

Supporting Information

Communicating assemblies of biomimetic nanocapsules

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1. Experimental Section

Chemicals. Titanium (IV) butoxide (TBOT, $M_w=340.32$ g/mol, $\geq 97\%$), tetraethyl orthosilicate (TEOS, $MW=208.33$ g/mol, $\geq 98\%$), dopamine hydrochloride ($M_w=189.64$ g/mol), poly(allylamine hydrochloride) (PAH, M_w avg ~ 50000 g/mol), poly(sodium 4-styrenesulfonate) (PSS, M_w avg ~ 70000 g/mol), Igepal CO-520 (polyoxyethylene nonylphenylether, M_w avg $=2200$ g/mol), cyclohexane ($M_w=84.16$ g/mol, $\geq 99\%$), sodium hydroxide, glycine, Rhodamine B (RhB), 1*H*-Benzotriazole (BTA) and aqueous ammonia solution (NH_4OH , $MW=40.08$ g/mol, 32 wt % in water). All materials were purchased from Sigma-Aldrich, U.K. and used without further purification. The Milli-Q deionized water was used in all experiment procedures.

Synthesis of light-responsive nanocapsules (TiO_2 -pH@PDA). The light-responsive nanocapsules were prepared by sol-gel method using reverse microemulsion as templates. First, 88.95 g cyclohexane, 9.78 mL CO-520, and 2.1 mL deionized water were mixed and stirred for 20 min at 800 rpm to generate an initial reverse microemulsion system. The initial microemulsion was pulse-ultrasonicated (model FB705, 20 kHz, Power 700 W, Fisher Scientific, USA) for 15 min (70% amplitude; 10 s on and 10 s off pulse regime) using a 1/2" tip in an ice cooling bath. Then, 600 μ L of TBOT was added into the mixture, followed by 400 μ L of ammonia hydroxide (32 wt%) to initiate the hydrolysis of TBOT. The mixture was stirred at room temperature for 24 h in a closed vial to complete the titanium shell formation. The synthesized titanium nanospheres were removed from the solution by centrifugation (12000 rpm, 15 min). The resulting solid samples were washed by ethanol and water three times to remove the surfactant. The titanium nanospheres were finally removed from the solution by centrifugation (12000, 10 min) and then dried at 60 °C. The dried samples were directly calcined at 450 °C for two hours to obtain crystalline titanium nanospheres.

The pH buffer (pH=10) was prepared by mixing 0.2 M aqueous solution of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and 0.2 M aqueous solution of sodium hydroxide (NaOH) at the volume ratio of 5:4.

The as-synthesized crystalline titanium nanospheres were dried at 100 °C under vacuum for 48 h to remove water and air from the inner volume. Then, 50 mg of titanium nanospheres were directly dispersed in 50 mL of pH buffer solution. The mixture was placed in a vacuum oven and evacuated using a vacuum pump at 20 °C. The vacuum cycle was carried out thrice to achieve maximum loading of pH buffer. Then, 50 mg of hydrochloride dopamine was directly added into the mixture, followed by stirring for 12 h. The obtained nanocapsules were separated by centrifugation (12000 rpm, 15 min) and washed with ethanol and water twice to remove the unpolymerized dopamine.

Synthesis of pH-responsive nanocapsules ($\text{SiO}_2\text{-BTA@PEs}$). The preparation method of pH-responsive nanocapsules is similar to $\text{TiO}_2\text{-pH@PDA}$ capsules using the reverse microemulsion as template. The reverse microemulsion system was made with 88.95 g of cyclohexane, 9.78 mL CO-520, 2.1 mL of deionized water. After ultrasonication, 600 μL of TEOS were added into the emulsion system under agitation for one hour. 1 mL of ammonia hydroxide (32 wt%) was added to trigger the hydrolysis and condensation of TEOS. After stirring for 24 h, the product was separated by centrifugation at 15 000 rpm for 15 min, followed by stirring in warm ethanol/water mixture solution at 50 °C for 30 min to wash out the surfactant and silicate oligomers. The silica nanospheres were removed from the solution by centrifugation (12000, 10 min) and then dried at 60 °C. The dried samples were directly calcined at 600 °C for 6 h to obtain the final silica nanospheres.

