Supporting Information

Bimetallic Coatings Synergistically Enhance the Speeds of Photocatalytic TiO_2 Micromotors

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1. Sample preparation and experiment details

Preparation of TiO_2 and TiO_2-metal microspheres. TiO_2 microspheres were prepared by a solvothermal method. 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. The solution was then transferred to a Teflon-lined autoclave and heated at 150 °C for 12 h. Then, TiO_2 microspheres were collected by centrifugation at 4000 rpm for 5 min and washed repeatedly with ethanol and pure 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 was 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-Au motors were prepared by depositing 50 nm of Au layer on top of the TiO_2 monolayer via electron beam evaporation (HHV TF500). Then a layer of Ag was sputtered on Au layer for various durations (SBC-12) to obtain TiO_2-Au/Ag motors. TiO_2-Ag motors were prepared by only sputtering Ag without Au coating. All TiO_2 Janus micromotors were then collected by sonication and resuspended in deionized water.

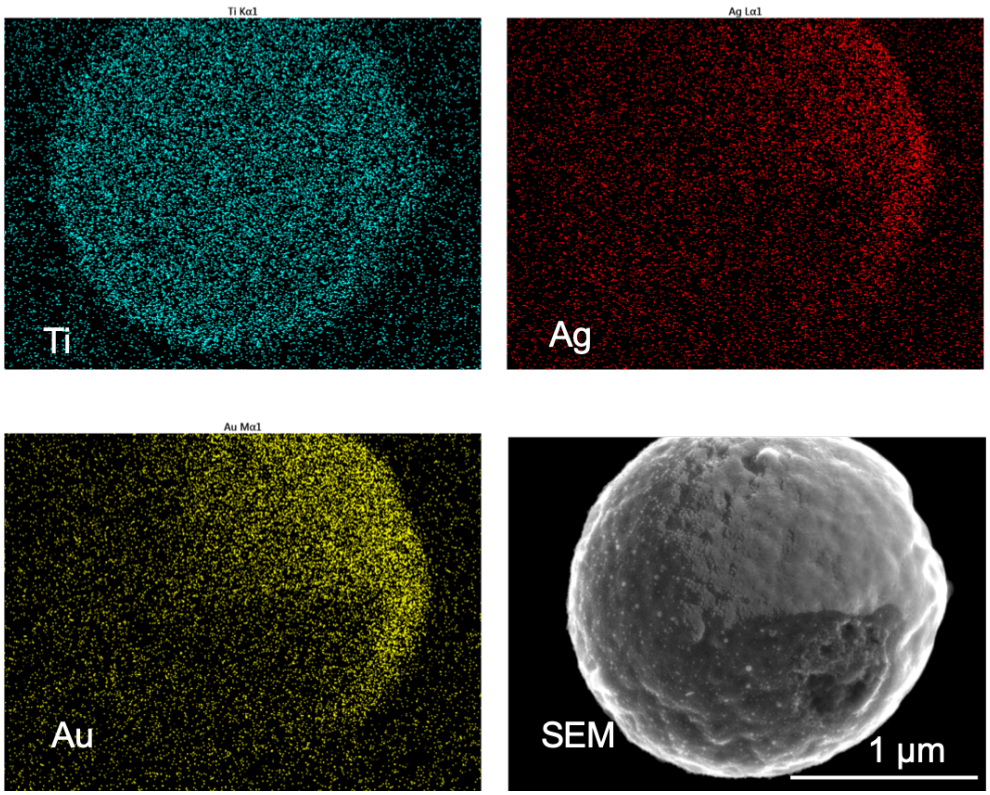

Figure S1 EDX mapping of TiO_2-Au/Ag Janus microparticle.

UV-Visible spectrum measurement UV/Vis diffuse reflectance spectra of TiO_2 films,

TiO_2-Au films, TiO_2-Ag films and TiO_2-Au/Ag films were conducted on a UV-3600 (Shimadzu) spectrometer by using blank glass film as the reference.

