Electronic Supplementary Information

Manipulating pH using near-infrared light assisted by upconverting nanoparticles

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Materials

Ytterbium(III) acetate hydrate (99.9%), thulium(III) acetate hydrate (99.9%), yttrium(III) acetate hydrate (99.9%), 1-octadecene (technical grade, 90%), oleic acid (technical grade, 90%), ammonium fluoride (99.99%), ruthenium(III) chloride trihydrate (technical grade), 2,2′-biquinoline (98%), acrylic acid (99%), N,N'-methylenebisacrylamide (99%) were purchased from Sigma-Aldrich. All solvents and other chemicals were purchased from Sigma-Aldrich or Fisher Scientific.

Characterization

UV-vis absorption spectra were collected using an Agilent Cary 4000 spectrometer. pH was measured using a Mettler Toledo pH meter. TEM images were collected on a JEOL JEM1400 transmission electron microscope. The upconversion photoluminescence was measured using a Spex Fluorolog II (212) spectrometer. A diode laser with a wavelength of 974 nm (type P976MF, PhotonTec Berlin GmbH) coupled with a 105-µm (core) fiber was used as the excitation light source. The diode laser was equipped with an adjustable fiber collimator (Changchun New Industries Optoelectronics Technology). The output power of the diode laser was controlled by a tabletop laser driver (device type ds11-la12v08-pa08v16-t9519-254-282, OsTech GmbH i.G.). The output power density of the diode laser was measured using an optical power meter (model 407A, Spectra-Physics Corp.) and a NIR indicator (Newport, model F-IRC1).

Synthesis

The synthesis of β-$NaYF_4$:0.5 mol% Tm^{3+}, 30 mol% Yb^{3+}/β-$NaYF_4$ core/shell UCNPs was reported in our previous work.[1] The details are provided below.

Synthesis of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} core nanoparticles. The NaYF4:TmYbcore nanoparticles were synthesized according to $Y(CH_3COO)_3$•xH_2O (372mg, 1.4 mmol), $Yb(CH_3COO)_3$•xH_2O (210 mg, 0.6 mmol) and $Tm(CH_3COO)_3$•xH_2O (3.5 mg, 0.01 mmol) were added to a 100 mL threeneck round-bottom flask containing octadecene (30 mL) and oleic acid (12 mL). The solution was stirred magnetically and heated to 120 °C under vacuum (heating rate: 3 °C/min) to form the lanthanide oleate complexes. The solution was degased at 120 °C for 15 min to remove residual water, acetic acid and oxygen. The temperature of the solution was then lowered to 50 °C and the reaction flask was placed under a gentle flow of Ar. During this time, a solution of ammonium fluoride (296 mg, 8.0 mmol) and sodium hydroxide (200 mg, 5.0 mmol) dissolved in methanol (20 mL) was prepared via sonication. Once the reaction mixture reached 50 °C, the methanol solution was added to the reaction flask and the resulting cloudy mixture was stirred for 30 min at 50 °C. The reaction temperature was then increased to ~70 °C and degased for 15 min to remove methanol in the reaction flask. Then, the reaction flask was placed under a gentle flow of Ar. Subsequently, the reaction temperature was increased to 300 °C (heating rate: 20 °C/min) under the Ar flow and kept at this temperature of 90 min. During this time the reaction mixture became progressively clearer until a completely clear, slightly yellowish solution was obtained. The mixture was allowed to cool to room temperature naturally. The nanoparticles were precipitated by the addition of ethanol (~80 mL). and isolated via centrifugation at 5000 rpm. The resulting pellet was dispersed in a minimal amount of hexane (5-10 mL) and precipitated with excess ethanol (~60 mL). The nanoparticles were isolated via centrifugation at 5000 rpm and then dispersed in hexane (10–15 mL) for the subsequent shell growth procedure.