BTA loading and encapsulation. Dried silica nanospheres (50 mg, 100 °C, vacuum, 48 h) were directly dispersed in BTA ethanol solution (10 wt%, 30 mL). The subsequent loading process was finished by three vacuum cycles. Then, loaded silica nanospheres were centrifuged and re-dispersed in deionized water saturated with BTA. Two PAH/PSS multilayers were assembled on the surface of BTA@SiO_2 by the layer-by-layer assembly (LbL) technique. 20 mL of PAH aqueous solution (2 mg/mL) was first added to the BTA@SiO_2 solution under agitation and allowed to self-assembled on the surface for 20 min, followed by centrifugation and washing three

times. The PSS was assembled on the surface of BTA@SiO₂ using the same procedure. pH-responsive nanocapsules with two PAH/PSS bilayers were obtained at the end of LbLshell assembly.

Dynamic Light Scattering (DLS) analysis. The size distribution of pure synthesized inorganic nanospheres and final cargo-loaded nanocapsules were measured by DLS employing NANOTRAC FLEX In-Situ Particle Size Analyzer (Microtrac Inc., USA). Three sub-runs per measurement were done at 25 °C and a backscattering angle of 180°.

Transmission electron microscopy (TEM). The morphology and structure of obtained samples were observed by TEM, JEOL 2100+ LaB6 operated at 200 kV. The testing samples were prepared by dispersing 10 mg of nanocapsules in ethanol under sonication. One drop of the suspension solution was added on the carbon-coated copper grids (Holey Carbon Film, 300 mesh Cu, Agar Scientific, Essex, UK) and dried under ambient conditions. The drop-dry cycles were repeated five times.

BET analysis. The surface area and pore volume of the capsules were measured by nitrogen adsorption and desorption at 77.3 K. Samples were placed in a vacuum at 120 °C for 20 hours to degas before testing. The isotherm measurements were conducted using a Micromeritics ASAP 2420 volumetric adsorption analyzer.

Fourier-transform infrared spectroscopy (FTIR) analysis. The characterization of chemical composition of the obtained samples was conducted by attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR, Bruker TENSOR II, U.K.). Absorbance measurements were taken from the pressed samples with 128 scans from 400 to 4000 cm⁻¹.

Thermogravimetric (TGA) analysis. TGA analysis was performed to analyze the mass change of samples during heating using a TA Q5000IR analyzer equipped with an automated vertical overhead thermobalance. Samples were heated to 800 °C with a rate of 10 °C/min under dry nitrogen gas flow.

UV-VIS analysis. The UV-vis spectroscopy (Evolution 201 UV-visible spectrophotometer, Thermo Scientific, U.K) was performed to characterize the light-responsive characteristic of TiO₂-pH@PDA capsules, pH-responsive property of SiO₂-BTA@Pes capsules, and the dynamic communication behaviors in the assemblies of

nanocapsules. In a typical testing process, 30 mg of $\text{TiO}_2\text{-pH@PDA}$ capsules was dispersed in 50 mL of an aqueous solution containing 2 mg of RhB. The mixed solution was stirred at 700 rpm in the dark for 30 min to reach the adsorption equilibrium. The solution was illuminated by visible light for 200 min using a 100W Xe lamp under continuous stirring. At the given interval of 20 min, the solution's pH change was tested using a pH meter. Subsequently, a small amount of solution was taken out and diluted with deionized water roughly 50-100 times to analyze changes of RhB concentration after centrifugation. The absorbance changes were analyzed by a UV-visible spectrophotometer (Evolution 201 UV-visible spectrophotometer, Thermo Scientific, U.K.) at the wavelength of 554 nm.