Motor Experiment. Three types of TiO_2 Janus micromotors were dispersed in de-ionized water before use. Various volumes of H_2O_2 (Alfa Aesar #33323) solution were added directly into the motor solution. Then a 5 μL motor and H_2O_2 mixture was dropped on a glass slide. The movement of motors were observed under an inverted optical microscope (Olympus IX73). UV light of 365 nm was generated by a LED (Thorlabs, M365LP1-C1) ranged from 300 to 600 mW/cm^2. Videos were taken by a Point Grey camera mounted on the microscope (FL3-U3-13E4C-C) at a frame rate of 30 per second. The videos were processed and analyzed by MATLAB.

Electrochemical Measurements. Linear sweep voltammetry of individual electrodes was performed to obtain the photocurrent between TiO_2 and metal with various intensities of UV illumination in a H_2O_2 solution (0.5% vol.). Au electrode was prepared by coating 50 nm Au film via electron beam evaporation on an ITO glass (1.25 cm*0.4 cm). Ag electrode was prepared by sputtering a layer of Ag on the same size ITO glass for 200 s. Au/Ag electrode was prepared by sputtering 50 s Ag on an Au electrode.

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 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 ITO glass by the dip coating method, and the sample was then heated at 450 °C for 2 h.

All the Au, Ag, Au/Ag and TiO_2 electrodes were connected to the working electrode of an electrochemical station (CHI 660E) and a Pt wire as counter electrode. Linear scanning voltammetry (LSV) was performed at a scan rate of 0.1V/s and rang from -1V to 2V. During the test, UV light at 365 nm was applied on the TiO_2 electrode.

2. No speed enhancement for TiO_2-Au/Ag micromotors by evaporation

To emphasize the importance of using sputtering method for the Ag coating, we used electron beam evaporation (HHV TF500) to produce the Ag layer for 50 nm and observed no speed enhancement in TiO_2-Au/Ag (evaporation) micromotors, shown in Figure S2.

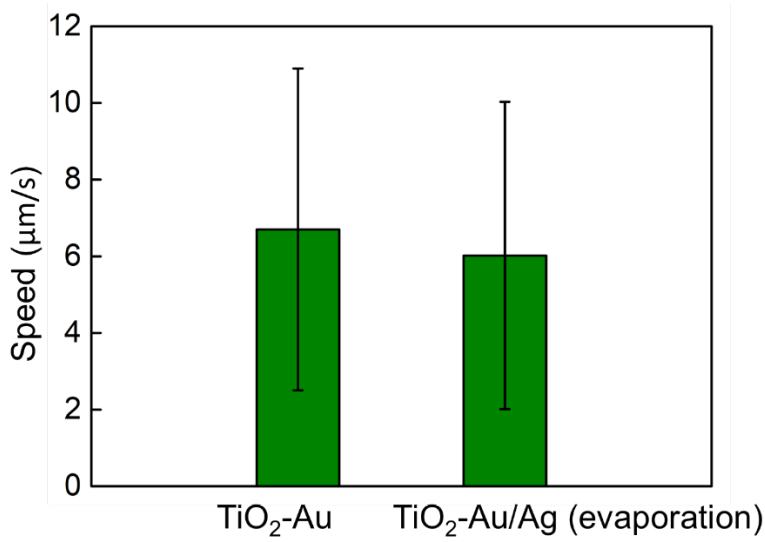

Figure S2. Average speeds of TiO_2-Au and TiO_2-Au/Ag(evaporation) micromotors moving in 0.5% H_2O_2.

3. Cross-sectional views of sputtered Ag films

Ag films were prepared as follows: first, a piece of silicon wafer was cleaned in ultrasound bath with isopropyl alcohol for 30 minutes, and then cleaned by plasma for 5 minutes. A layer of Ag was sputtered on the silicon wafer for various duration to obtain Ag films.