Synthesis of β-$NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} /β-$NaYF_4$ core/shell nanoparticles. $Y(CH_3COO)_3$•xH_2O (479 mg, 1.8 mmol) was added to a 100 mL threeneck round-bottom flask containing octadecene (30 mL) and oleic acid (12 mL). The solution was stirred magnetically and heated to 120 °C under vacuum (heating rate: 3 °C/min) and maintain at 120 °C for 15 min. The temperature of the reaction flask was lowered to 80 °C and the reaction flask was placed under a gentle flow of Ar. Then, the dispersion of $NaYF_4$: 0.5 mol% Tm^{3+}, 30 mol% Yb^{3+} core nanoparticles in hexane, which was synthesized by the procedure shown above, was added to the flask. The resulting solution was heated to 110 °C (heating rate: 5 °C/min) and degased for 15 min to remove hexane in the reaction flask. The reaction mixture was cooled to 50 °C and the flask was place under a gentle flow of Ar. Then, a solution of ammonium fluoride (259 mg, 7.0 mmol) and sodium hydroxide (175 mg, 4.4 mmol) in methanol (20 mL) was added. The resulting cloudy mixture was stirred at 50 °C for 30 min. The reaction temperature was then increased to ~70 °C and degased for 15 min to remove methanol in the reaction flask. Then, the reaction flask was placed under a gentle flow of Ar. Subsequently, the reaction temperature was increased to 300 °C (heating rate: 20 °C/min) and kept at this temperature for 90 min under the Ar flow. The mixture was allowed to cool to room temperature naturally. The nanoparticles were precipitated by the addition of ethanol (~80 mL) and isolated via centrifugation at 5000 rpm. The resulting pellet was dispersed in a minimal amount of hexane (5-10 mL) and precipitated with excess ethanol (~60 mL). The nanoparticles were isolated via centrifugation at 5000 rpm and then dried in the vacuum oven.

Synthesis of [Ru(bpy)$_2$(PPh$_3$)(BuNH$_2$)] (Ru-A)

The synthesis of Ru-A was according to the previous work of one of the authors.[2] The details are shown below.

Synthesis of Ru(bpy)$_2$Cl$_2$. The synthesis of Ru(bpy)$_2$Cl$_2$ is according to the literature.[3] RuCl$_3$•3H$_2$O (807.4 mg), 962.5 mg (6.2 mmol) of 2,2′-bipyridine, and 0.9 g LiCl were dissolved in 7 mL of DMF. The solution is refluxed for 8 h and cooled to room temperature. After adding 35 mL of acetone, the solution was kept in a freezer overnight. The crystalline product was filtered and washed with cool water and dried in the vacuum oven at room temperature.

Synthesis of Ru(bpy)$_2$(PPh$_3$)Cl. The synthesis of Ru(bpy)$_2$(PPh$_3$)Cl is according to the literature.[4] Ru(bpy)$_2$Cl$_2$ (682 mg, 1.3 mmol) was dissolved in methanol (45 mL). Triphenylphosphine (410 mg, 1.5 mmol) was added, and the mixture was stirred until complete dissolution. After this, water (20 mL) was added, and the mixture was heated at reflux for 2 h. Once the reaction was complete, the solution was concentrated by rotary evaporation. The solid was resuspended in acetone (50 mL), which first produced the dissolution of [Ru(bpy)$_2$Cl]$^+$ and then the precipitation of [Ru(bpy)$_2$Cl]Cl. The solution was kept at 0 °C for one hour before filtration. The red solid was washed with cold acetone and diethyl ether.

