Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Design a plasmonic micromotor for enhanced photo-remediation of polluted anaerobic stagnant waters

Experimental Section

Materials: Ethanol, acetonitrile, ammonium hydroxide ($NH_3•H_2O$), chloroplatinic acid (H_2PtCl_6), chlorauric acid ($HAuCl_4$), styrene, potassium persulfate (KPS), polyvinylpyrrolidone (PVP K-30) and methacrylic acid (MAA) were purchased from Beijing Chemicals (Beijing, China). Trisodium citrate, dopamine hydrochloride (DA), tris(hydroxymethyl)aminomethane (Tris), titanium butoxide (TBOT) and Polyethylenimine (PEI, MW 1800) were purchased from Aladdin Chemistry Co., Ltd. (China). Methylene blue (MB), Rhodamine B (RB), methyl orange (MO), p-nitrophenol, fluorescein, direct red, acid fuchsin, 1-aminoanthraquinone, p-benzoquinone, brilliant black and astrazon orange were purchased form sigma. All these reagents were of analytical reagent grade and were used as received without further purification. Azodiisobutyronitrile (AIBN) was purchased from Beijing Chemicals (Beijing, China) and purified by recrystallization from ethanol. Nanopure water (18.2 MΩ; Millpore Co., USA) was used throughout the experiment.

General techniques: X-ray measurements were performed on a Bruker D8 FOCUS Powder X-ray Diffractometer (XRD) using Cu Ka radiation. SEM images were obtained with a Hitachi-4800 FE-SEM. The diffuse reflectance UV-vis spectra were recorded on a Hitachi U-4100 spectrophotometer (Japan). Microscopic videos were captured using an Olympus BX-51 optical equipped with a CCD camera. A 300 Watt quartz halogen lamp was used as artificial solar source all through the experiments.

Synthesis of template polystyrene spheres (PS): PS were synthesized as previously described.[1] Briefly, 50 ml ethanol solution of 0.375 g PVP K-30 was placed into a 100 mL three-necked round-bottom glass reactor with nitrogen purging. Then, a mixture of AIBN (0.125 g), styrene (14.5 g) and MAA (0.127 g) solution was added to the reactor. The polymerization was conducted for 24 h at 70 ^{o}C with stirring. After cooling down to room temperature, the resulting beads were washed with ethanol and DI water three times each. Finally, the beads were dried in a vacuum oven at 60 ^{o}C for 24 h.

Coating PS with PDA: PS (2 mg mL^{-1}) was resuspended and stirred in a Tris buffer solution (pH 8.5, 10 mM) of 2 mg mL^{-1} dopamine hydrochloride for 3 h. Then the PS were collected with centrifugation and resuspended again in the dopamine hydrochloride solution for a second coating. PDA coated PS (PS@PDA) were purified from the PDA aggregates formed in solution by centrifugation.

In situ growth of PtNPs: 200 mg PS@PDA was dispersed in 200 mL deionized water containing 0.3 mM H_2PtCl_6, then the mixture was heat to 90 ^{o}C and maintained for 24 h with stirring. The final product PS@PDA@PtNPs was collected by centrifuging and washing with nanopure water for three times.

Encapsulation of PS@PDA@PtNPs with TiO_2 layer: The coating reaction was performed in a mixed solvent of ethanol and acetonitrile at room temperature by hydrolysis of TBOT in the presence of ammonia. In a typical experiment, 20 mg of PS@PDA@PtNPs composites were dispersed in ethanol/acetonitrile (3:1, v/v) mixture and then added 200 μL of ammonia at room temperature. Finally, 400 μL titanium butoxide (TBOT) was added to the above suspension under stirring. After reacting for 24 h, the product PS@PDA@PtNPs@TiO_2 was obtained after centrifuging and washing.

Synthesis of gold nanoparticles (AuNPs): AuNPs were synthesized by the standard G. Frens's citrate reduction method. Briefly, 150 mL of water solution containing 1.5 mL of $H[AuCl_4]_3 \cdot 3H_2O$ (1 % w/v) were heated to boiling and a 6 mL of 1% w/v sodium-citrate solution (containing 0.05% w/v citric acid) was added quickly under vigorous stirring. The solution was kept boiling for about 5 min to get a wine red color and was then allowed to cool down.

