

Supporting Information

Thermoresponsive Polymer Brush Photocatalytic Substrates for Wastewater Remediation

Kirsten Bell,^a Yiwen Guo,^a Samuel Barker,^a Seong H. Kim,^{a,b,c} Christian W. Pester^{*,a,b,c}

^a Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA.

^b Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA.

^c Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA.

Table of Contents

General Material and Reagent Information	2
General Analytical Information.....	2
Surface Functionalization	3
<i>General procedure for the synthesis of a RAFT CTA surface initiator</i>	<i>3</i>
<i>General procedure for the functionalization of planar substrates.....</i>	<i>4</i>
<i>General procedure for the functionalization of glass beads</i>	<i>5</i>
Synthesis of Dual Responsive Polymer Brush Functionalized Substrates	5
<i>Random Copolymerization p(FIA-co-NIPAAm).....</i>	<i>5</i>
<i>Thermal SI-RAFT Polymerization on wafers for LCST control experiments - PNIPAAm.....</i>	<i>6</i>
<i>Thermal SI-RAFT Polymerization on wafers for LCST control experiments - PFIA</i>	<i>6</i>
Surface characterization of Dual Responsive Polymer Brush Functionalized Substrates	9
Dual responsive heterogeneous catalysis for wastewater treatment	12
<i>Degradation of tetracycline hydrochloride (TC).....</i>	<i>12</i>

General material and reagent information

(3-Aminopropyl)triethoxysilane (APTES), fluorescein *o*-acrylate, *N*-isopropylacrylamide (NIPAAm), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride, 2,2'-azobis(2-methylpropionitrile) (AIBN), tetracycline hydrochloride (TC) were purchased through Sigma Aldrich. 4-Cyano-4-[dodecylsulfanylthiocarbonyl]sufanyl] pentanoic acid (CDTPA) was purchased through Boron Molecular. Sulfuric acid (98%) was purchased through VWR and used as received. Glass beads, acid-washed $\leq 106 \mu\text{m}$ were purchased through Sigma Aldrich and used as received. The solvent anhydrous dimethylformamide (DMF) was purchased through Sigma Aldrich and stored in a nitrogen atmosphere glovebox. The solvents toluene, dichloromethane (DCM), acetone, ethyl acetate, hexane, isopropanol, and methanol were used as received from Sigma Aldrich. The solvent ethanol was purchased through VWR and used as received. Deionized water (DIW) used was from in house at the Pennsylvania State University's Chemical and Biomedical Engineering building. Silicon wafers with native oxide (1.55 nm) layer was purchased from WaferPro, LLC (San Jose, CA). Glass slides were purchased through Chemglass with a thickness of 1/8" and cut to desired size. LED light strips ("30/m 5050 flexible LED strip, 12V") in natural white were purchased through LEDlightinghut.com. The LED light intensity was controlled via a "LED strip light dimmer, DC 12V-24V dimmer switch for single color strip lights" purchased through Amazon. Lux light intensity was determined with the "Trendbox Digital Light Meter Tester Luxmeter Luminometer Photometer High Accurate 200000 Lux/FC HS1010A with LCD Display Handheld Portable" purchased through Amazon.com at the center of the light bath. The reactions were heated via GE 250-watt dimmable R40 heat lamp incandescent light bulbs purchased from Lowes.

General analytical information

Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVIII-HD-500. All ^1H NMR experiments are reported in δ units, parts per million (ppm), and were normalized to the signal for deuterated solvent DMSO (2.5 ppm) or CDCl_3 (7.26 ppm) unless otherwise noted.

X-ray photoelectron spectroscopy (XPS) for elemental analysis measurements were performed using a Physical Electronics PHI VersaProbe II Spectrometer with a monochromatic Aluminum K_α X-ray source (1486.6 eV) under a vacuum of 10^{-8} Torr. Spectra were analyzed using CasaXPS software (Casa Software Ltd.).

Ultraviolet-visible spectroscopy (UV/vis) measurements were performed on a lambda 950 UV-Vis-NIR spectrometer (Perkin Elmer) equipped with a standard detection module (3300nm-190nm). Samples were diluted with 3 mL DIW and measured in a 3.5 mL quartz cuvette with a 10 mm path length (Sterna cells Inc). Transmittance was measured from 250 nm to 700 nm in 1 nm steps and absorbance calculated by referencing to pure DIW.

UV/vis Diffused Reflectance (DR) was performed on a Shimadzu UV-2600 with an ISR-2600 integrating sphere configured to the relative reflectance with respect to the reference Barium Sulfate. The samples were made by loading into a powder cup with no dilution.

Water contact angle measurements were performed by using an in-house set-up and analyzed through ImageJ.

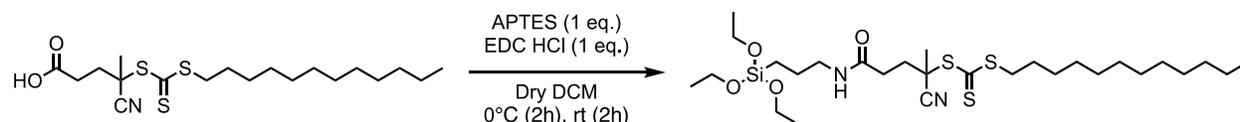
Film thickness were measured by using a J.A. Woollam RC2-D variable-angle spectroscopic ellipsometer (VASE) at 55°, 65°, and 75° incident angles and a wavelength of 400 to 1000 nm. The CompleteEASE software package (J.A. Woollam Co., Inc.) was used for fitting the optical constants and thicknesses. Unless otherwise noted, a three-layer model containing (1) a silicon substrate layer at the bottom, followed (2) a 1.55-nm-thick native silicon oxide layer and then (3) a polymer film layer were used. Thicknesses of polymer film layers were fitted by using a general Cauchy model. For thermal film thickness measurements, a 5 mL heated liquid cell attachment on a J.A. Woollam M-2000 ellipsometer at 75° was used with a wavelength of 300 – 900 nm. The thicknesses were fitted with a general Cauchy model and with the same three-layer model in DIW as the solvent material. Both the substrate and material fit temperature as a variable.

Fluorescence emission and lifetime analysis were collected via a Leica SP8 DIVE multiphoton confocal microscope set up with sensitive hybrid detectors (HyDs).

