

Electronic Supplementary Information

Plasmonic-redox controlled atom transfer radical polymerization

*Yuyang Guo,^{a, c} Yu Zou^{*b, c} and Jiang Jiang^{*b, c}*

^aDepartment of Polymer Materials, College of Materials Science and Engineering, Shanghai University, Nanchen Street 333, Shanghai, 200444, China

^b*i*-Lab, CAS Key Laboratory of Nano-Bio Interface, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, 215123, China

^cSchool of Nano-Tech and Nano-Bionics, University of Science and Technology of China, Hefei, 230026, China

Experimental Methods

Materials

Methyl methacrylate (MMA) was purchased from Sigma-Aldrich. TiO₂, ethyl α -bromoisobutyrate (EBIB), CuBr₂ and N,N',N',N'',N''-pentamethyldiethylenetriamine (PMDETA) were purchased from Aladdin. Acetonitrile (MeCN), acetone, methanol (MeOH), tetrahydrofuran (THF), HAuCl₄·4H₂O, ethanol (EtOH) and urea were purchased from Sinopharm Chemical Reagent Co., Ltd. The MMA monomer was passed through a basic alumina column (100-200 mesh, purchased from Aladdin) to remove inhibitors before use. Other chemicals were used as received, and deionized water (Millipore, Milli-Q grade) was used in all experiments.

Synthesis of the plasmonic photocatalyst

The plasmonic photocatalyst was prepared by the typical deposition-precipitation method. Commercial TiO₂ (1.0 g, rutile, ~40 nm) powder was first mixed with an aqueous solution (100 mL) of HAuCl₄ (1 mM) and urea (0.42 M). After TiO₂ was dispersed by gentle stirring under room temperature, the suspension was transferred to a 353 K oil bath, and kept under stirring for 4 h in the dark. The solution was then centrifuged, washed with water for 3 times, and dried at 333 K under vacuum overnight. Finally, the powery sample was calcined at 673 K for 4 h in a muffle furnace.

SiO₂ coated r-TiO₂ was prepared by a modified Stober method. TiO₂ (1.0 g, rutile, ~40 nm) was dispersed in an NH₃·H₂O-EtOH mixed solution (1.34 mL NH₃·H₂O mixed with 10 mL EtOH) by ultra-sonification in a vial, covered by a Parafilm. TEOS

(1.9 mL) was added dropwise by a syringe pump in 45 min, under vigorously magnetic stirring at room temperature. After the addition was completed, the suspension was kept stirring overnight, and then the suspension was centrifuged, washed with EtOH 3 times, and dried at room temperature under vacuum overnight. The molar ratio of Si/Ti = 0.68.

General procedures for LSPR-ATRP of MMA

In a typical reaction setting, Au/TiO₂ (10 mg), MMA (2 mL), MeCN (0.5 mL), CuBr₂ stock solution (5.2 μL, 180 mM in MeCN), and PMDETA stock solution (10.4 μL, 270 mM in MeCN) were charged and sealed in a vial with a plug-type rubber stopper. The Cu(II) loading was 59.47 ppm. After degassing by gentle pure-N₂ bubbling for 30 min, and ultrasonic treatment for 1 min to sufficiently disperse the plasmonic photocatalyst, the reaction vial was placed on a magnetic stirrer, next to a laser-diode pumped all-solid-state CW 532 nm laser (MGL-FN-532-1.5W, Changchun New Industries Optoelectronics Technology Co., Ltd.). After irradiating the reaction mixture with the laser (1.5 W) under stirring (1000 rpm) at room temperature for 4 h, it was diluted by acetone or THF and centrifuged, with the resulting supernatant collected and precipitated in MeOH-H₂O (v/v = 1:1). After 2 rounds of purification through centrifugation and redissolution in acetone or THF, the polymer was collected and dried at 318 K in a vacuum oven overnight. The monomer conversion was measured gravimetrically, and the molecular weight and dispersity were analyzed by gel permeation chromatography.

For kinetics studies, aliquots were taken out at 0.5 h intervals for analysis using a pre-degassed syringe.

