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Supporting information

Better Fuels for Photocatalytic Micromotors: A Case Study of Triethanolamine

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1. Synthesis of Janus micromotors

All reagents were used without further purification.

Preparation of TiO_2 and TiO_2-metal microspheres. TiO_2 microspheres were prepared by a solvothermal method.[1] First, 1.3 mL of titanium isopropoxide (Aladin #T105735) was dissolved in 30 mL of ethanol (Aladin #E111994); then, 0.35 mL formic acid (Aladin #F112038) was added to obtain a transparent solution. Transfer the well-mixed solution to a Teflon-lined autoclave and heated at 150 °C for 2 h. The last step is to wash and collect the TiO_2 microspheres. TiO_2 microspheres were collected by centrifugation at 4000 rpm for 5 min and washed repeatedly with ethanol and deionized water (18.2 MΩ·cm) each for three times. Anatase TiO_2 microspheres were obtained after annealing for 2 h at 450 °C.

A monolayer of TiO_2 microspheres was obtained by a drop-casting method. TiO_2 microspheres were first suspended in ethanol (20 μL) and dispersed by ultrasound. The suspension was drop-casted on a piece of glass slide that has been previously cleaned by plasma (PCE-6 model) for 300 s. TiO_2-Pt motors were prepared by depositing 20 nm of Pt layer or Au layer on top of the TiO_2 monolayer via plasma sputtering to obtain TiO_2-Pt or TiO_2-Au motors. All TiO_2 Janus micromotors were then collected by sonication and resuspended in deionized water.

Preparation of ZnO and ZnO-Pt microspheres. ZnO microspheres were prepared by a hydrothermal method.[2] Typically, 0.03 M zinc nitrate hexhydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Aladin # Z118841) was dissolved in 75 mL deionized water, followed by the addition of 25 mL of triethanolamine (TEOA, Aladin # T108150). After 15 minutes of stirring, the mixed solution was transferred into Teflon reaction vessels and reacted at 180 °C for 4 h. The reaction was terminated by slowly cooled down the Teflon vessel to room temperature. Then, ZnO microspheres were cleaned by multiple cycles of centrifugation, using ethanol and deionized water (18.2 MΩ·cm) each three times.

The preparation of Janus microspheres of ZnO is the same as that of TiO_2, and the same casting method is used to spread ZnO microspheres in a monolayer on a substrate on which precious metals are plasma sputtered. All ZnO Janus micromotors were then collected by sonication and resuspended in deionized water.

Preparation of Cu_2O and Cu_2O-Au microspheres. Cu_2O microspheres were prepared based on a previously reported method.[3] In a typical synthesis, 1 g of copper acetate (Aladin # C105400) was dissolved in 40 mL of deionized water (18.2 MΩ·cm) and mixed with 40 mL of absolute ethanol at 70 °C with stirring. Then, 1.4 g of sodium hydroxide (Aladin #S111509) and 1.2 g of glucose (Aladin #L115560) were added to the solution; the solution was heated for another 30 min at 70 °C and then allowed to cool to room temperature. The precipitate was collected by centrifugation at 3000 rpm for 4 min and washed with deionized water and ethanol three times each. The precipitate was collected and then further dried in vacuum for 1 h. 0.1 g of the Cu_2O microspheres was re-dispersed in 1 mL ethanol and drop-cast onto a glass slide to form a monolayer of Cu_2O spheres. The spheres were subsequently coated with 20 nm of gold by using plasma sputtering. The final Cu_2O-Au micromotors were sonicated and collected in water for motility experiments.

Preparation of TiO_2-SiO_2 microspheres. We refer to the preparation methods previously reported in the literature.[4] We first spread the commercial SiO_2 (2 μm) microspheres on the substrate in a single layer using the casting method. The substrate-supported monolayers were

transferred to the vacuum system where a 40 nm TiO_2 film was deposited by e-beam evaporation at normal incidence. After deposition, the Janus particles were annealed at 450 °C for 2 h in air. Then all TiO_2-SiO_2 Janus micromotors were collected by ultrasonic treatment and have been subsequently done for motion experiments.

2. Motor Experiment

All micromotors used in the motion tests were dispersed in deionized water prior to use. The motor suspension was first dropped on a glass slide. In case the effect of the fuel was examined, different volumes of solutions were added to the motor suspension dropwise with pipets, such as H_2O_2 (Alfa Aesar #33323), NaCl solution (Aladin # S298765), TEOA (Aladin # T108150) solution, and H_2Q (Aladin #H108945) solution. The movement of motors was observed under an inverted optical microscope (Olympus IX73). UV light of 365 nm was generated by a LED (Thorlabs, M365LP1-C1) with a power output that is tunable from 50 to 650 mW/cm^2 (measured by a power meter Thorlab S175C). Videos were taken by a Point Grey camera (FL3-U3-13E4C-C) mounted on the microscope at a frame rate of 30 per second. The videos were processed and analyzed by MATLAB codes courtesy of Prof. Hepeng Zhang at Shanghai Jiaotong University.