Sum frequency generation (SFG) spectroscopy measurements were obtained by scanning picosecond SFG spectrometer (EKSPILA, Lithuania). The SFG beam ($\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$) was produced by overlapping a visible ($\lambda = 532$ nm) laser beam from a picosecond laser and a tunable infrared (IR) laser beam from an optical parametric generator and amplifier (OPG/OPA) at a fixed frequency at the air/polymer interfaces. The incident angles of the IR and visible beams were approximately 56° and 60° to the surface normal, respectively. The step scan was 4 cm^{-1} among 2700–3100 cm^{-1} , and 10 cm^{-1} among 3100–3900 cm^{-1} . The data point was an average of 200 pulses each. The *ssp* (s-polarized SFG signal, s-polarized visible laser beam, and p-polarized IR laser beam in reference to the plane of laser incident plane) and *ppp* (p-polarized SFG signal, p-polarized visible laser beam, and p-polarized IR laser beam in reference to the plane of laser incident plane) polarization combination were used in SFG measurements. SFG plots were normalized to the IR intensity and visible laser intensity measured by the internal detectors and were fitted using non-linear fitting program with Mathematica. The relative humidity (RH) was controlled by mixing dry nitrogen with a saturated water vapor- nitrogen gas flow to 70% RH. The measurements were carried out at room temperature (~22 °C) and at 40 °C.

Surface functionalization

General procedure for the synthesis of a RAFT CTA surface initiator



A 250 mL flask equipped with a magnetic stir bar and rubber septum was charged with 4-Cyano-4-[dodecylsulfanylthiocarbonyl)sufanyl] pentanoic acid (CDTPA, 403.7 mg, 1 mmol) and dry dichloromethane (DCM, 50 mL). *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC HCl) (191.7 mg, 1 mmol) dissolved in dry DCM (10 mL) was then added dropwise. The

solution was cooled and stirred at 0°C for 10 min before APTES (0.23 mL, 1 mmol) was added dropwise. The reaction mixture was stirred at 0°C for 2 hours, then at room temperature for another 2 hours, and then concentrated in vacuo. The crude product was purified with silica gel column chromatography (1:1 v/v ethyl acetate and hexanes) to provide a viscous orange/yellow liquid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.86 (s, 1H), 3.83 (q, 6H), 3.32 (t, 2H), 3.26 (q, 2H), 2.49 (m, 3H), 2.38 (m, 1H), 1.89 (s, 3H), 1.66 (m, 4H), 1.38 (m, 2H), 1.26 (m, 25H), 0.88 (t, 3H), 0.64 (m, 2H).

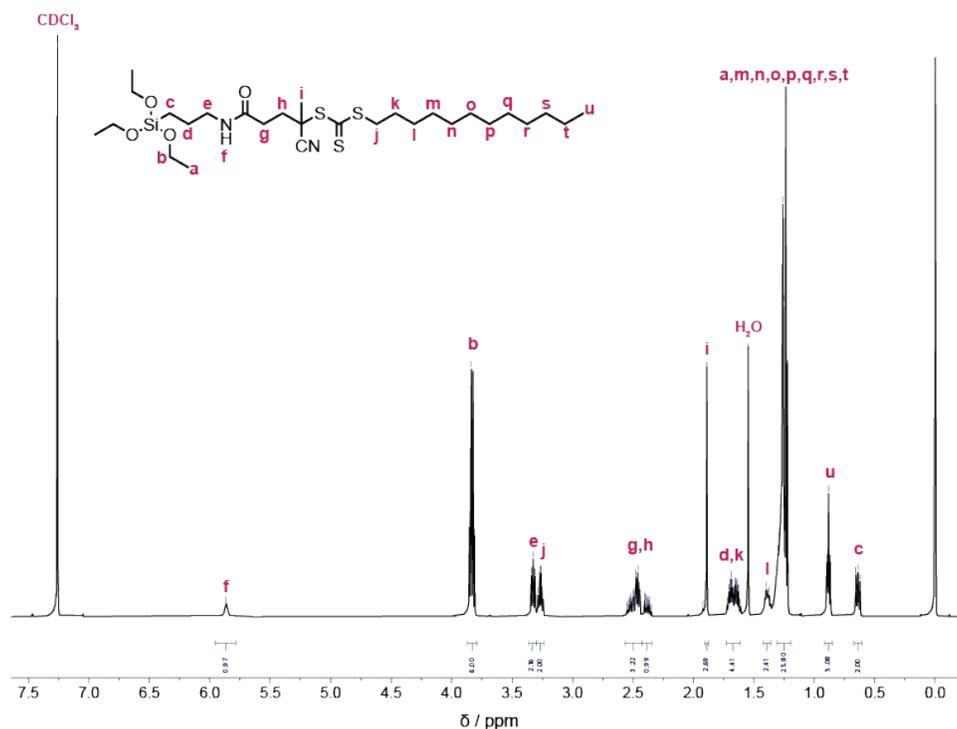


Figure S1. ¹H NMR spectrum of CDTPA-derived RAFT CTA surface initiator.

General procedure for the functionalization of planar substrates

Silicon wafers/glass slides were broken into pieces of ~1 cm × 1 cm and sonicated for 10 minutes in toluene followed by 10 minutes in isopropanol to remove any preexisting residues. They were then dried with a stream of nitrogen and arranged in a Petri dish, avoiding overlap. In the uncovered Petri dish, substrates were treated with an air plasma cleaner (PDC-001, Harrick Plasma) under 300 mTorr vacuum for 15 minutes. During this time, a dilute (0.05% v/v) solution of CDTPA surface initiator (20 μL) in dry toluene (40 mL) was prepared. Promptly after removing the open Petri dish from the plasma cleaner, the CDTPA solution was poured into the dish and covered. It then was protected from natural light with aluminum foil and left to soak in solution for 40 h at room temperature. After the allotted time the wafers/glass slides were rinsed with toluene followed by ethanol and dried under a stream of nitrogen. To maintain surface initiator integrity, substrates were stored in an inert nitrogen glovebox prior to use.

Disclaimer: For LCST studies, silicon wafers were broken into ~ 1.5 cm × 3.5 cm for the larger liquid cell.

Table S1. Experimental molar ratios for different polymer brush thicknesses.