For $\text{SiO}_2\text{-BTA@Pes}$ capsules, the release profile of BTA at different pH was continuously tested using the spectroscopic setup shown in Figure S8. The samples were placed in an aluminium crucible with small holes in it with a dialysis membrane. A small stirring bar was added to the cuvette. Then, deionized water (pH=7 or 10) was added to the cuvette until the bottom of the crucible was immersed into water. The released BTA's fluorescence spectra were collected at 10 min intervals during the duration experiment. The fluorescence intensity at the emission maximum of BTA was plotted as a function of time to obtain release profiles.

Fluorescence analysis. To measure the dynamic communication behavior in nanocapsule assemblies, the $\text{SiO}_2\text{-BTA@PEs}$ were firstly dispersed in water with a concentration of 1 mg/mL, then the $\text{TiO}_2\text{-pH@PDA}$ with different concentrations (1 mg/mL, 3 mg/mL, 5 mg/mL and 10 mg/mL) were added. A typical procedure was as following: 50 mg of $\text{TiO}_2\text{-pH@PDA}$ capsules and 10 mg of $\text{SiO}_2\text{-BTA@PEs}$ capsules were mixed together in 10 mL of aqueous solution. The solution was illuminated by visible light for 400 min using a 100W Xe lamp under continuous stirring. A small amount of solution was taken out and diluted with deionized water roughly 50 times. The released BTA's fluorescence spectra were collected after centrifugation. The fluorescence intensity at the emission maximum of BTA was plotted as a function of time to obtain communication-controlled release profiles. The different weight ratios of $\text{TiO}_2\text{-pH@PDA/SiO}_2\text{-BTA@PEs}$ capsules (1:1, 3:1, 5:1 and 10:1) were also prepared to measure the communication behaviors using the same procedures.