When conducting light on-off experiments, the laser source was turned on and off periodically, starting at t_0 when the laser irradiated the reaction vial for the first time, with aliquots of samples taken by a pre-degassed syringe for analysis.

Calculation of theoretical MW and initiator efficiency

The theoretical molecule weights were calculated based on the ratio of monomer and the ATRP initiator EBIB, by the following equation:

$$M_{n,th} = [MMA]_0/[EBIB]_0 \times \text{Conversion}(\%) \times M(MMA) + M(EBIB)$$

The initiator efficiency was calculated as the ratio of theoretical molecular weight to experimental molecular weight:

$$\theta_{ini.} (\%) = M_{n,th}/M_{n,exp} \times 100\%$$

Characterizations

The optical property of the plasmonic photocatalysts and the ATRP system was measured by a UV-3600 Plus UV-vis-NIR spectrophotometer. Morphologies of plasmonic photocatalysts were analyzed under a transmission electron microscope (TEM, Hitachi HT7700). High-angle annular dark-field imaging (HAADF) images were taken with a FEI Technai G2 S-Twin instrument at an accelerating voltage of 200 kV. Elemental mapping was conducted on a JEOL JEM-2100F. XRD analyses were performed using a Bruker D8 Advance X-ray diffractometer (with Cu Ka radiation at 0.154 18 nm). Varian NMR System 400 MHz NMR Spectrometer with automated triple broadband (ATB) probe was used for ¹H-NMR measurements of the polymers, typically with 5-10 mg purified polymer samples dissolved in 0.5 mL

CDCl_3 . Gel permeation chromatography (GPC) analysis was performed on an Agilent PL-GPC50 GPC system, with THF as eluent and poly(ethylene glycol) of low dispersity as standards. The GPC system is equipped with two PL aquagel-OH mixed $8\ \mu\text{m}$ columns and a refractive index detector. The sample loading was $100\ \mu\text{L}$ of $2\ \text{mg mL}^{-1}$ polymer solution in THF, and the test temperature was $30\ ^\circ\text{C}$.

Supplementary Figures and Tables

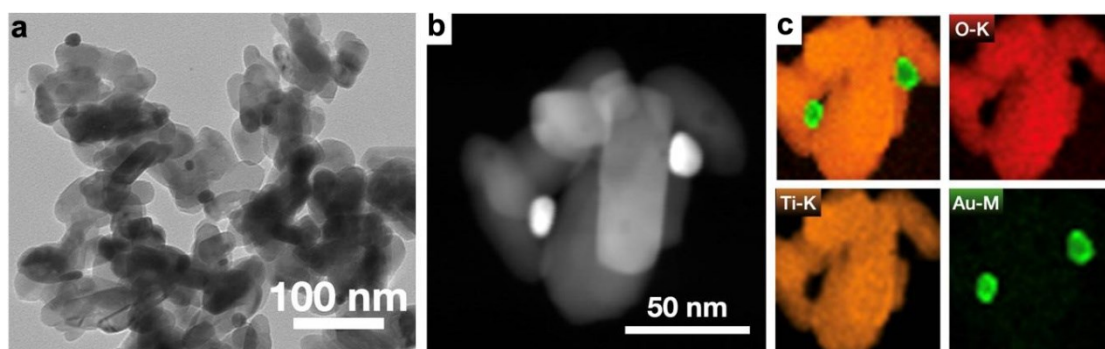


Fig. S1 (a) Transmission electron microscope (TEM) image, (b) HAADF image, and (c) elemental mapping of Au/r-TiO₂.

