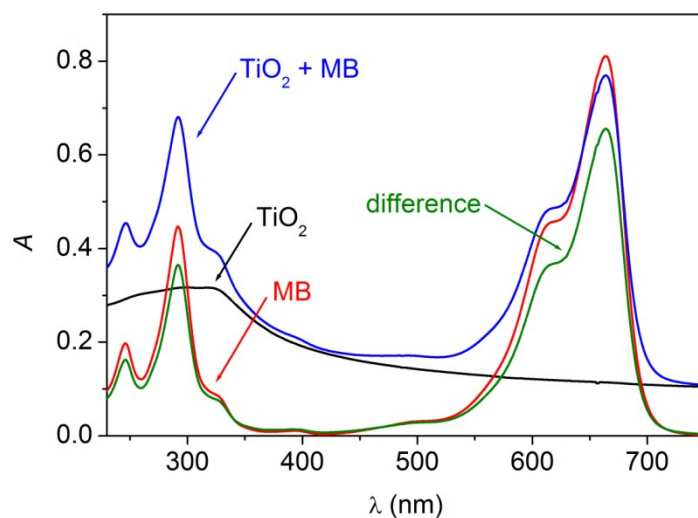


Fig. S10 Demonstration of the lack of additivity of absorbance values in the heterogeneous system containing anatase and methylene blue in a Agilent 8453 diode array spectrophotometer (stirring: 1000 rpm). MB: homogeneous solution of methylene blue; TiO_2 : suspension of anatase in water; $\text{TiO}_2 + \text{MB}$: suspension of anatase in a solution of methylene blue; difference: the difference of spectra $\text{TiO}_2 + \text{MB}$ and TiO_2 .

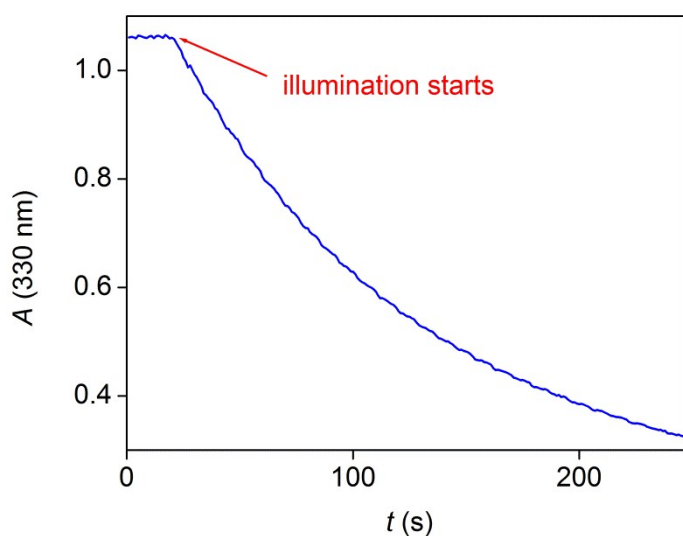


Fig. S11 Kinetic trace observed at 330 nm during the illumination of the actinometric solution. The illumination started after a 30-second initial dark period. 15 mg of solid $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ was dissolved in 25 cm^3 of 0.050 M H_2SO_4 to prepare the actinometric solution, 2.50 cm^3 of which was irradiated for 250 s in the experiment shown. $T = 25.0^\circ\text{C}$; stirring: 800 rpm.