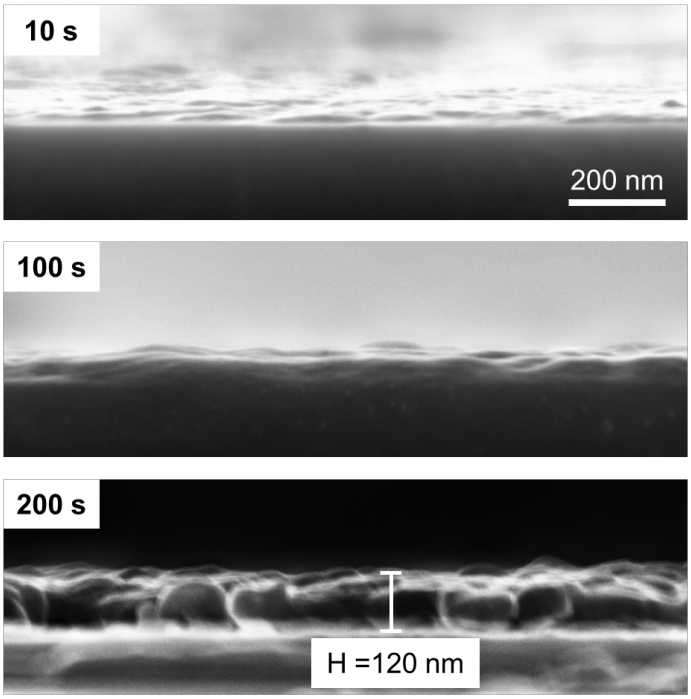

Figure S3. Cross-sectional views of the sputtered Ag films acquired at 10 s, 100 s and

200 s sputtering time respectively.

4. Electrochemical experiment

In a typical electrochemical measurement, one indium-tin oxide (ITO) glass slide was coated with a compact TiO_2 layer by the same solvothermal method as used before, and a second ITO slide was coated with the metal being studied. The coated ITO slide is then immersed in 0.5 % H_2O_2, and connected to an electrochemical station, where linear sweep voltammetry was performed (Figure S4). The photocurrent collected on a TiO_2 photoanode under different UV light intensities is plotted in Figure S5, showing a typical increase in current as light intensity increased. The cathodic currents on electrodes coated with different metals are also plotted in the same figure. The intersections between a photoanodic curve (i, ii, iii, iv), acquired with TiO_2 at different light intensities, and a photocathodic curve, acquired with electrodes coated with different metals, then represents the photocurrent when a TiO_2 anode and a metal cathode are electrically connected. This method of acquiring an intersection value has been reported in previous photoelectrochemical studies.[1]

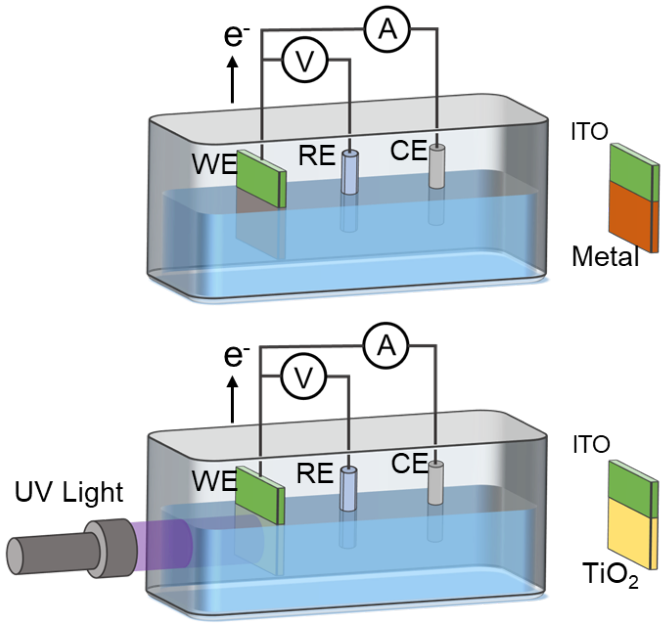

Figure S4. Two electrochemical setups used to measure the cathodic (top) and anodic (bottom) current. WE is the working electrode. Ag/AgCl is used as the reference electrode (RE). All electrodes are immersed in 0.5% wt H_2O_2. Counter electrodes (CE) are platinum wires.