Speed calculations. All motor speeds, except those in Fig. 4c, were calculated by deviding the displacement between two frames with the time interval between two frames (0.033s), i.e. their instantaneous speeds. Data in Fig. 4c were acquired by fitting their MSD rather than calculating instantaneous speeds, because the motors in Fig. 4c were moving too slow for instantaneous speeds to be accurate.

Error bars in reporting motor speeds and photocurrents: Although both standard deviation and standard error can be used to describe how accurate a measurement is, we have chosen *standard error* for reporting our speed and photocurrent data in the main text, because if reflects not the spread our measurements were (which was also useful, see Fig. S1), but how accurate our calculated mean from our sample was to the true mean of the entire population. The standard error of the mean ($\sigma_{\bar{x}}$) of motor speeds is calculated by:

$$\left(\sigma_{\bar{x}}\right) = \frac{\sigma_x}{\sqrt{n}}$$

where σ_x is the standard deviation of the 20 measurements, given by

$$\sigma_x = \sqrt{\frac{\sum_i^n (V_i - \bar{V})^2}{n-1}}$$

where V_i is the speed for the ith motor, and $\bar{V}$ is the average speed of motors. In a typical report in this study, n=20.

To give readers a sense of the spread of our measurements, the following figure shows the speed distribution of 20 TiO_2-Pt motor under UV light (650 mW/cm^2) and 0.5 mM TEOA, which we used to calculate our average and standard error.

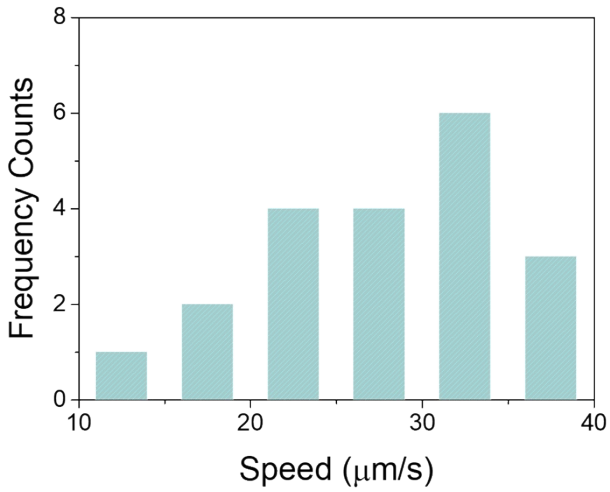

Fig. S1 The velocity distribution of the TiO_2-Pt motor under UV light (650 mW/cm^2) and 0.5 mM TEOA.

3.Optimization of concentrations for H_2O_2 and H_2Q fuels

Before comparing with TEOA, the speeds of TiO_2-Pt motors in H_2Q and H_2O_2 were explored to determine the optimal concentration for both. 50 mM H_2Q was chosen as the optimal concentration, beyond which speeds reach a plateau. 100 mM H_2O_2 was chosen as the optimal concentration, beyond which TiO_2-Pt could move by the decomposition of H_2O_2 on Pt even without light illumination.

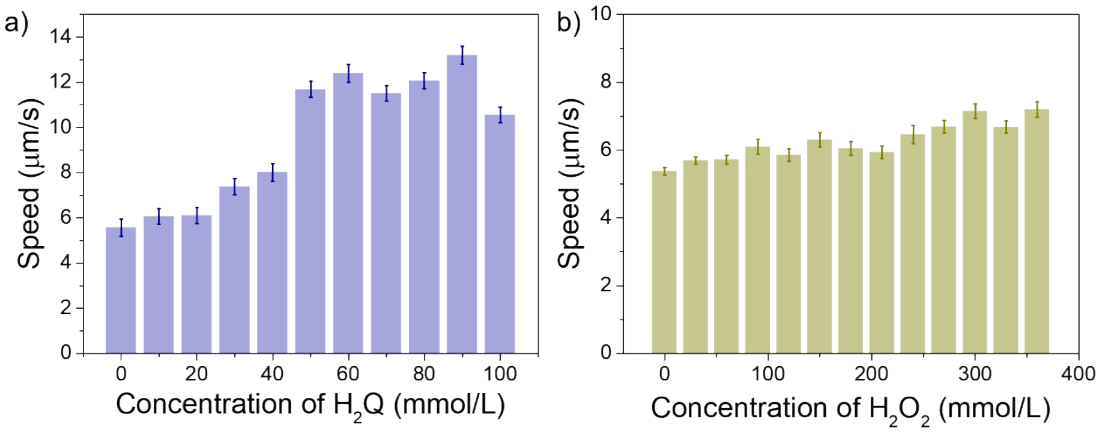

Fig.S2 Speeds of TiO_2-Pt micromotors in different concentrations of H_2Q (a) or H_2O_2 (b) under UV light intensity of 650 mW/cm^2. Error bars represent standard errors from 20 independent measurements

4. Electrochemical measurements

Preparation of TiO_2 photoelectrodes. The TiO_2 electrode was prepared as follows: 0.2 mL of concentrated HCl (36.5%−38% by weight) and 5 mL of titanium butoxide (Aladin #T104104) were added to 60 mL of absolute ethanol in a 100 mL round-bottom flask. The mixture was refluxed under constant stirring for 12 h to form a TiO_2 sol. The TiO_2 thin film was coated on the FTO glass (Place of Origin: China, Luoyang Tengjing Glass Co. Resistance range: 7-20 Ω.) by the dip coating method, and the sample was then heated at 450 °C for 2 h.