Decorating of PS@PDA@PtNPs@TiO_2 with AuNPs: PS@PDA@PtNPs@TiO_2 was first immobilized with PEI to form a positive surface. Then 100 mL suspension containing 300 mg PEI-functionalized PS@PDA@PtNPs@TiO_2 was dispersed in the 100 mL AuNPs suspension prepared above. The mixture was stirred for about 8 h before centrifugation.

Calcination to obtain the motor plasmonic photocatalyst (MPP): The organic cores were removed by calcination. The calcination was performed in air condition at 500 ^{o}C for 6 h with a heating rate of 5 ^{o}C min^{-1}. Finally, the MPP could be obtained by a moderate ultrasonic treatment.

Synthesis of photocatalysts TiO_2: TiO_2 were prepared using the similar method as for MPP but without the PtNPs growth and AuNPs decorating step.

Mixing test: Typically, 2 mL of 2% H_2O_2 solution (containing 0.5 mg mL^{-1} MPP) was added in a 6 well culture-plates. Then a drop of 3 mg mL^{-1} MB solution was add carefully to the static H_2O_2 solution, and the photographs were taken at intervals.

Photocurrent measurement: The photocurrent was tested in 100 mM $NaSO_4$ solution at an applied bias 0.5 V versus Ag/AgCl. A three-electrode configuration was used: a platinum column as the counter electrode, Ag/AgCl as the reference electrode and the TiO_2 or MPP film modified ITO was employed as the working electrode. For preparation of the working electrode, suspension of catalyst was dropped on the ITO glass surface, after drying at room temperature nafion was dropped to immobilize the film. A 300 Watt quartz halogen lamp was used as light source with the distance between the lamp and the electrode being fixed at 20 cm.

Photocatalytic degradation: MB, RB and MO were used as model organic compounds**.** A 300 Watt quartz halogen lamp was used as artificial solar source. The distance between the lamp and the reactor was fixed at 20 cm. In a typical measurement, 6.67 mL aqueous solution containing 80 μg MB (RB/MO) and 4 mg MPP was placed in a 25 mL jacketed beaker. Prior to photo irradiation, the suspension was magnetically stirred in the dark for 40 min to establish adsorption-desorption equilibrium. Then 1.33 mL 30 % H_2O_2 was added just before irradiation. 0.5 mL of the suspension was collected and centrifuged every 10 min. After centrifugation, the residual concentration in the supernatant was analyzed through measuring the absorbance at 600 nm (550 nm for RB and 450 nm for MO). To perform the photocatalytic under anaerobic conditions, the dissolved oxygen was removed by bubbling nitrogen for 30 min before irradiation, and the samples were kept under a nitrogen atmosphere during photo irradiation by flowing nitrogen gas over the liquid surface. For the complex organic mixture photocatalytic degradation, a super organic mixture containing equal amount of eleven different organics (MB, RB, MO, p-nitrophenol, fluorescein, direct red, acid fuchsin, 1-aminoanthraquinone, p-benzoquinone, brilliant black and astrazon orange) was first prepared. In the photocatalytic degradation measurement the organic mixture (1.5 μg mL^{-1} each) along with 0.5 mg mL^{-1} of photocatalyts and 5% H_2O_2 was irradiated for 1.5 h. After centrifugation the supernatant was collect and the absorption spectrum was measured.