Supporting Figures

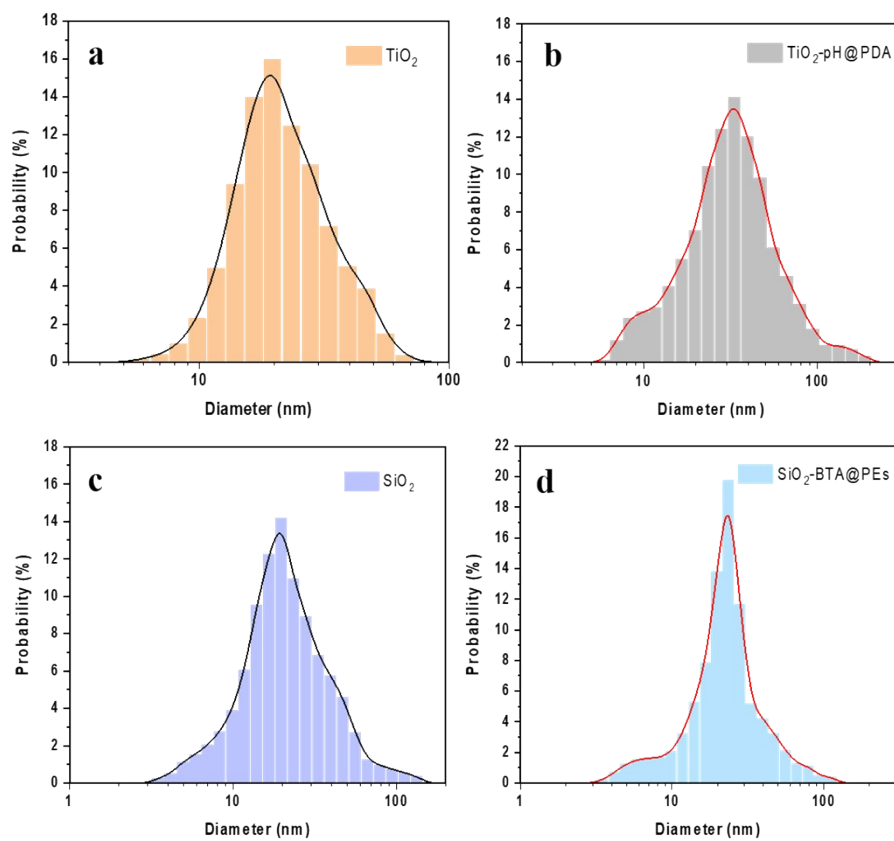


Figure S1. Nanospheres' diameter distributions before and after encapsulation. (a) TiO_2 nanospheres; (b) $\text{TiO}_2\text{-pH@PDA}$ capsules; (c) SiO_2 nanospheres; (d) $\text{SiO}_2\text{-BTA@PEs}$ capsules.

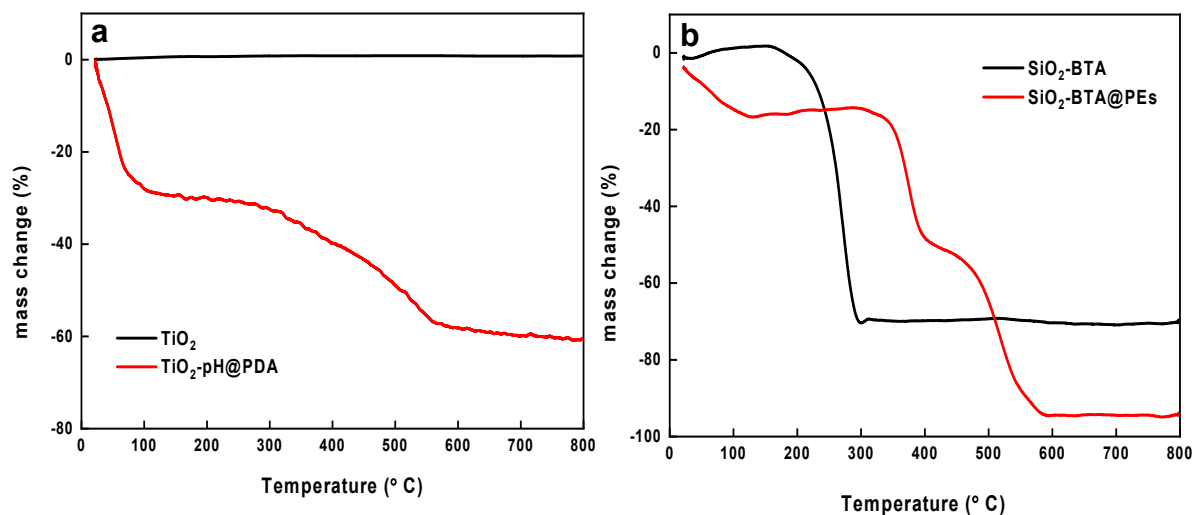


Figure S2. TGA curves for (a) TiO_2 nanospheres and $\text{TiO}_2\text{-pH@PDA}$ capsules; (b) SiO_2 loaded BTA and $\text{SiO}_2\text{-BTA@Pes}$ capsules.