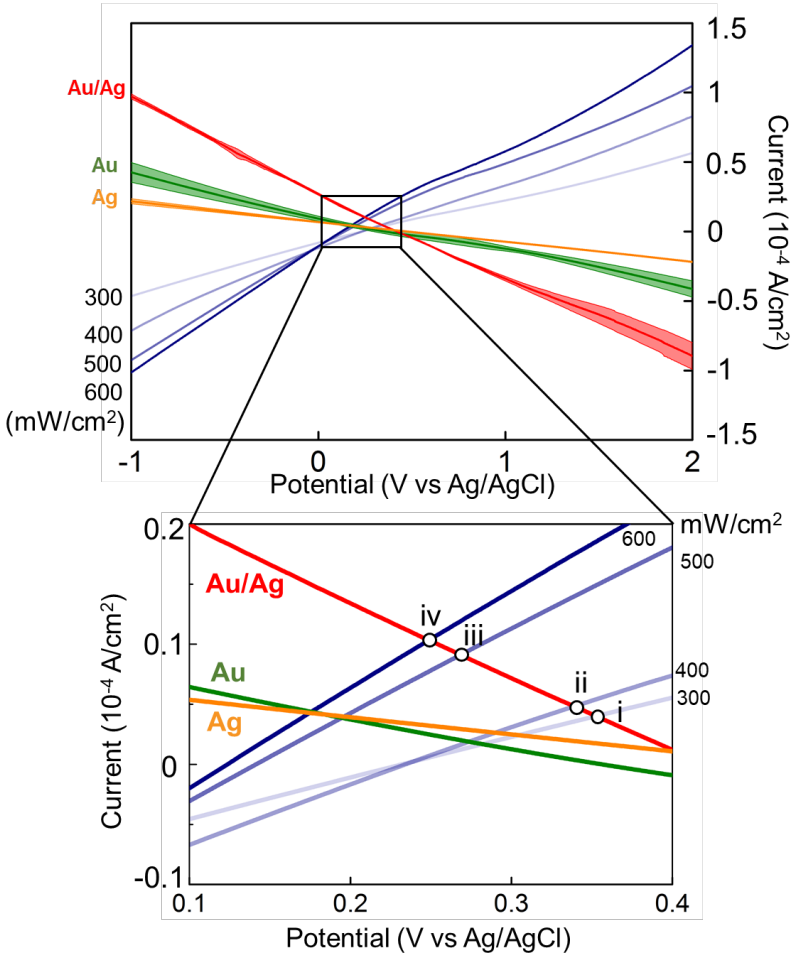

Figure S5. I-V curve of TiO_2 anode (purple lines, at light intensities of 300-600 mW/cm^2) and three metal cathodes (Au, Ag and Au/Ag), acquired by the two setups in Fig. S3 respectively. Bottom: a magnified view of the center region of the top I-V plot. The red Au/Ag curve intersects with purple TiO_2 currents at various points, yielding the data used to plot the red columns in Fig. 4 in the main text. Similarly, intersections between the green Au or the orange Ag lines with TiO_2 curves yield the green and orange columns in Fig. 4, respectively.

5. Speed enhancement on PS-Pt and TiO_2-Pt micromotors

We coated a layer of Ag on PS-Pt and TiO_2-Pt micromotors by sputtering (SBC-12) for 50 s, and in both cases the speed of motors after Ag sputtering showed significant enhancements (Fig. S6 and S7). PS-Pt motors were immersed in 5% H_2O_2, while TiO_2-Pt micromotors moved in 5% H_2O_2 and under UV light of 600 mW/cm^2.