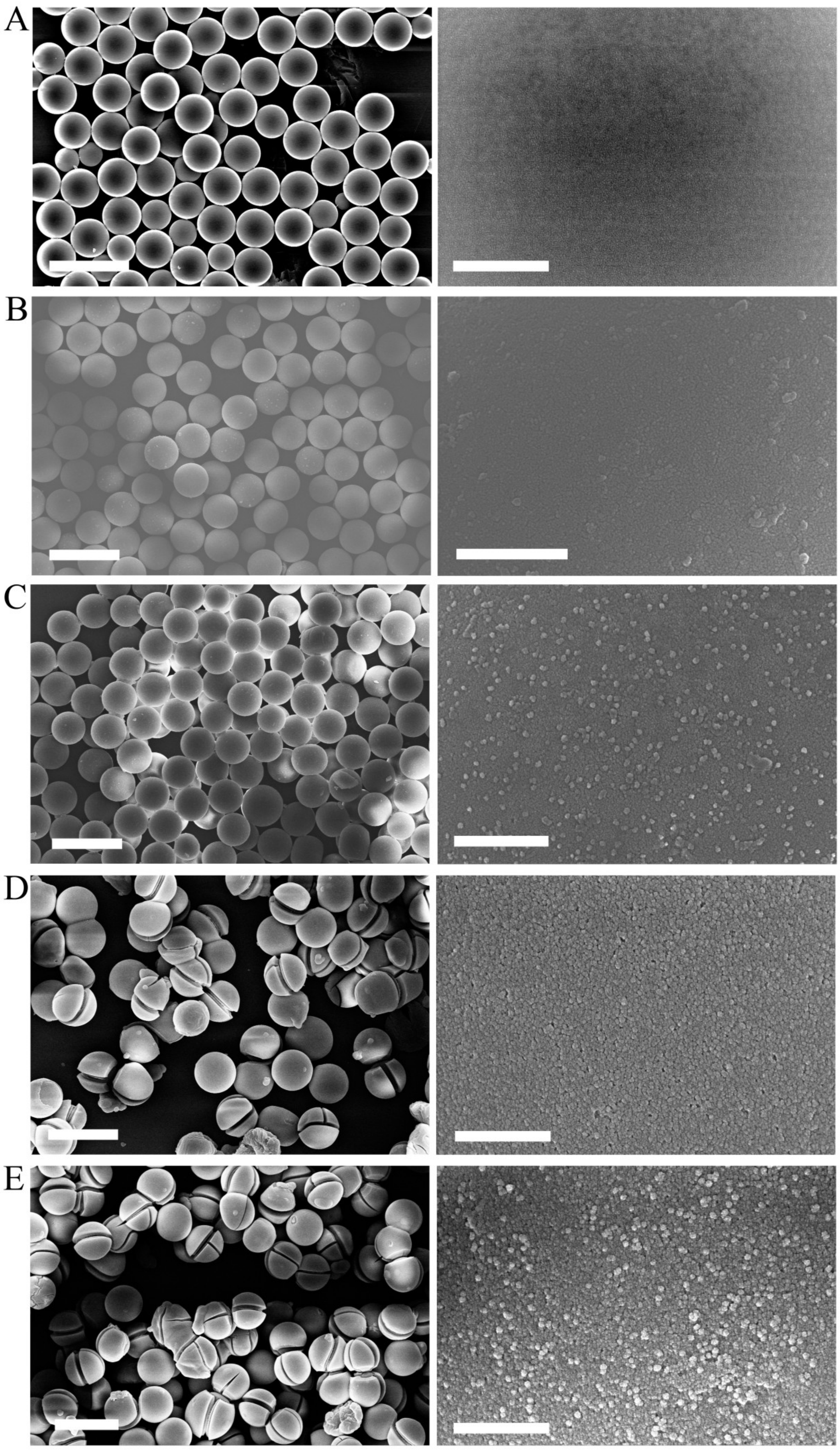
A
B
C
D
E

Fig. S1 SEM images (left) and typical surfaces high-resolution SEM images (right) of PS, PS@PDA, PS@PDA@PtNPs, PS@PDA@PtNPs@TiO_2, PS@PDA@PtNPs@TiO_2@AuPNs (A-E). Scale bar = 10 μm (left) and 500 nm (right).

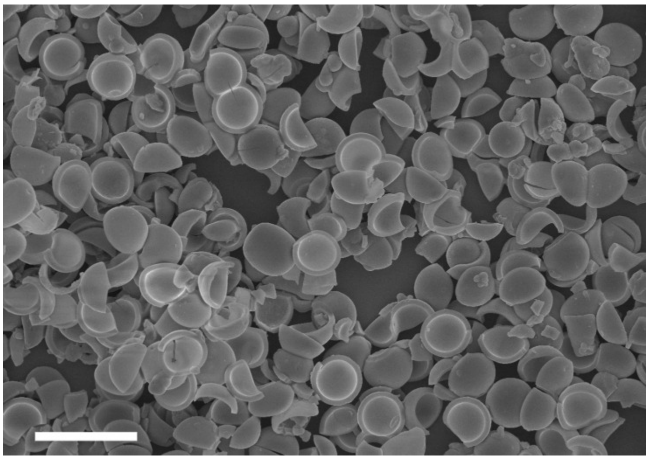

Fig. S2 SEM image of TiO_2 particles (scale bar = 10 μm).