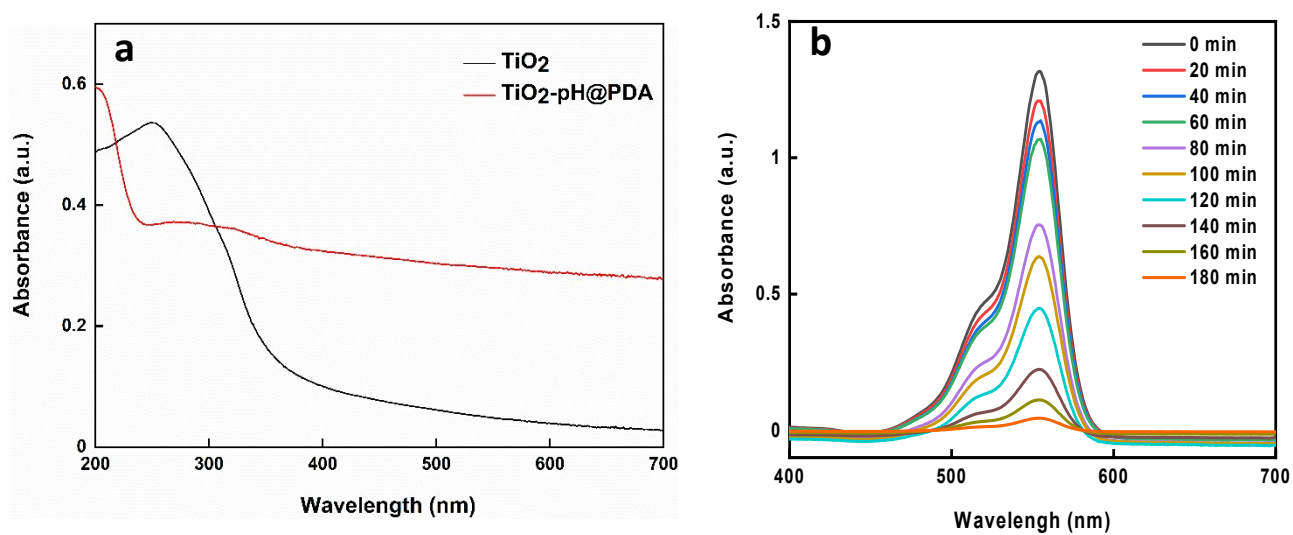


Figure S3. UV-vis absorption spectra of (a) pure TiO_2 and $\text{TiO}_2\text{-pH@PDA}$; and (b) photodegradation of RhB using $\text{TiO}_2\text{-pH@PDA}$ capsules.

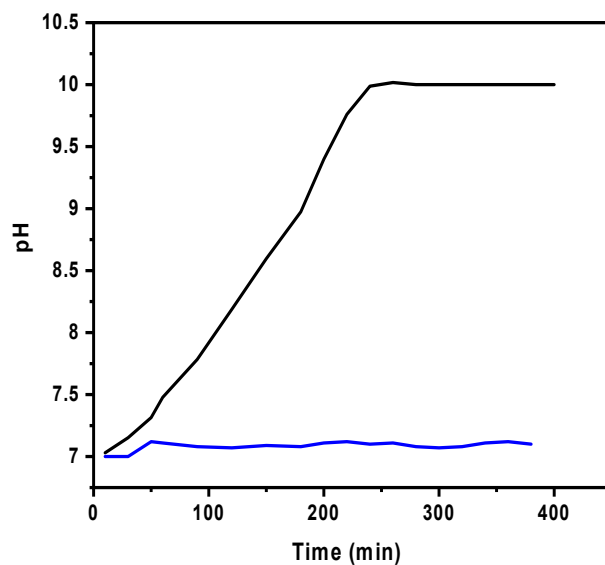


Figure S4. pH change of TiO_2 -pH@PDA capsule dispersion with visible light irradiation (black line) and without visible light irradiation (blue line).