Target Thickness (<i>d</i> , nm)	[NIPAAm]:[FIA]:[CDTPA]:[AIBN]
5	[250]:[25]:[1]:[0.25]
15	[500]:[50]:[1]:[0.25]
25	[1000]:[100]:[1]:[0.25]

Thermal SI-RAFT polymerization on wafers for LCST control experiments - PNIPAAm

A stock solution was prepared for the monomer NIPAAm, CDTPA, and 2,2'-azobis(2-methyl-propionitrile) (AIBN), with a molar ratio of [NIPAAm]:[CDTPA]:[AIBN] equivalent to [1000]:[1]:[0.25]. The stock solution was transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into a jar that carried the functionalized CDTPA large wafer. Once the substrates were fully covered with reaction solution, the jar was then capped and heated to 75°C. After 24 hours, the PNIPAAm wafer was washed with methanol and dried under a stream of nitrogen. The solution was precipitated in hexanes to further analyze the polymer made in solution.

Thermal SI-RAFT polymerization on wafers for LCST control experiments - PFIA

A stock solution was prepared for the monomer fluorescein *o*-acrylate, CDTPA, and 2,2'-azobis(2-methyl-propionitrile) (AIBN), with a molar ratio of [FIA]:[CDTPA]:[AIBN] equivalent to [100]:[1]:[0.25]. The stock solution was transferred into the glovebox. In the glovebox, anhydrous dimethylformamide (DMF) was added to the stock solution as a solvent before the solution was distributed into a jar that carried the functionalized CDTPA large wafer. Once the substrates were fully covered with reaction solution, the jar was then capped and heated to 75°C. After 24 hours, the PNIPAAm wafer was washed with DCM and dried under a stream of nitrogen. The solution was precipitated in methanol to further analyze the polymer made in solution.

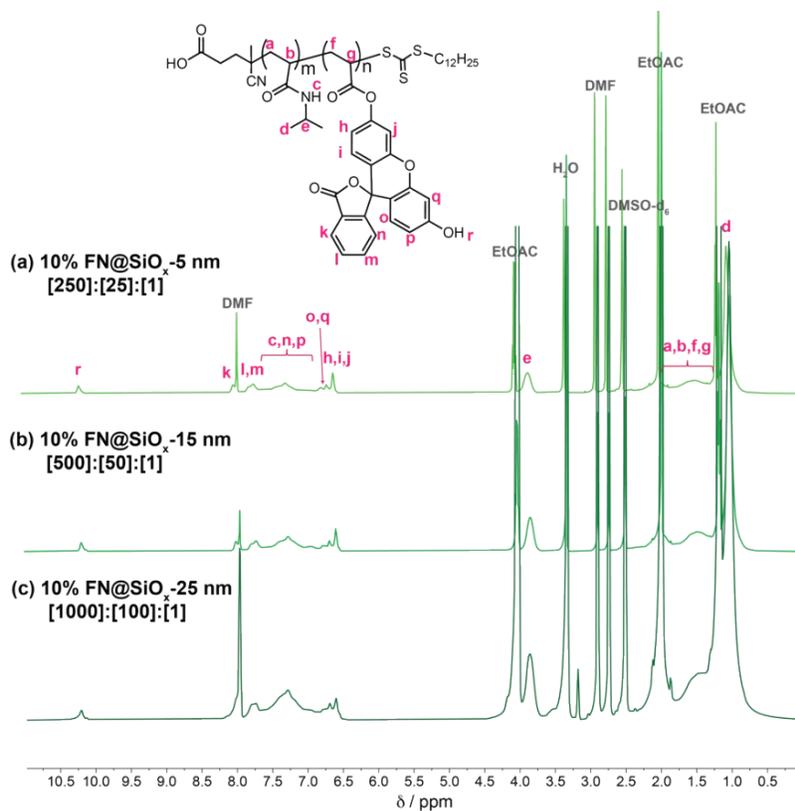


Figure S2. ¹H NMR Spectra in DMSO-d₆ of the precipitated product p(FIA-co-NIPAAm) polymerized in solution for the increasing molar ratios of [NIPAAm]:[FIA]:[CDTPA] (a) [250]:[25]:[1] targeting 5nm, (b) [500]:[50]:[1] targeting 15nm, and (c) [1000]:[100]:[1] targeting 25nm.

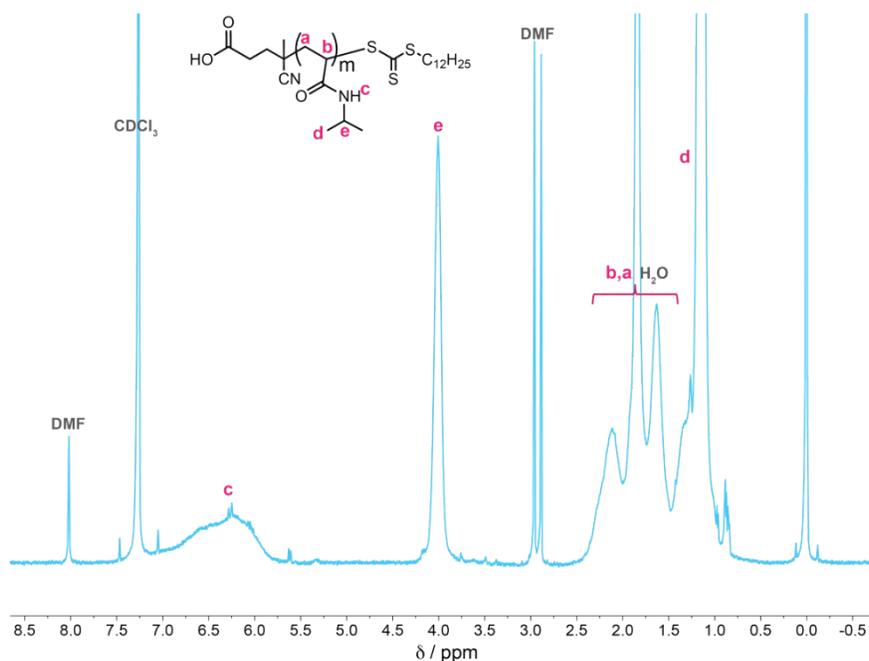


Figure S3. ^1H NMR Spectra in CDCl_3 of the precipitated product PNIPAAm polymerized in solution.