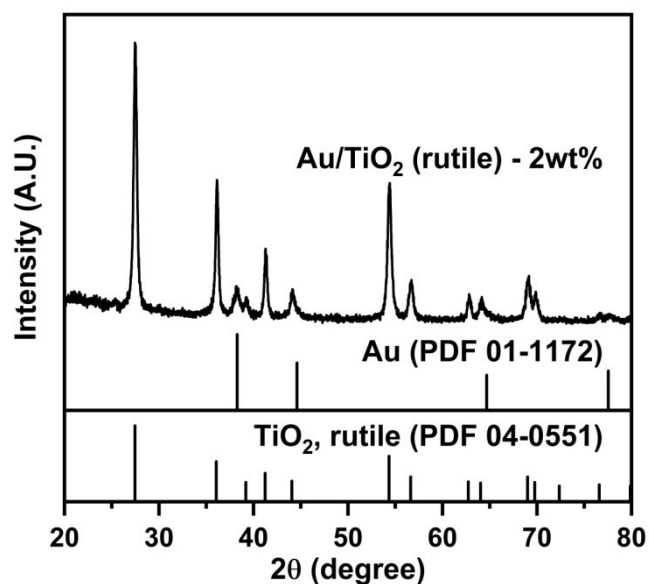


Fig. S2 X-ray diffraction of the Au/r-TiO₂ heterostructure.

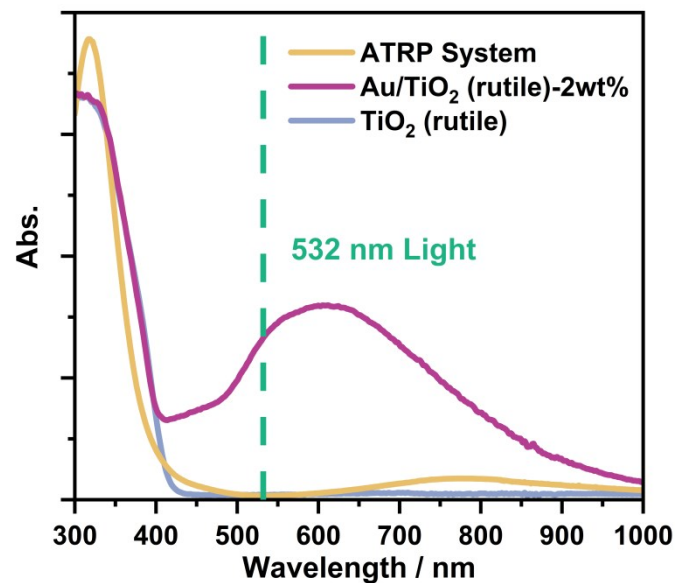


Fig. S3 UV-vis absorption spectra of r-TiO₂ and Au/r-TiO₂ in H₂O, and the ATRP reaction mixture with [MMA]₀: [EBIB]₀: [CuBr₂]₀: [PMDETA]₀ = 200:1:0.01:0.03 in MeCN.

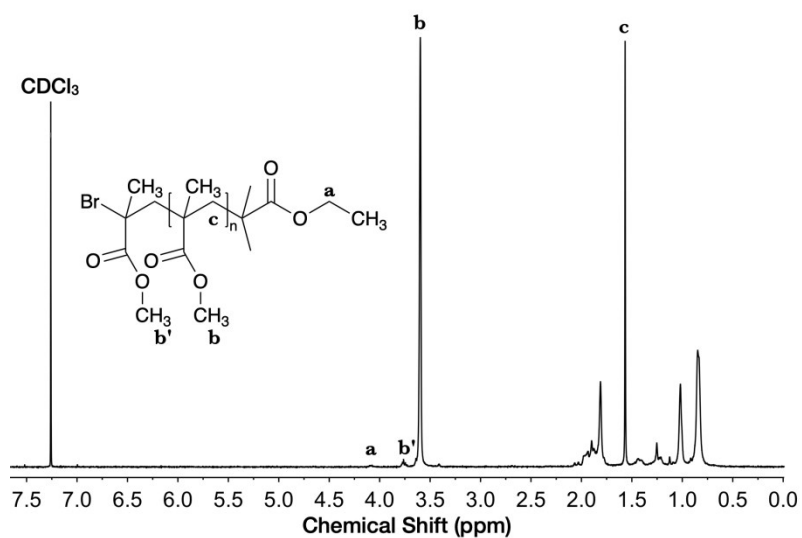


Fig. S4 ¹H-NMR spectrum of PMMA which is dissolved in CDCl₃, showing characteristic signals from initiator (CH₃CH₂-), subunits (-OCH₃, -CH₂-) and bromide end group (CH₂C(CH₃)(C=O-OCH₃)-Br).