Synthesis of [Ru(bpy)$_2$(PPh$_3$)(BuNH$_2$)] (Ru-A). A total of 200 mg of [Ru(bpy)$_2$(PPh$_3$)Cl]Cl was dissolved in 20 mL of water and heated to 80 °C. The formation of the [Ru(bpy)$_2$(PPh$_3$)-(H$_2$O)]$^{2+}$ complex was determined by its absorption band at 425 nm which moves to 450 nm at pH > 12. After formation of the aquo complex, a mixture of 20 equiv of n-butylamine (BuNH$_2$) and 5 equiv of p-toluenesulfonic acid previously dissolved in 5 mL of water was added. The solution was heated at 80 °C in a sealed tube and monitored by UV-Vis during about 4 h, until no further spectral changes were observed. All the following procedures were done in darkness. The solution was filtered to remove any insoluble particles and the EtOH and the excess of BuNH$_2$ were removed under vacuum. The aqueous solution was precipitated with saturated KPF$_6$. Ru-A is non-fluorescent.

NIR-Controlled pH change of the dispersion of UCNPs and Ru-A

Ru-A (30 mg) was dissolved in 0.2 mL acetone. UCNPs (100 mg) were dispersed in 3 mL water with the assistance of ultrasonic treatment (Figure S3, see the process in Video S1). The acetone solution of Ru-A was added to the dispersion of UCNPs to prepare the dispersion of UCNPs and Ru-A. The pH change was measured while irradiating the suspension with CW

974 nm laser with the working power densities fixed at 5.5 W cm^{-2} with magnetic stirring. The temperature of the system was controlled by an ice bath to exclude the influence of photothermal effect caused by NIR irradiation.

Preparation of hydrogel containing UCNPs and Ru-A

A solution containing 200 mg/mL AA, 0.5 mg/mL MBA, 3 mL H_2O, 33 mg/mL UCNPs, 10 mg/mL Ru-A, and 33 mg/mL APS was bubbled with nitrogen for 30 mins. Then, the precursor solution was added to the tubes which were subsequently sealed and kept at the room temperature for 12 h. The resulting hydrogels were removed from the glass tubes and soaked in distilled water for half an hour to remove the unreacted monomer. The hydrogel was stored in a sealed bottle in dry condition in the dark until use.

Preparation of hydrogel containing Ru-A or UCNPs Only

The procedure and amount were the identical to the preparation of hydrogel containing both UCNPs and Ru-A except excluding either UCNPs or Ru-A.

NIR-controlled swelling of hydrogel in ice bath

Before the NIR irradiation experiment, the nanocomposite hydrogel was equilibrated in water (pH = 3.5) for 4 h. The temperature of the system was held constant by an ice bath to exclude the influence of heating caused by NIR laser. As a control experiment, the hydrogel was left in the water solution (1.5 mL, pH = 3.5) for an additional 15 mins without NIR irradiation.