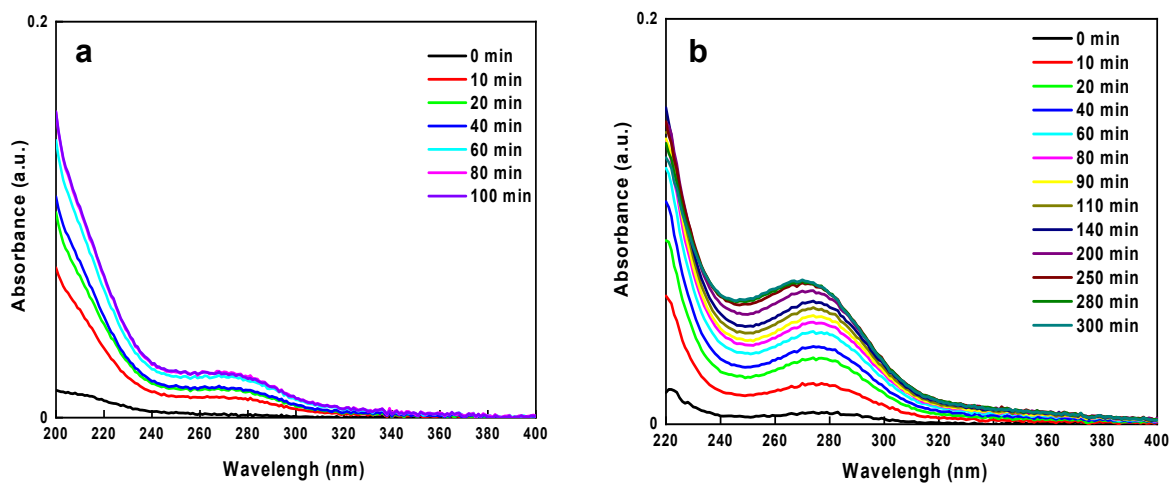


Figure S5. UV-vis absorption spectra showing fluorescence intensity of BTA at different pH: (a) pH=7; (b) pH=10.

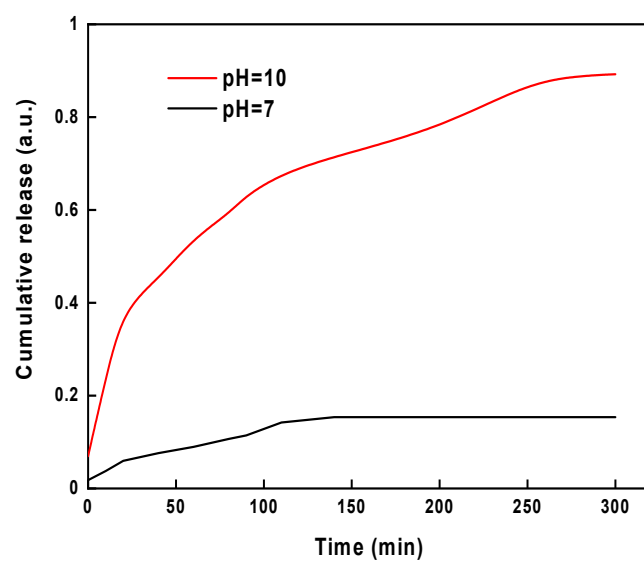


Figure S6. Release profile of BTA at different pH: pH =7 (black line); pH=10 (red line).