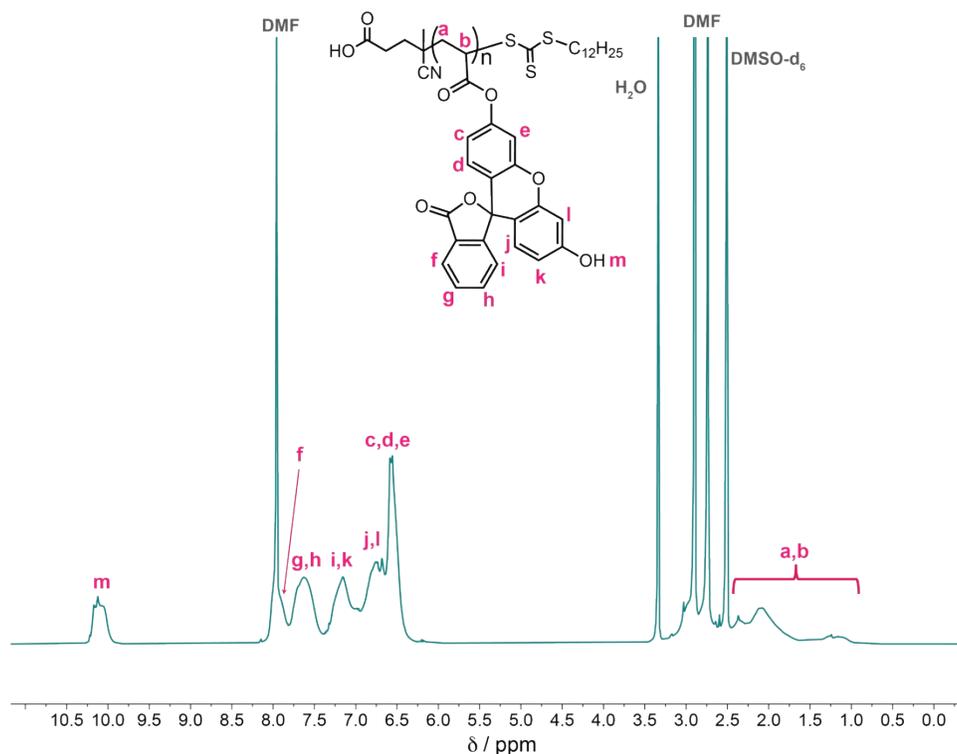


Figure S4. ^1H NMR Spectra (DMSO-d_6) of the precipitated product PFlA polymerized in solution.

Surface characterization of dual responsive polymer brush functionalized substrates

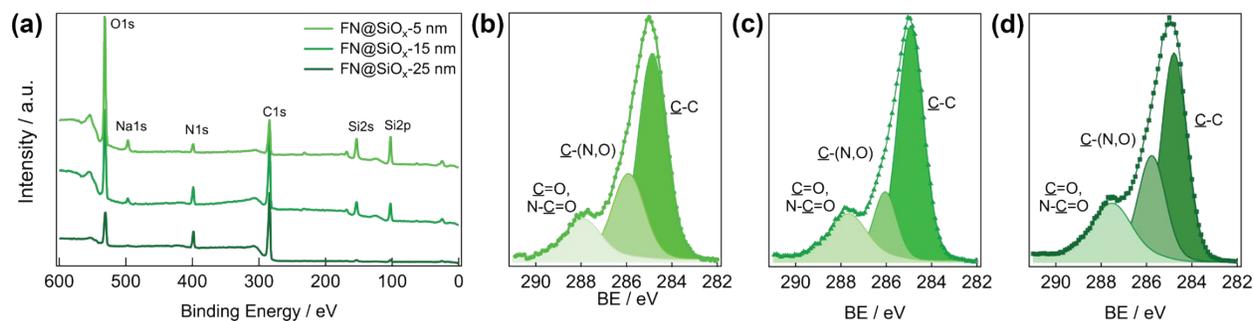


Figure S5. (a) XPS survey for the varying 10% FN@SiO_x functionalized glass beads and their high-resolution carbon spectra for (b) FN@SiO_x -5 nm, (c) FN@SiO_x -15 nm, and (d) FN@SiO_x -25 nm.

Table S2. Summary of actual C1s and N1s composition on the FN@SiO_x beads.

Substrate	C1s (%)	N1s (%)	N1s:C1s signal ratio
FN@SiO_x - 5nm	30.6	3.9	0.13
FN@SiO_x - 15nm	52.2	6.6	0.13
FN@SiO_x - 25nm	72.4	8.8	0.12

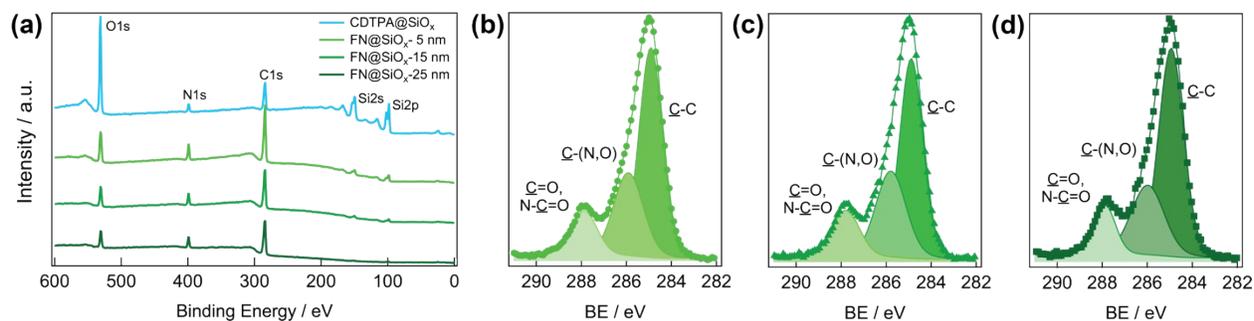


Figure S6. (a) XPS survey for the varying 10% FN@SiO_x functionalized silicon wafer thicknesses and their high-resolution carbon spectra for (b) FN@SiO_x-5 nm, (c) FN@SiO_x-15 nm, and (d) FN@SiO_x-25 nm.

Table S3. Summary of actual C1s and N1s composition on the FN@SiO_x silicon wafers.