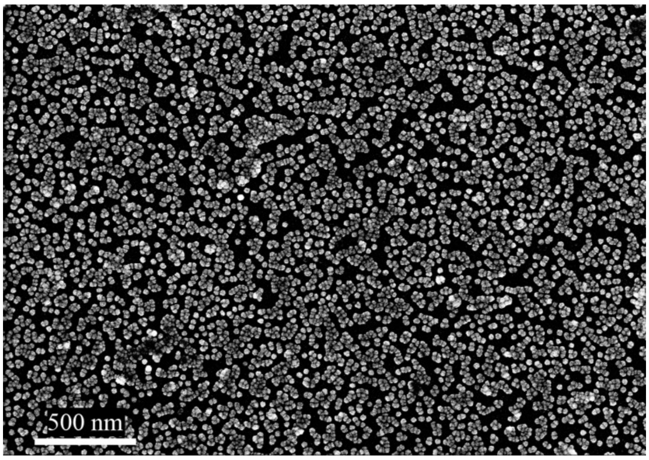

Fig. S3 SEM image of AuNPs.

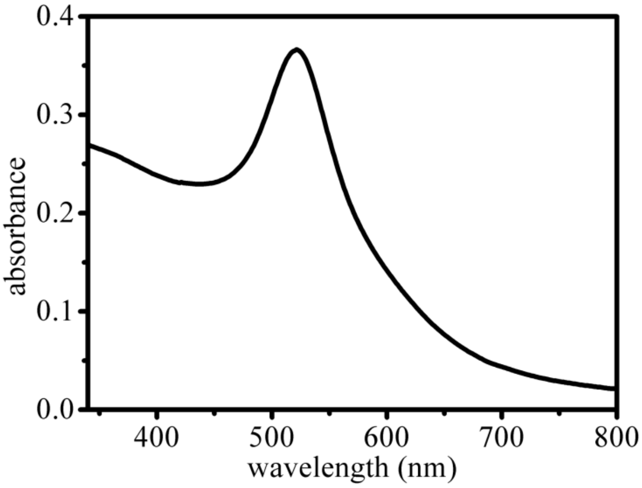

Fig. S4 UV-vis absorption spectrum of AuNPs.

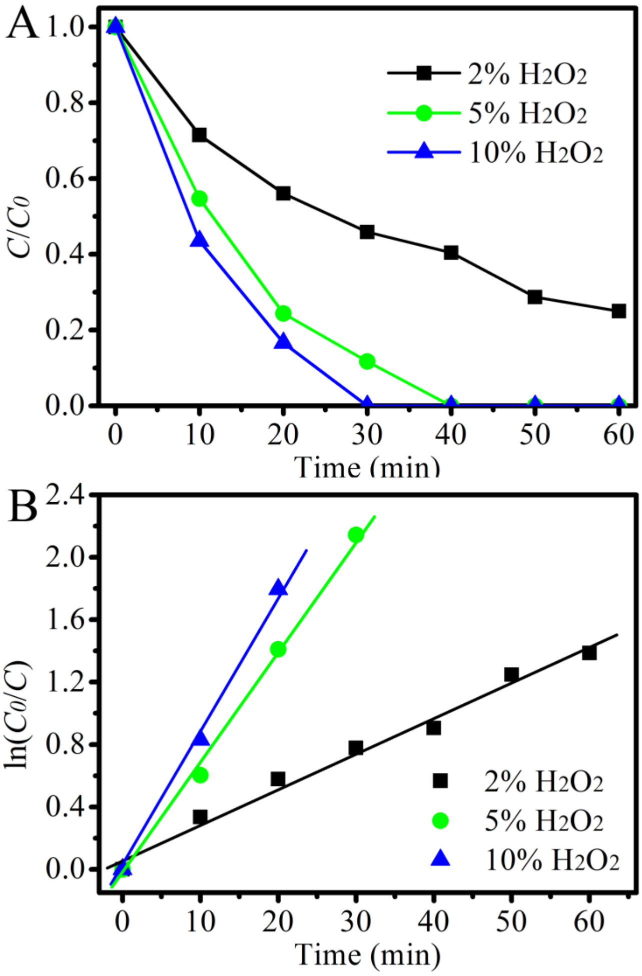

Fig. S5 H_2O_2 concentration dependent degradation of MB (10 μg mL^{-1}) with 0.5 mg mL^{-1} MPP under solar irradiation. The degradation rate constants of 2%, 5% and 10% H_2O_2 were 0.0898, 0.0724 and 0.0225 min^{-1}, respectively.