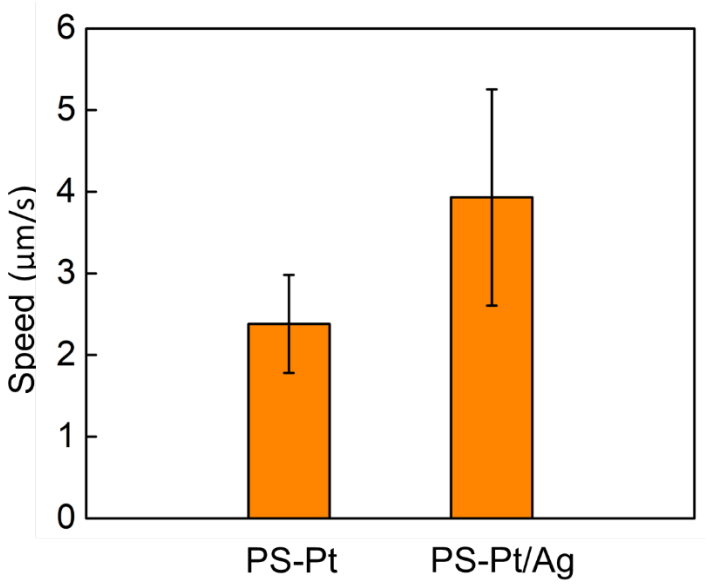

Figure S6. Average speeds of PS-Pt and PS-Pt/Ag micromotors moving in 5% H_2O_2.

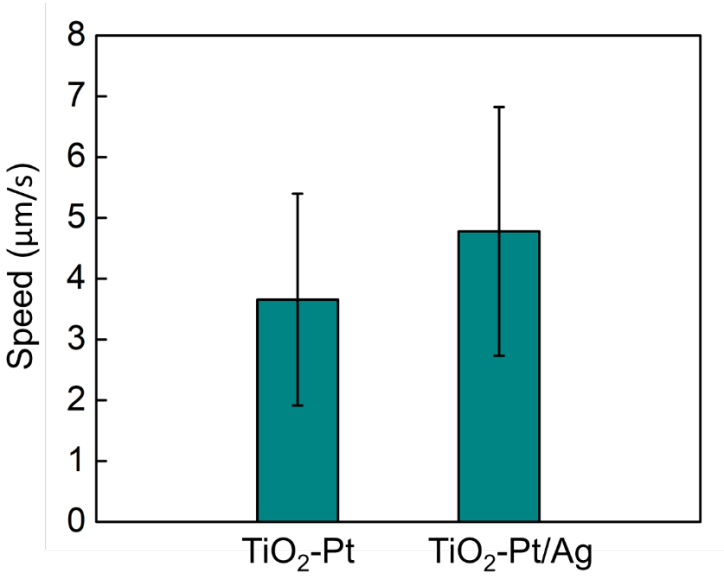

Figure S7. Average speeds of TiO_2-Pt and TiO_2-Pt/Ag micromotors moving in 5% H_2O_2.

6. Control experiments to eliminate drift and convective transport

Three types of TiO_2 Janus micromotors (TiO_2-Au, TiO_2-Ag, TiO_2-Au/Ag) were dispersed in de-ionized water or 0.5% H_2O_2 before use. Then a 5 μL motor and H_2O_2 mixture was dropped on a glass slide. The movement of motors in the absence of UV light were observed under an inverted optical microscope (Olympus IX73). Videos were taken by a Point Grey camera mounted on the microscope (FL3-U3-13E4C-C) at a frame rate of 30 per second. The videos were processed and analyzed by MATLAB.

The movement of 2 μm PS microspheres in de-ionized water and in the presence or absence of UV light were observed and analyzed as the same as TiO_2 motors.

TiO_2-Ag microsphere in H_2O_2 (Fig. S8c) showed a small amount of self-propulsion and a slightly increased diffusion coefficient. This is perhaps due to the catalytic performance of Ag towards decomposition of H_2O_2, but this effect is too small to account for the speed increase we report.