Substrate	C1s (%)	N1s (%)	N1s:C1s signal ratio
FN@SiO _x - 5nm	65.4	8.6	0.13
FN@SiO _x - 15nm	70.5	9.4	0.13
FN@SiO _x - 25nm	74.9	10.6	0.14

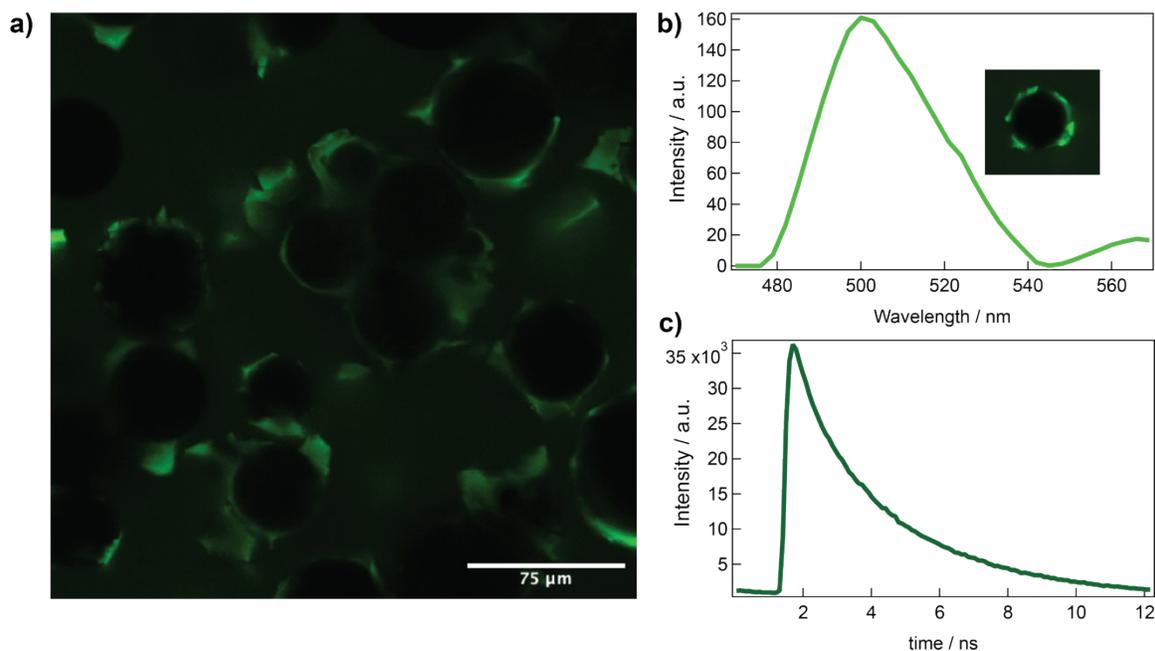


Figure S7. Fluorescence emission determination of the (a) FN@SiO_x functionalized beads under confocal fluorescence microscope and its (b) spectra with a maximum at $\lambda = 500$ nm. (c) Lifetime of the fluorescein photocatalyst on the surface was determine with the Leica's integrated fluorescence lifetime imaging microscope (FLIM) FALCON to be 3.3 ns.

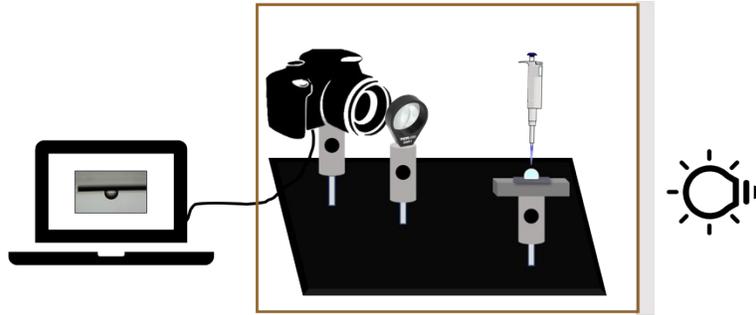


Figure S8. Schematic of setup for house set-up for in lab water contact angle measurements, employing a USB webcam (Hotpet 5 MPixel webcam) connected to a laptop, plano-convex lens with focal length $f = 50$ mm, and sample platform. A micropipette was used to deposit a drop of $5 \mu\text{L}$ of DIW onto the sample surface for imaging. The webcam was then adjusted as needed to focus and optimize sharpness. Then the setup was covered with a cardboard box with the front panel replaced with a white sheet of polypropylene. A fluorescent utility lamp was used as a backlight outside of the box, passing through the sheet of polypropylene for a uniform, lighted background. Images were captured using the webcam on the laptop. The substrates were dried with a stream of air between each measurement. The WCA was measured three times on one substrate on different areas of the wafer. WCAs were fit using the “Both Bestfits” option within the contact angle plugin for ImageJ developed by Macro Brugnara (<https://imagej.nih.gov.ezaccess.libraries.psu.edu/ij/plugins/contact-angle.html>)

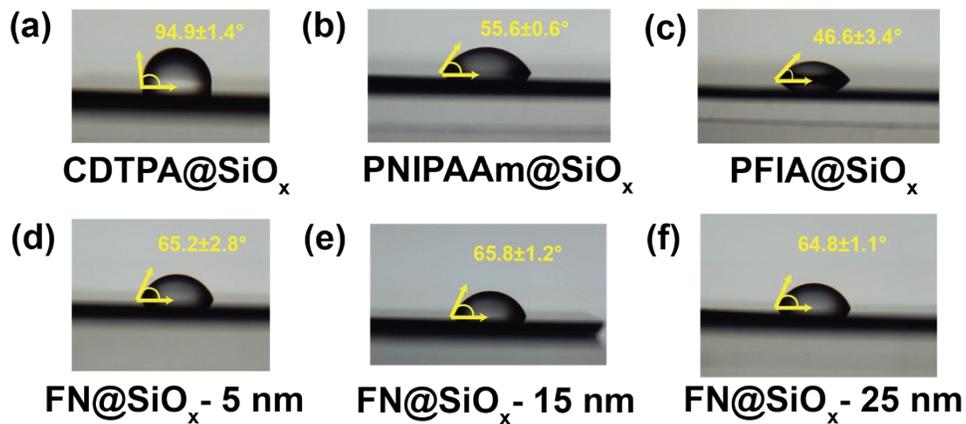


Figure S9. Water contact angles measured using the contact angle plugin in the ImageJ software for control wafers (a) CDTPA CTA wafer only, (b) PNIPAAm, and (c) PFIA to compare to the p(FIA-co-NIPAAm) polymer brushes of different thicknesses (d) 5 nm, (e) 15 nm, and (f) 25 nm.