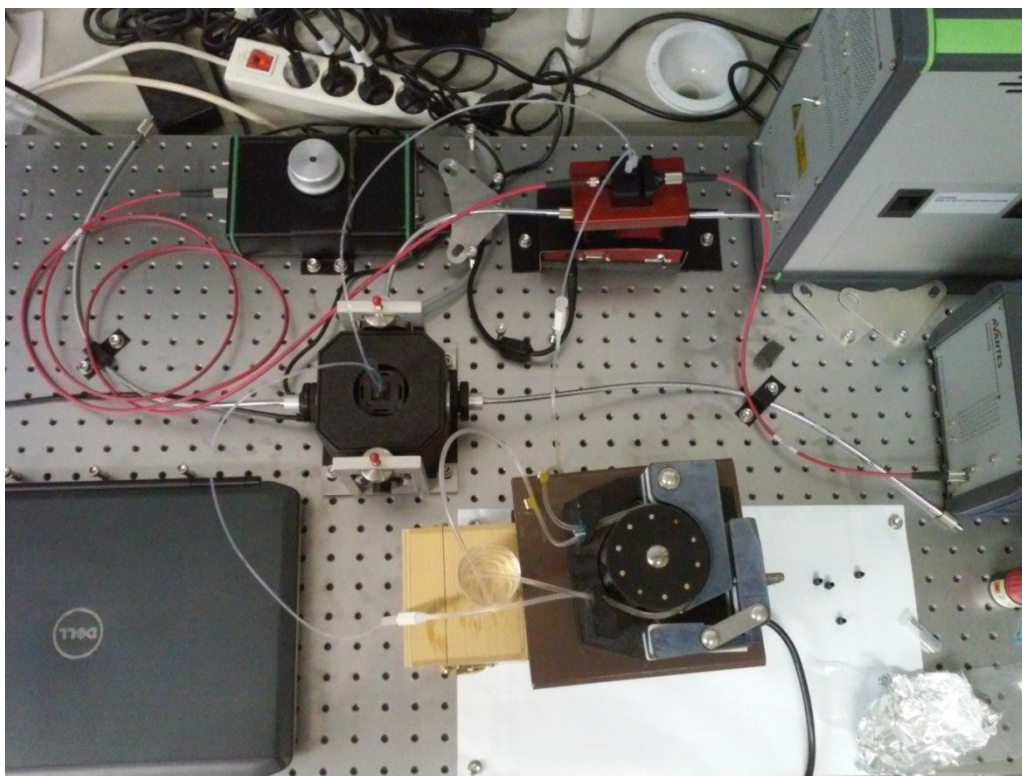


Fig. S12 Photo of the experimental setups with flow-through arrangement

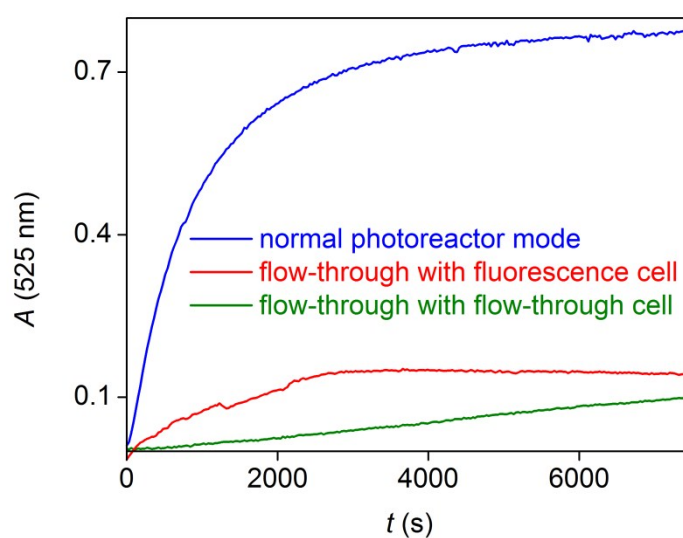


Fig S13 Kinetic traces detected during the demonstration experiments using the flow-through setup of the instrument. Test reaction: $\text{Ru}(\text{bipy})_3^{2+}$ -sensitized aqueous photochemical oxidation of 2,4,6-trichlorophenol (TCP) in the presence of $\text{S}_2\text{O}_8^{2-}$ as an oxidant. $[\text{K}_2\text{S}_2\text{O}_8] = 20 \text{ mM}$; $[\text{HCl}] = 1.0 \text{ mM}$; $[\text{Ru}(\text{bipy})_3^{2+}] = 3.33 \text{ }\mu\text{M}$; $[\text{TCP}] = 0.56 \text{ mM}$; path length 1.00 cm ; $T = 25.0 \text{ }^\circ\text{C}$. Flow rate (for red and green curves: $3.53 \text{ cm}^3/\text{min}$; ; stirring (for blue and red curves): 800 rpm .