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Supporting Information

H_2O_2-Sensitized Single-Component TiO_2 Micromotors: Blue-Light-Driven Propulsion and Collective Cell Manipulation

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Experimental Section

Fabrication of Pristine Anatase TiO_2 and Peroxide-TiO_2 Microparticles. Monodisperse TiO_2 colloidal microspheres were synthesized based on the previously reported strategy.[1, 2] Typically, formic acid (0.35 mL) was first mixed with ethanol (30 mL), followed by adding titanium(IV) isopropoxide (TTIP, 0.425 mL). After continuous magnetic stirring for 10 min, the mixed solution was then transferred to a 50 mL Teflon-line stainless steel autoclave to undergo solvothermal reaction at 150 ℃ for 1 h. The obtained white precipitate was washed three times by conducting centrifugation and sonication with ethanol and water. Next, the sample was dried at 60 ℃ for 12 h. Finally, the anatase TiO_2 microspheres were collected after calcination at 300 ℃ for 2 h. The peroxide-TiO_2 microspheres were fabricated by dispersing the anatase TiO_2 sample within H_2O_2 aqueous solution with different concentration for 10 min. Formic acid, ethanol, and H_2O_2 were purchased from Sinopharm (China). TTIP was purchased from Sigma-Aldrich. All chemicals were used without further purification.

Characterization. Scanning electron microscopy (SEM) images were obtained from a Hitachi S-4800 field-emission SEM (Japan). X-ray diffraction (XRD) patterns were tested by using a Rigaku Ultima IV diffractometer (Japan) with a 2ϑ scanning range of 10–80° and a scanning rate of 10° min^{-1}. The wavelength of Cu Kα radiation source is 1.5406 Å. The voltage and current were set as 40 kV and 200 mA, respectively. UV–vis diffuse spectra (DRS) were characterized by a UV–vis spectrometer (Persee, TU-1950, China) with a scanning range of 240-800 nm. Fourier transform infrared (FTIR) spectrums were obtained using a FTIR Spectrometer (INVENIO S, Bruker). The I-V curves were measured by using a electrochemical workstation (CHI660) at ambient temperature. Reference electrode is Ag/AgCl.

Phototaxis and Collective Behaviors of Peroxide-TiO_2 Micromotors under Blue Light Navigation. A 100 μL mixed suspension of the anatase TiO_2 micromotors (0.005 mg/mL) and H_2O_2 aqueous solution (0.001, 0.01, 0.1, 1, and 5 wt%) was dropped onto a glass slide (Citotest 1A5107), followed by attaching a glass coverslip to alleviate the disturbance. LED light sources (SZ Lamplic Technology, China, wavelength: 420 nm, light intensity: 0–290 mW cm^{-2}) were placed above the glass slide. The light intensities were determined by using a light intensity meter (PM100D, Thorlabs). The incident angle of the light was set as 45°. The concentration of anatase TiO_2 micromotors was adjusted to 0.5 mg/mL for the observation of collective behaviors. All light-driven propulsion experiments were conducted under ambient temperature conditions. The micromotors' motion was observed and recorded using

an inverted optical microscope, with LED light sources fixed at the microscope's observation stage to ensure consistent illumination. All obtained videos were analyzed by Tracker and ImageJ. MATLAB was applied to delineate the corresponding color-coded trajectory plots. For the cell capture and transportation experiment, an additional dead cell suspension (A549) was added into the above solution.

Numerical Simulation. A 2D model was built using COMSOL Multiphysics software (6.1) based on the *transport of diluted species* and *creeping flow* modules. TiO_2 microspheres (2 μm in diameter) was immersed in the H_2O_2 solution near the surface of a square substrate (60×60 μm). The particle surface produces oxygen (O_2) molecules by decomposing H_2O_2 according to the proposed propulsive mechanism upon blue light irradiation. The flux (J_{O_2}), diffusion coefficient (D_{O_2}) of O_2, and the convection governs the O_2 distribution. The conservation equation is:

$$J_{O_2} = -D_{O_2}\nabla_{c_{O_2}} \#(1)$$

c_{O_2} and $\nabla_{c_{O_2}}$ are the concentration and concentration gradient of O_2 molecules, respectively.

In this model, we neglected the inertial effect and treated the fluid as incompressible. The initial flow velocity was set as zero, so does the fluid pressure. The chemiosmotic slip near the TiO_2 microparticle is determined by the $\nabla_{c_{O_2}}$ according to equations (2-3).

$$u = -b_p(I - nn)\nabla_{c_{O_2}} \#(2)$$

$$\nabla \cdot u = 0 \#(3)$$

Here, u and b_p denote the flow fluid velocity and the chemiosmotic slip mobility on the TiO_2 particle surface, respectively. $(I - nn)$ represents the tangential component the ∇C where I is the unit tensor.