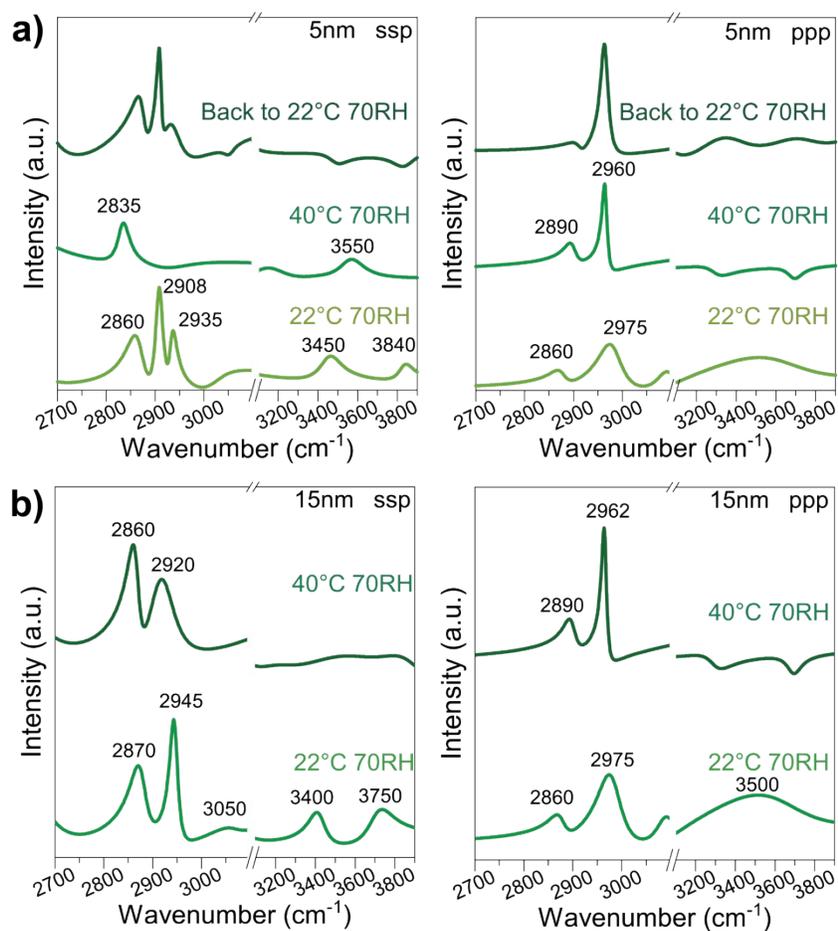


Figure S10. The sum frequency generation (SFG) spectra for FN@SiO_x (a) 5 nm and (b) 15 nm films at 22°C and 40°C in air at 70% relative humidity.

Dual responsive heterogeneous catalysis for wastewater treatment

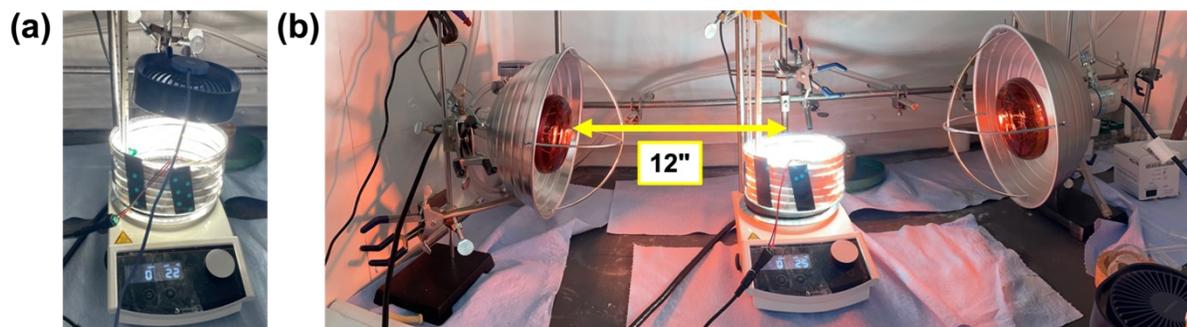


Figure S11. Experimental LED photoreactor set up for (a) the room temperature ($T = 22^\circ\text{C}$) cooled dan with the SmartDevil small personal USB desk fan at the highest setting from amazon and the (b) heated ($T = 50^\circ\text{C}$). The reaction was heated by GE 250-watt dimmable R40 heat lamp incandescent light bulbs purchased from Lowes 12 inches away from center of light bath. Lux light intensity was set to 18,000 lux for both heated and cooled reactions, determined with the

“Trendbox Digital Light Meter Tester Luxmeter Luminometer Photometer High Accurate 200000 Lux/FC HS1010A with LCD Display Handheld Portable” from Aamazon.com at the center of the light bath. Reactions were taped down in the center of the light reactor under vigorous stirring.

Degradation of tetracycline hydrochloride (TC)

Disclaimer: The heat lamps were turned on a half hour before use to ensure proper heating.

A stock solution of 25 ppm tetracycline hydrochloride (TC) was prepared in deionized water (DIW). In a 4 mL vial equipped with a stir bar, ~550 mg of FN@SiO_x glass beads were added with 2.5 mL of the TC stock solution. The reaction vials were placed in their respective light baths (either room temperature or heated depending on the specific study) and stirred in the dark for 15 minutes to mix antibiotic solution. Before the LEDs were turned on, the first aliquot started after the dark mixing with 100 μL in 3 mL DIW for further characterization via UV/vis. Aliquots were continued as desired.

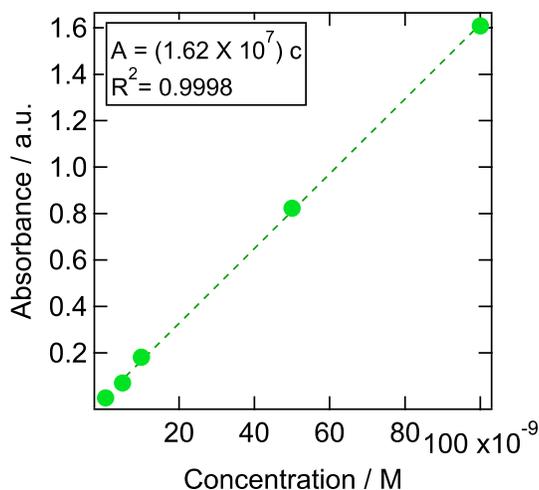


Figure S12. Calibration curve for tetracycline hydrochloride (TC) at $\lambda = 356$ nm, the observed absorption maximum.