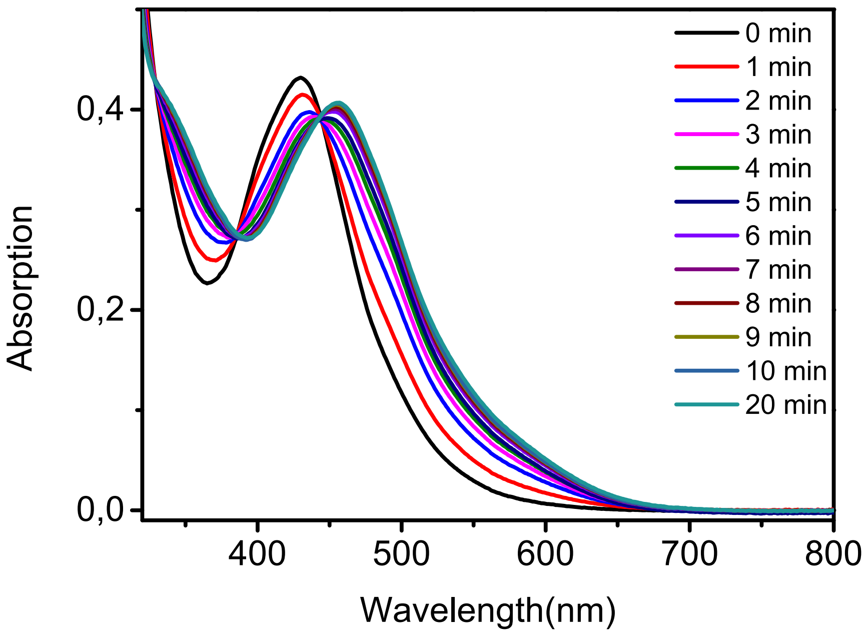

Figure S1. UV/Vis absorption spectra of Ru-A (0.1 mg/mL, 0.5/99.5 acetone/water) upon 470 nm light exposure (1 mW cm^{-2}). The spectral change shows 470 nm light efficiently triggered the release of n-butylamine.[2]

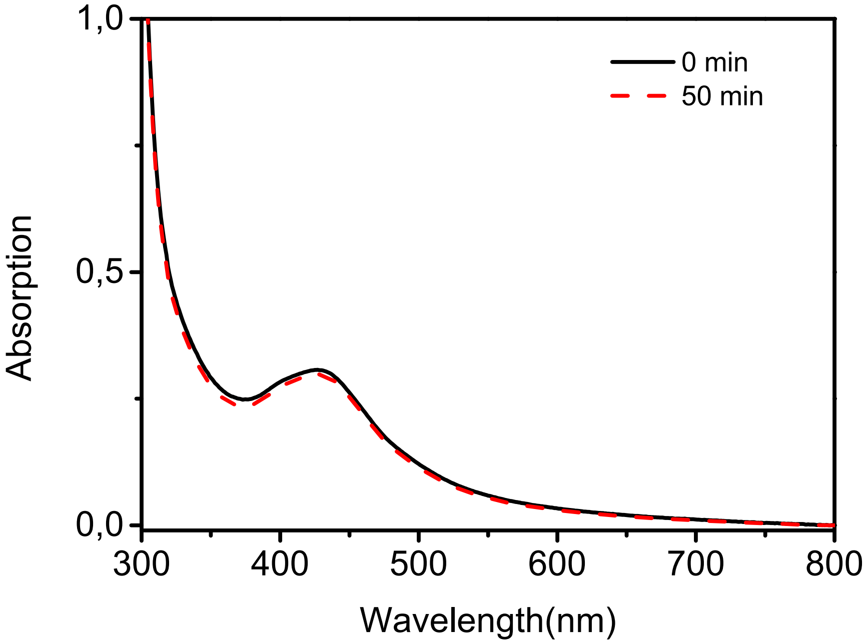

Figure S2. UV/Vis absorption spectra of Ru-A (0.1 mg/mL, 0.5/99.5 acetone/water) upon NIR light exposure (5.5 W cm^{-2}).

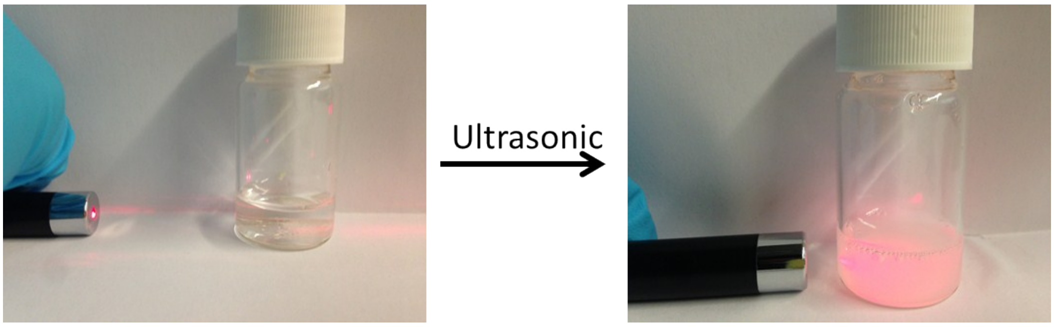

Figure S3. An aqueous dispersion of UCNPs (33 mg/mL) prepared by ultrasonic treatment. Before ultrasonic treatment (left), nearly no scattering was observed, which indicates UCNPs were not dispersed in water. After ultrasonic treatment, strong scattering was observed which indicates UCNPs were dispersed in water.