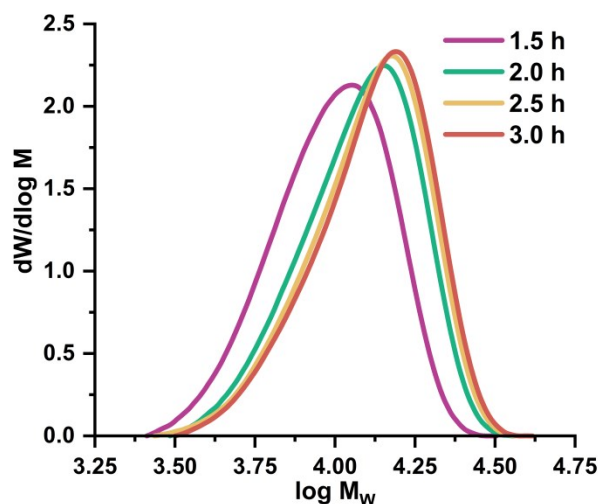


Fig. S5 Temporal evolution of PMMA molecular weights in kinetic studies.

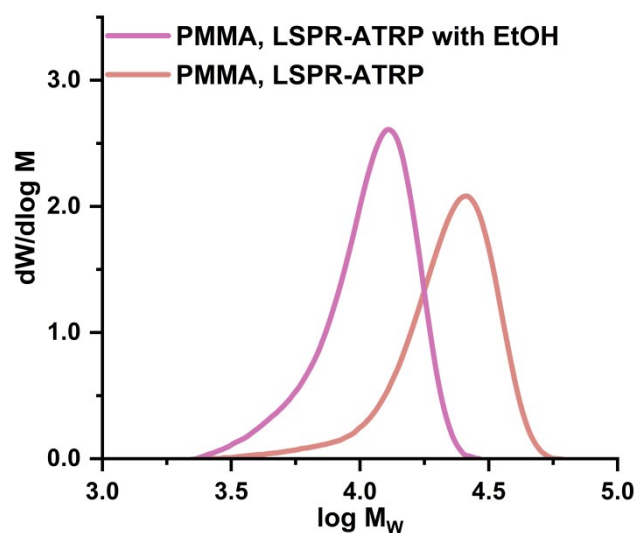


Fig. S6 Changes in molecular weights of LSPR-ATRP with and without EtOH.

Table S1 ATRP reaction conducted under different conditions

| Condition | Au/r-TiO ₂ | CuBr ₂ | Conversion / % | M _{n,exp} | M _{n,th} | Đ | θ _{ini./} % |
|-----------|-----------------------|-------------------|----------------|--------------------|-------------------|------|----------------------|
| dark | + | + | 0 | - | - | - | - |
| light | - | + | 0 | - | - | - | - |
| light | + | + | 13.02 | 20053 | 2604 | 1.18 | 13.96 |
| light | + | - | 12.87 | 136727 | 2574 | 3.56 | 2.03 |

Polymerization reactions were performed in 20% MeCN in the dark or under visible light (532 nm) irradiation for 4 h, with [MMA]₀: [EBIB]₀: [PMDETA]₀ = 200:1: 0.03, [CuBr₂]₀ either 0 or 0.01 equiv., and Au/r-TiO₂ (10 mg) if it was used. The “+” and “-” signs indicate the presence and absence of Au/r-TiO₂ or CuBr₂.

Table S2 ATRP reaction conducted using Au on different supports

| Entry | Condition | Conversion / % | M_{n,exp} | M_{n,th} | D | θ_{ini.} / % |
|--------------|----------------------------|-----------------------|--------------------------|-------------------------|----------|-----------------------------|
| 1 | Au/SiO ₂ | 0 | - | - | - | - |
| 2 | Au/rutile@SiO ₂ | 0 | - | - | - | - |
| 3 | Au/anatase | 1.60 | 11736 | 514 | 1.13 | 4.38 |

Polymerization reactions were performed in 20% MeCN under visible light (532 nm) irradiation for 4 h, with [MMA]₀: [EBIB]₀: [CuBr₂]₀: [PMDETA]₀ = 200:1:0.01:0.03.