The default parameters used in this work included the following values. The surface mobility over the particle surface (b_p) is deduced to be 8.5×10^{-11} m^5 mol^{-1} s^{-1}. The diffusion coefficients of O_2 in water is set to be 1.97×10^{-9} m^2 s^{-1}. The J_{O_2} is set as 8.32×10^{-5} mol m^{-2} s^{-1} that was calculated according to the previously reported method.[3, 4]

Supporting Figures

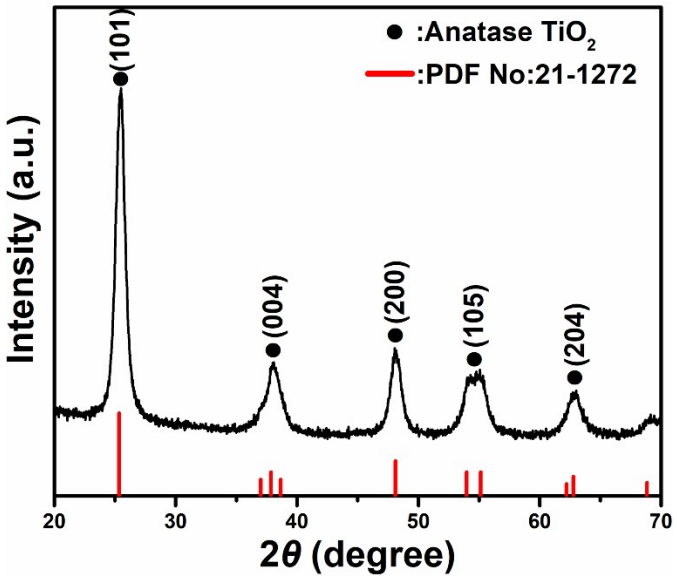

Figure S1. The XRD pattern of the obtained anatase TiO_2 microparticles.

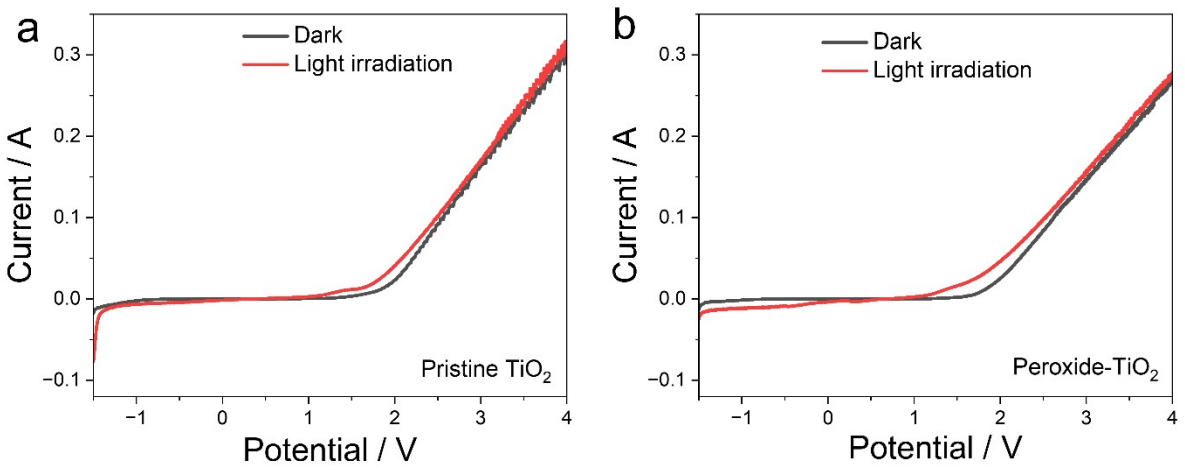

Figure S2. Current–voltage curves of pristine (a) and H_2O_2-sensitized TiO_2 (b) under dark and blue-light (420 nm) irradiation, respectively.