The sample preparation process was also shown in Video S1. In the preparation process, water (3 mL) was added to dry upconverting nanoparticles (100 mg). The nanoparticles were then dispersion in water by ultrasonic treatment.

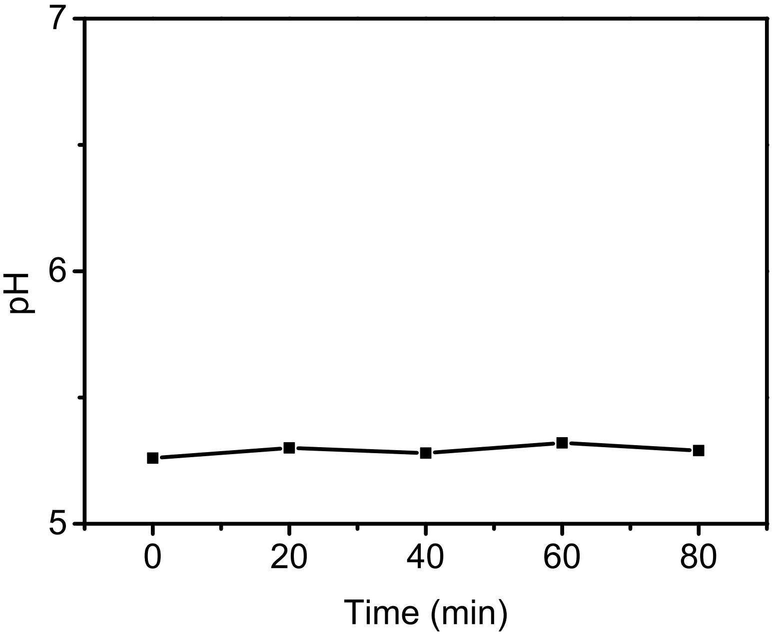

Figure S4. (a) pH change of a dispersion of Ru-A (10 mg/mL) in acetone/water mixture (6/94, V/V) upon NIR light irradiation (5.5W cm^{-2}) in an ice bath.

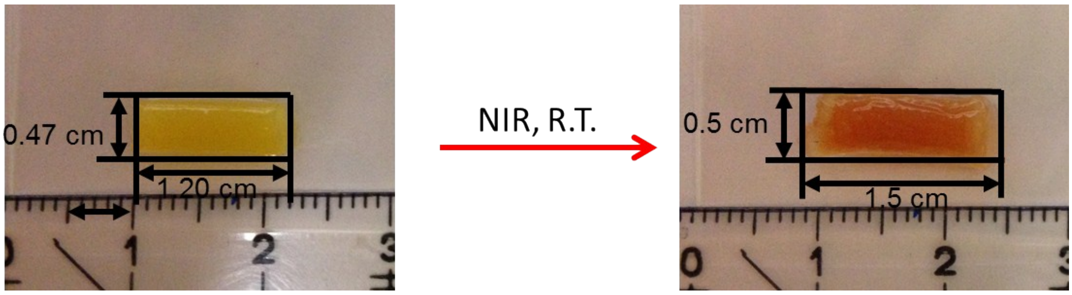

Figure S5. Nanocomposite hydrogel in the water solution (1.5 mL, pH = 3.5) before and after NIR light irradiation (5.5 W/cm^2, 15 min) at room temperature.