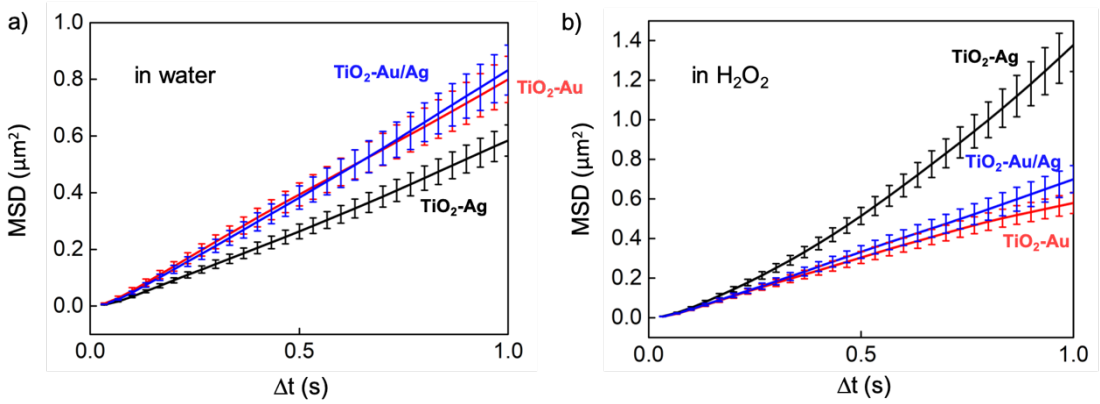

Figure S8 MSD of TiO_2-Au, TiO_2-Ag and TiO_2-Au/Ag Janus particles in water (a) and 0.5% H_2O_2 (b) in the absence of UV light.

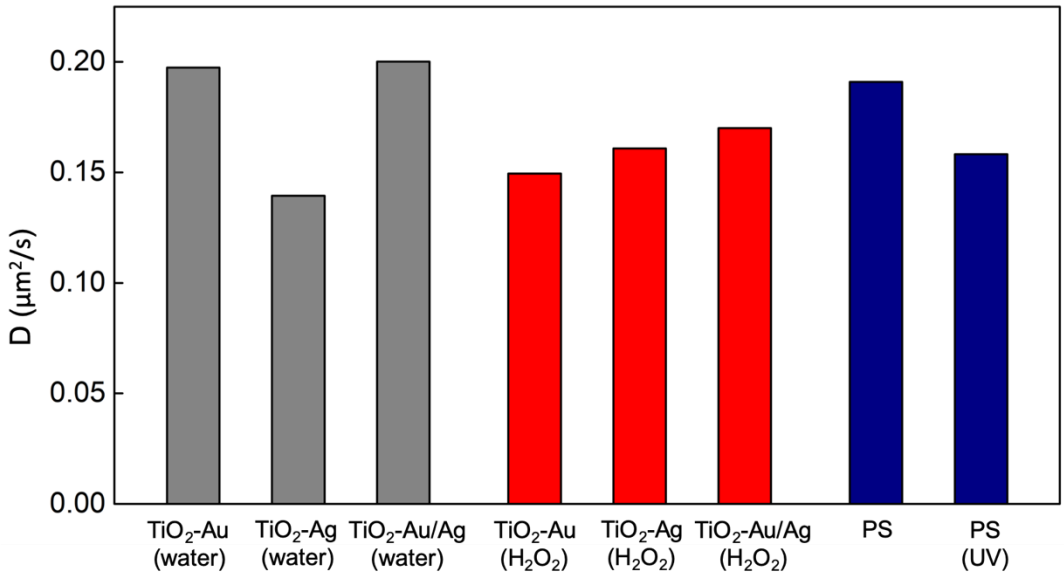

Figure S9 Diffusion coefficients calculated from MSD of various samples. Results of TiO_2-metal samples are extracted from Fig. S8. PS microspheres are suspended in water and in the presence or absence of UV light (600 mW/cm^2).

7. Supporting videos

Video S1: TiO_2-Au/Ag, TiO_2-Au, TiO_2-Ag and TiO_2 moving in 0.5% H_2O_2 under 600

mW/cm^2 UV light

Video S2: TiO_2-Au/Ag, TiO_2-Au and TiO_2-Ag moving in DI water under 600 mW/cm^2 UV light

Video S3: TiO_2-Au/Ag in 0.5% H_2O_2 without UV light

Video S4: Part 1: Diffusion of TiO_2-Au, TiO_2-Ag and TiO_2-Ag/Ag in water or H_2O_2 in the absence of UV light. A weak white ambient lighting is applied for video capturing. Part 2: Diffusion of 2 μm PS microspheres in water and in the presence (or absence) of 600 mW/cm^2 UV light.

Reference

1. C. Liu, J. Tang, H. M. Chen, B. Liu and P. Yang, *Nano Lett.*, 2013, **13**, 2989-2992.