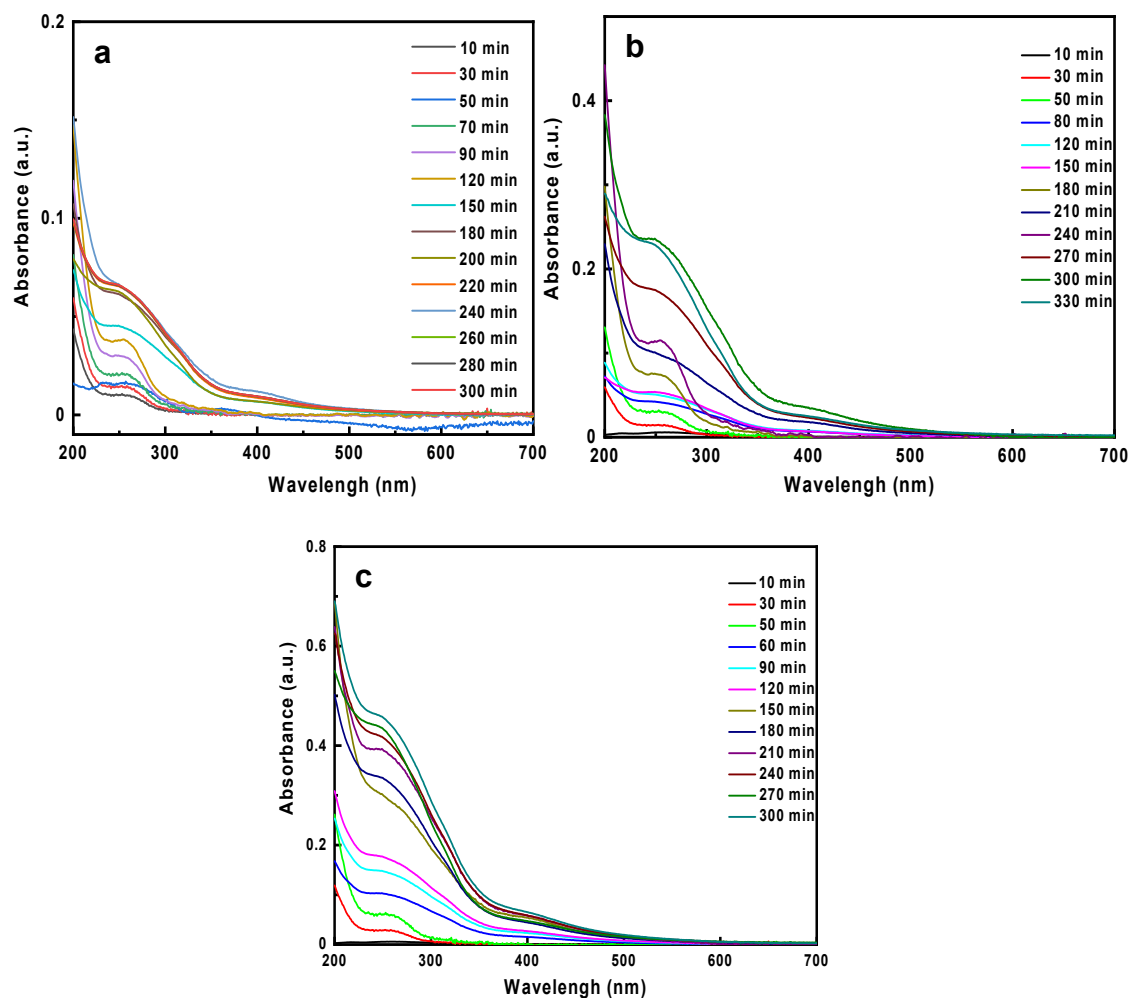


Figure S7. UV-vis absorption spectra showing fluorescence intensity of BTA released by communication-controlled under different mass ratios of $\text{TiO}_2\text{-pH@PDA/SiO}_2\text{-BTA@PEs}$ capsules, (a) 1:1; (b) 3:1; (c) 10:1.

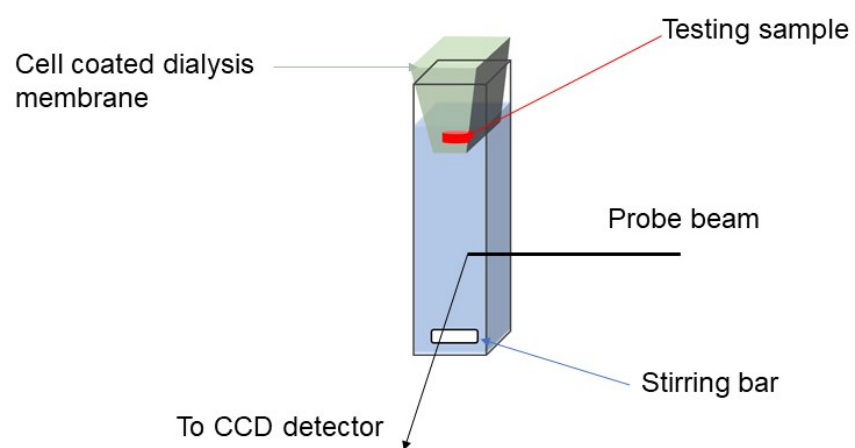


Figure S8. Spectroscopic setup for the continuous testing of BTA release.