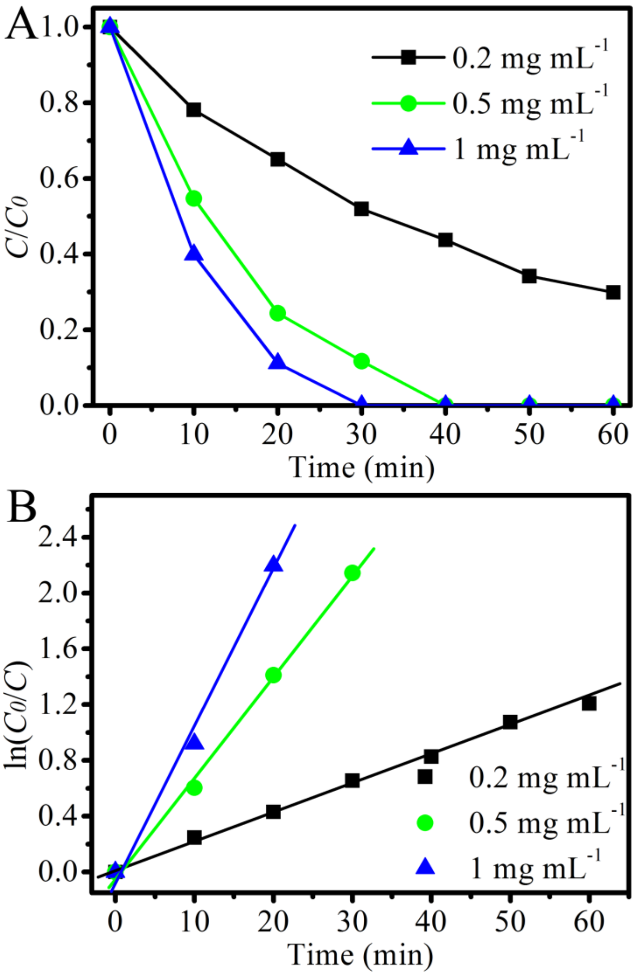

Fig. S6 MPP concentration dependent degradation of MB (10 μg mL^{-1}) with 5% H_2O_2 under solar irradiation. The degradation rate constants of 0.2, 0.5 and 1 mg mL^{-1} were 0.1098, 0.0724 and 0.0203 min^{-1}, respectively.

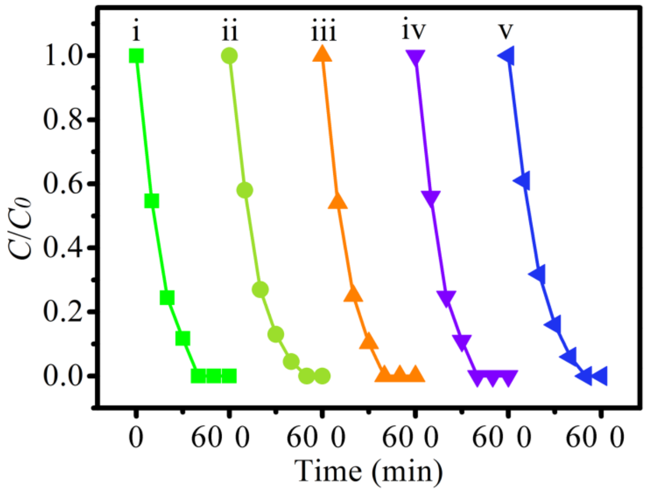

Fig. S7 Photocatlytic degradation of MB (10 μg mL^{-1}) using recovered MPP (0.5 mg mL^{-1}) with 5% H_2O_2 for five cycles.

Table S1. Elemental analysis results: pure water (a); the supernatant of 0.5 mg mL^{-1} MPP (b) and the supernatant of a mixture containing 0.5 mg mL^{-1} MPP, 5% H_2O_2 and 10 μg mL^{-1} MB after being photo irradiated for 1 h (c). These results were obtained from three parallel samples by inductively coupled plasma mass spectrometry (ICP-MS). The supernatant was collected by a low-speed centrifugation through which the detached small nanoparticles could be kept in the supernatant. "-" represented the concentration was undetectable.

	a	**b**	**c**
Ti (ng mL^{-1})	519.3±14.4	534.8±22.7	515.7±17.2
Au (ng mL^{-1})	-	-	-
Pt (ng mL^{-1})	-	-	6.34±0.41

The results in Table S1 showed the high stability of the plasmonic photocatalysts. Very few PtNPs were found to leach out during the photocatalytic reaction. This detaching didn’t cause any detectable decreasing in the photocatalytic activity (Figure S7).

Reference:

1 Z. Zhang, Y. Long, J. Pan and X. Yan, *J. Mater. Chem.*, 2010, **20**, 1179-1185.