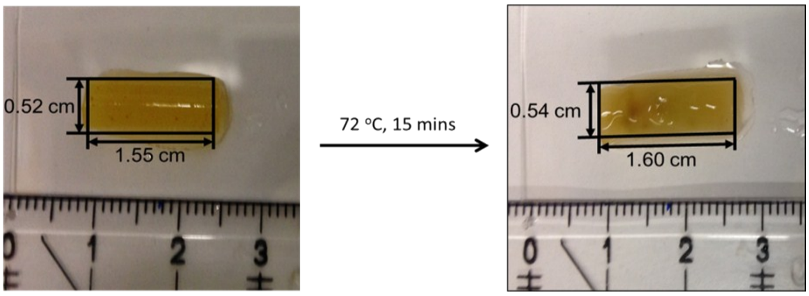

Figure S6. Nanocomposite hydrogel (1.5 mL, pH = 3.5) before and after heating at 72 ^{o}C for 15 min in an aqueous solution.

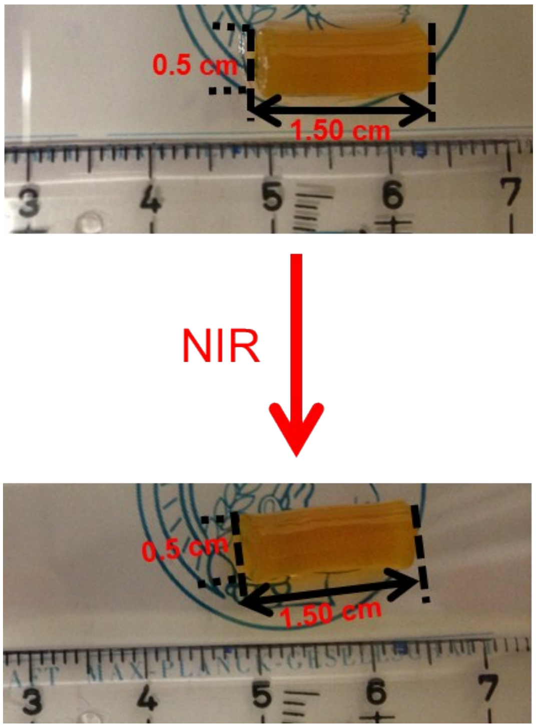

Figure S7. Hydrogel only incorporated with Ru-A (10 mg/mL) before and after NIR light exposure (5.5 W cm^{-2}). The sample in an aqueous solution was placed in an ice bath and irradiated by NIR light.

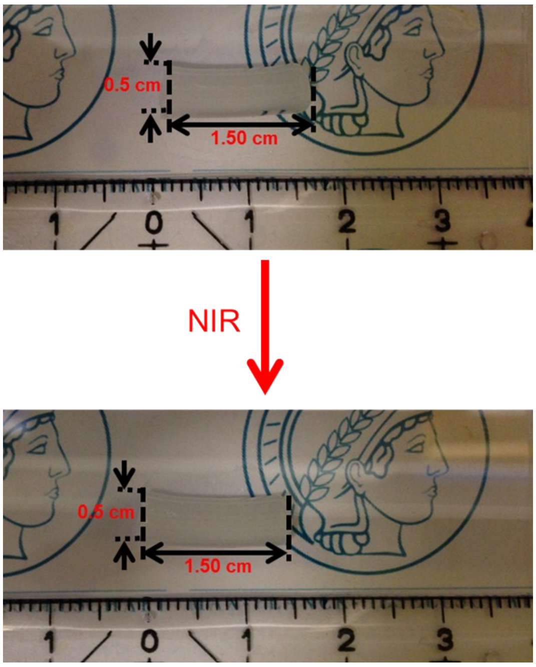

Figure S8. Hydrogel only incorporated with UCNPs (33 mg/mL) before and after NIR light exposure (5.5 W cm^{-2}). The sample in an aqueous solution was placed in an ice bath and irradiated by NIR light.

Video 1: Preparation of an aqueous dispersion of UCNPs

UCNPs (100 mg) were put in a vial. Water (3 mL) was then added to the vial. Nearly no light scattering was observed. The vial was put into an ultrasonic bath for 15 min. After that, a dispersion of UCNPs in water was obtained. Strong light scattering can be observed.

References

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