Transient Photocurrent Response. Photocurrents were measured using an electrochemical analyzer (CHI 660 E Instruments) in a standard three-electrode system with the prepared samples as the working electrodes with an active area of ca. 1 cm^2, a Pt wire as the counter electrode, and Ag/AgCl (saturates KCl) as a reference electrode. UV LED (Thorlabs, M365LP1-C1) as the excitation light source, the switch of the light source is controlled by the function generator. A 0.5 mM Na_2SO_4 aqueous solution was used as the electrolyte.

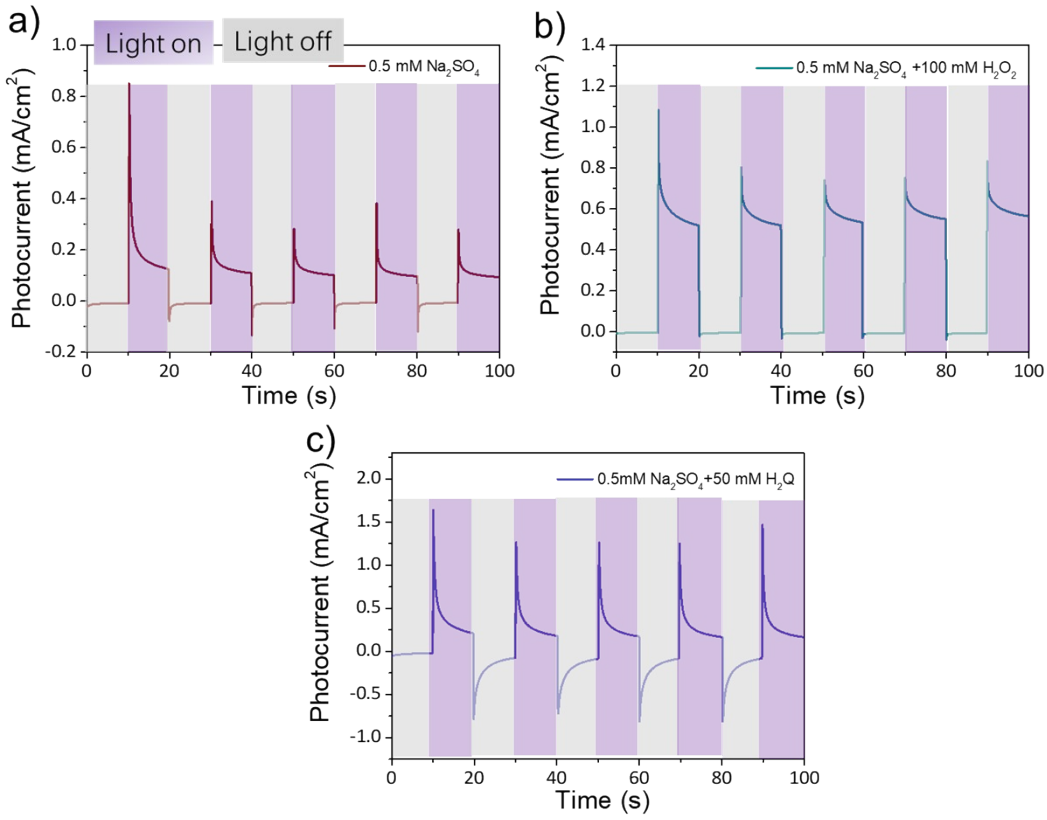

Fig. S3 Transient photocurrents of TiO_2 electrode in 0.5 mM Na_2SO_4 (a), 100 mM H_2O_2 (b), and 50 mM H_2Q (c) at a UV light intensity of 650 mW/cm^2

5. MSD plots for Au-Cu_2O motors (Fig. 4c in the main text)

6. Supporting videos

All videos are played at the original speed.

Video S1: The motion of TiO_2-Pt motors during switching on/off of UV light in 0.5 mM TEOA

Video S2:The motion of TiO_2-Pt in water, 100 mM H_2O_2, 50 mM H_2Q and 0.5 mM TEOA，respectively, at a UV light intensity of 650 mW/cm^2

Video S3: TiO_2-Au and ZnO-Pt micromotors moving in water or 0.5 mM TEOA under 650 mW/cm^2 UV light.

Video S4: Cu_2O-Au moving in water, 0.5 mM TEOA, 500mM H_2O_2 or 20 mM BQ under 650 mW/cm^2 UV light.

Video S5: The motion of SiO_2-TiO_2 in water, 0.5 mM TEOA, 100 mM H_2O_2 and 50 mM TEOA, respectively, at a UV light intensity of 650 mW/cm^2.

References

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