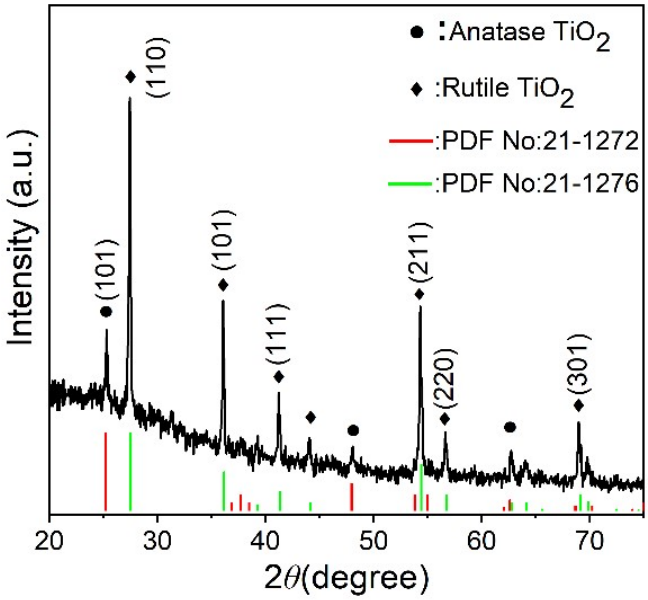

Figure S3. The XRD pattern of the obtained anatase/rutile TiO_2 microparticles.

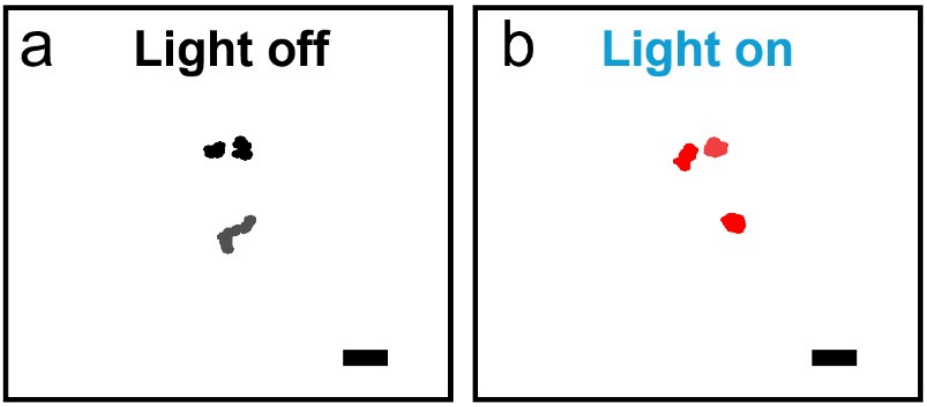

Figure S4. The 3 s motion trajectories of anatase/rutile TiO_2 microparticles without (a) and with (b) blue light irradiation. H_2O_2 concentration: 5 wt.%. Scale bars: 10 μm.

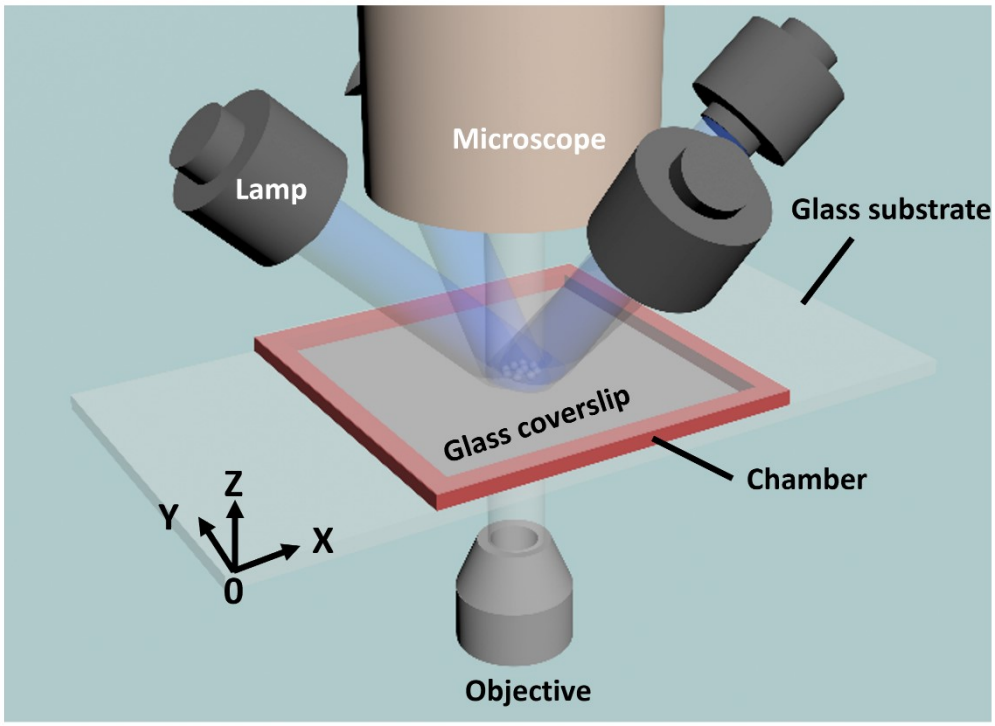

Figure S5. Schematic diagram of the experimental setup.