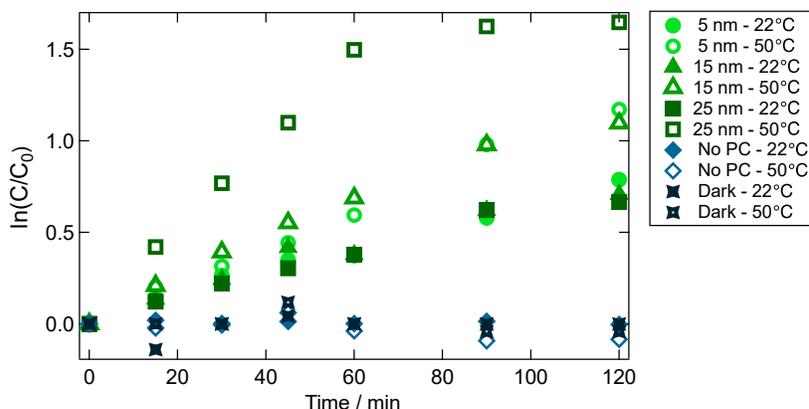


Figure S13. Degradation of tetracycline hydrochloride (TC) with varying the thickness of a dual responsive heterogeneous catalyst at different temperatures. [●] FN@SiO_x-5nm at room

temperature, [○] FN@SiO_x-5nm heated, [▲] FN@SiO_x-15nm at room temperature, [△] FN@SiO_x-15nm heated, [■] FN@SiO_x-25nm at room temperature, and [□] FN@SiO_x-25nm heated.

Table S4. Summary of rate constants for the pseudo-first order kinetic model in the degradation of TC for the varying thicknesses above and below the determined LCST.

Catalyst	Room Temperature ($T = 22^{\circ}\text{C}$)		Heated ($T = 50^{\circ}\text{C}$)	
	k (min^{-1})	R^2	k (min^{-1})	R^2
FN@SiO _x -5nm	0.0067	0.9927	0.0101	0.9968
FN@SiO _x -15nm	0.0066	0.9798	0.0103	0.9857
FN@SiO _x -25nm	0.0062	0.9885	0.0175	0.9385

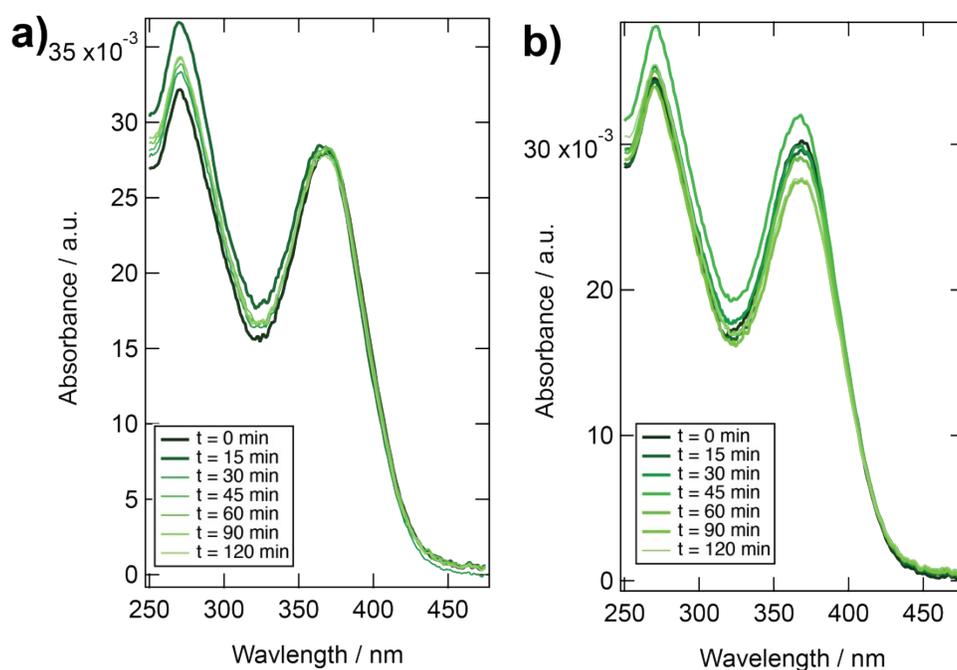


Figure S14. Raw UV/vis data for the control experiment of no photocatalyst in the degradation of TC at (a) room temperature and (b) heated to 50 °C.

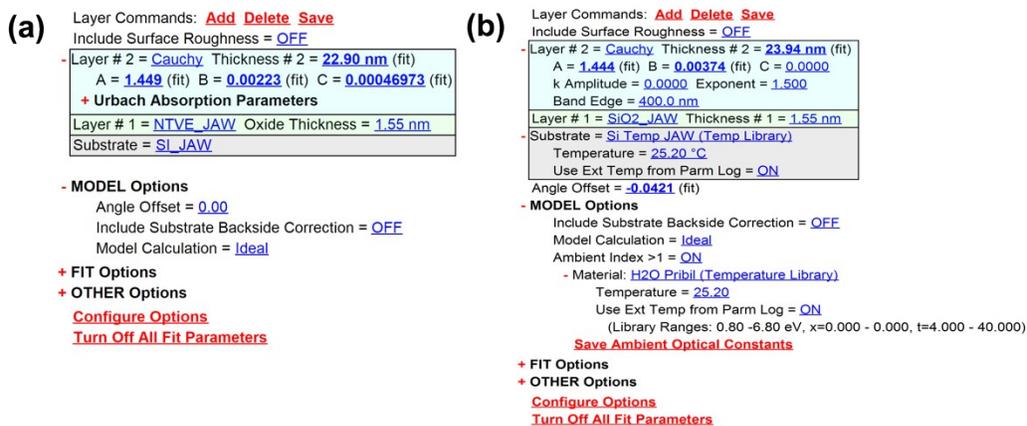


Figure S15. Example of an ellipsometry fitting model for (a) normal, dry wafers on VASE and (B) heated DIW samples for LCST on the M-2000.