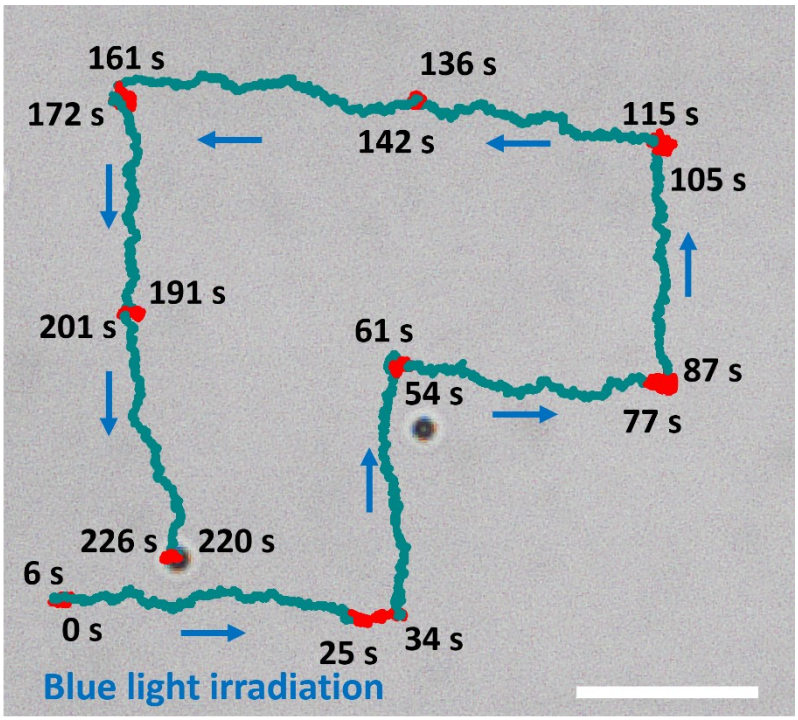

Figure S6. The negative phototactic motion of a peroxide-TiO_2 micromotor under the pulseed blue light navigation. The green and red lines represent the motion trajectories of the motor with the blue light on and off, respectively. Scale bar: 20 μm.

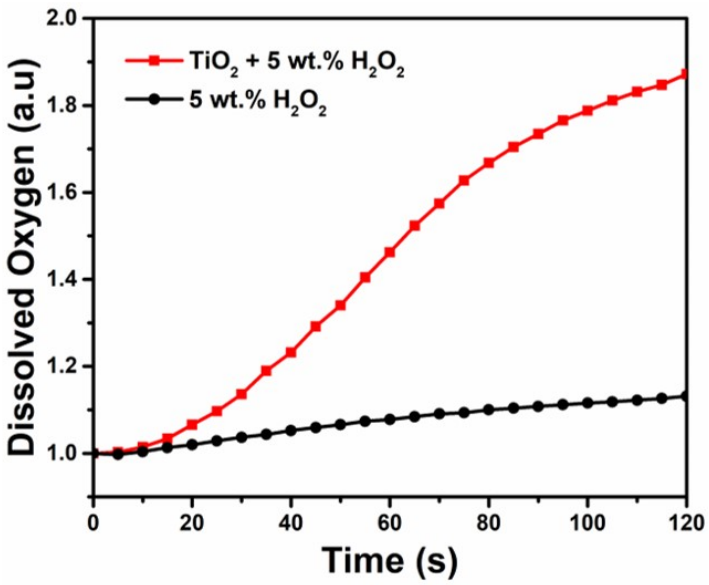

Figure S7. The dissolved oxygen changes of the 5 wt.% H_2O_2 solution with/without TiO_2 micromotors (0.05 mg/mL) over time upon blue light irradiation (I = 290 mW/cm^2).

Supporting Videos

Video S1: Directional on/off trajectories of a peroxide-TiO_2 micromotor in 0.01 wt.% H_2O_2 aqueous solution under the global navigation of blue light.

Video S2: Blue-light-driven motions of the micromotors over 10 s at different C_f.

Video S3: Phototactic locomotion of dozens of peroxide-TiO_2 micromotors (0.02 mg/mL).

Video S4: Collective behavior of a peroxide-TiO_2 micromotor swarm before and after blue light exposure in water.

Video S5: Collective behavior of a peroxide-TiO_2 micromotor swarm before and after blue light exposure in H_2O_2.

Video S6: Cell capture and removal by a peroxide-TiO_2 micromotor swarm under blue light modulation.

References

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