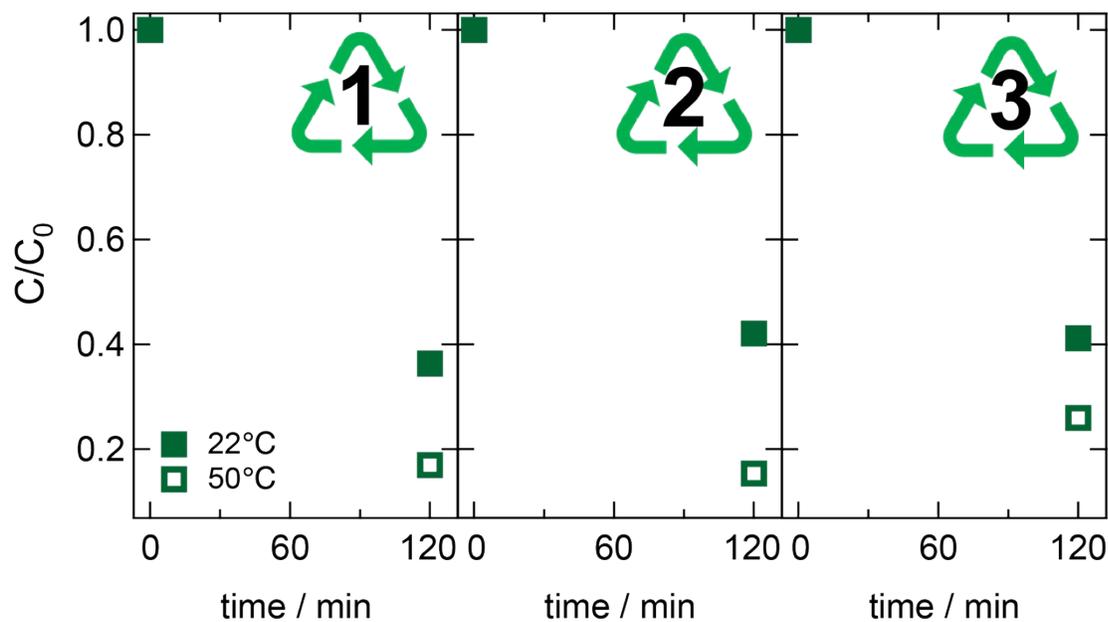


Figure S16. FN@SiO_x-25 nm recycled in the degradation of tetracycline hydrochloride (TC) three times. The glass beads were filtered off and rinsed with deionized water (DIW) 5 times, followed by ethanol, and then dried in vacuo before repeating the degradation reaction process.

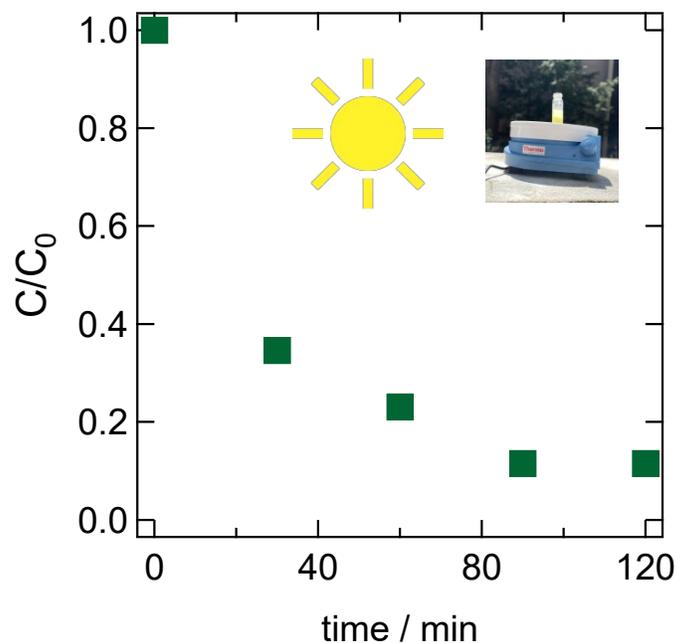


Figure S17. The degradation of tetracycline hydrochloride (TC) with FN@SiO_x-25 nm dual responsive catalysts irradiated with natural sunlight, outside at 20°C.

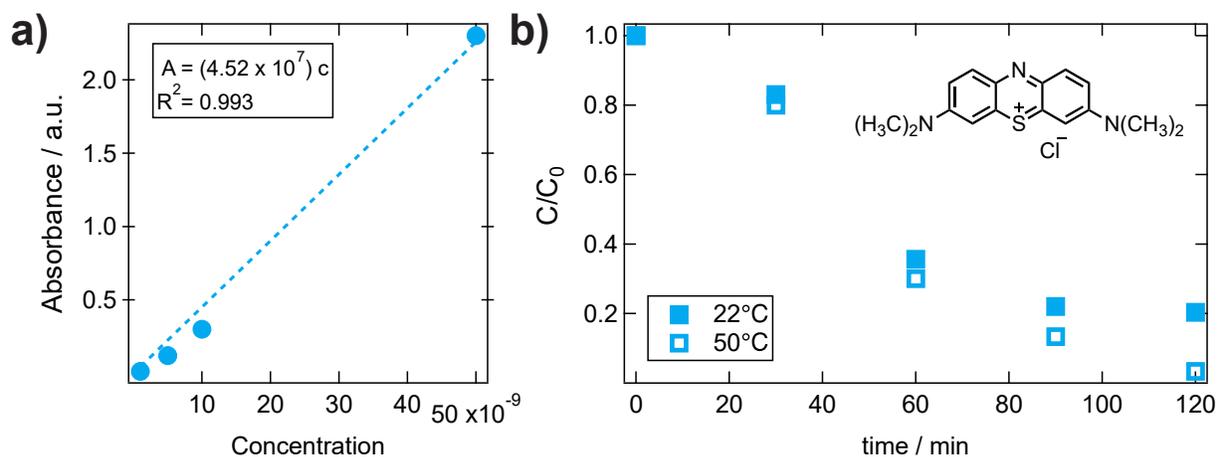


Figure S18. (a) Calibration curve for methylene blue (MB) at $\lambda = 664$ nm, the observed absorption maximum. (b) Photocatalytic degradation of MB catalyzed by FN@SiO_x-25 nm heterogeneous dual-responsive catalysts at room temperature and elevated temperatures.