

Supplementary Information for

Self-assembled Janus Plasmene Nanosheet as

Flexible 2D Photocatalysts

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Experimental section

Materials. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), hexadecyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH_4), L-ascorbic acid (AA), trisodium citrate (TC), silver nitrate (AgNO_3), cetyltrimethylammonium chloride solution (CTAC, 25 wt % in H_2O), polyvinylpyrrolidone (PVP, average $M_w \sim 55,000$), potassium bromide (KBr , $\geq 99.9\%$), sodium chloride (NaCl , 99.99%), palladium chloride (PdCl_2 , 99%), 4-nitrophenol (4-NP) and were obtained from Sigma-Aldrich. Ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25 wt %), hydrogen peroxide (H_2O_2 , 30 wt %) and chloroform was purchased from Merck Millipore. Tetrahydrofuran (THF), methanol (MeOH), acetone and hydrochloric acid (HCl, 32 wt %) was purchased from Thermal fisher scientific (Ajax Finechem). Thiol-functionalized polystyrene (PS, $M_n = 50,000$ and $20,000$ g/mol) was obtained from Polymer Source. Indium tin oxide-coated glass slides (ITO glass, $30\text{-}60 \Omega/\text{sq}$) were purchased from South China Science & Technology Company Limited, China. Milli-Q water was obtained from Milli-Q Advantage A 10 water purification System. All materials were used without any further purification.

Synthesis of gold nanocubes (Au NCs). Seed-mediated method was used to synthesize Au NCs according to literature.¹ For the synthesis of seeds, 7.65 mL of 0.1 M CTAB was firstly added into a 20 mL glass vial. Then, 0.1 mL of 25 mM HAuCl_4 and 0.6 mL of freshly prepared ice-cold 0.01 M NaBH_4 were added into the vial. The vial with mixed solution was heated in a 30 °C water bath under 500 rpm stirring for 30 s. After that, the solution was kept undisturbed for 1 hour in the 30 °C water bath. The prepared seed solution was diluted 10 times by adding 1 mL of seed solution to 9 mL of MQ water. To grow Au NCs, 12 mL of MQ water was firstly added in to a 50 mL tube. Then, 2.4 mL of 0.1 M CTAB, 0.3 mL of 10 mM HAuCl_4 and 1.8 mL of 10 mM AA were added into the tube with a gentle shake after each addition. After

mixing all precursor solutions, the solution was kept undisturbed in the 30 °C water bath overnight. Finally, the Au NCs were collected by centrifuging at 7800 rpm for 10 min and then redispersed in 15 mL MQ water for further use.

Synthesis of gold nanobipyramids (Au NBPs). Au NBPs were synthesised by a seed-mediated method reported in literature with small modifications.² For the synthesis of seeds, 4.9 mL of 0.1 M CTAC was added into a 20 mL glass vial. Then, 5 mL of 10 mM TC, 0.1 mL of 25 mM HAuCl₄ and 0.25 mL 25 mM NaBH₄ were added subsequently into the vial. The mixed solution was stirred at room temperature for 2 min followed by keeping in an 80 °C water bath under 300 rpm stirring for 90 min. The seed solution was then cooled down to room temperature for further use. For the growth of Au NBPs, a growth solution was prepared by mixing 50 mL of 0.1M CTAB solution with 1 mL of 25 mM HAuCl₄, 0.5 mL of 10 mM AgNO₃, 1 mL of 1.0 M HCl and 0.4 mL of 0.1 M AA. 0.4 mL of seed solution was then added to the as-prepared growth solution. After that, the mixed solution was kept in the 30 °C water bath for 2 hours. The as-prepared Au NBPs solution was collected by centrifuging at 7830 rpm for 10 min. In order to get highly pure Au NBPs, the as-prepared Au NBPs were further purified by the method described in literature with small modifications.³ In detail, the above collected Au NBPs were firstly redispersed in 70 mL of 80 mM CTAC, followed by adding 44 mL of 20 mM Ag NO₃ and 22 mL of 0.2 M AA. The mixed solution was kept under stirring at 500 rpm in a 60 °C water bath for 4 hours. The solution was then cooled down to room temperature for the further use. The bimetallic Au/Ag product was collected by centrifuging at 6000 rpm for 10 min and then redispersed in 50 mL of 50 mM CTAB. The solution was kept undisturbed for 2 hours to precipitate the Au@Ag nanorods to the bottom of the container. The supernatant which mainly contains spherical-like nanoparticles was discarded. The precipitate was then redispersed in 20 mL of water and gently mixed with 3 mL of NH₃·H₂O and 3 mL of H₂O₂. The mixed solution was kept undisturbed until the Ag shell was completely etched away. The

clear supernatant was carefully taken out and centrifuged at 8200 rpm for 10 min. The highly pure Au NBPs were finally redispersed in 25 mL of 50 mM CTAB for further use.

Synthesis of palladium nanocubes (Pd NCs). Pd NCs were synthesized according literatures with small modifications.⁴ 105 mg of PVP, 600 mg of KBr and 66 mg of AA were added into 7.564 mL MQ water. The mixture was stirred at 500 rpm for 15 min in an 80 °C water bath to get a clear solution. After that, 3.436 mL of 0.05 M Na₂PdCl₄ was added into the above solution. 0.05 M Na₂PdCl₄ solution was prepared by dissolving 0.5 g PdCl₂ and 0.3 g NaCl in 50 mL of MQ water under stirring at 800 rpm at room temperature until the fully dissolve of PdCl₂. The mixed solution containing Pd precursor was kept stirring at 500 rpm in an 80 °C water bath. After 3 hours, the Pd NCs were washed with MQ water by centrifuge (14000 rpm, 5 min) for 3 times and then redispersed in 22 mL MQ water for further use.

Fabrication of Au NC plasmene nanosheets. The plasmene nanosheets were prepared by a two-step drying-mediated method reported by our group.⁵ The Au NCs was centrifuged at 7800 rpm for 10 min, redispersed in 5 mL of 4 mg/mL PS ($M_n = 20,000$ g/mol) in THF solution and kept undisturbed overnight to exchange the ligand from CTAB to PS. The PS-capped Au NCs were then washed with THF and chloroform to remove the residual PS ligands. The final PS-capped Au NCs in chloroform was concentrated to about 10 μ L by centrifuge. Finally, one drop of concentrated PS-capped Au NCs was spread on the surface of a convex-shaped water droplet sitting on a Si wafer (or ITO glass or PET film). After the water completely evaporated, a continuous monolayer Au NC nanosheet was formed on the substrate.

Fabrication of Au NBP plasmene nanosheets. 5 mL of Au NBPs aqueous solution were diluted to 10 mL with MQ water, centrifuged at 8200 rpm for 10 min and finally redispersed in 4 mg/mL PS in THF solution. PS with molecular weight of $M_n = 50,000$ g/mol was used for H-NBP plasmene nanosheets and $M_n = 20,000$ g/mol was for V-NBP plasmene nanosheets.

The Au NBPs solution were kept undisturbed overnight to finish the ligand exchange. The PS-capped Au NBPs were washed with THF for 2 times and chloroform once to remove the residual PS ligands. The final PS-capped Au NBPs in chloroform was concentrated to about 10 μ L after centrifuge. The fabrication of Au NBPs plasmene nanosheets followed the same procedure of Au NCs plasmene nanosheets as described above.

Fabrication of Pd NC nanosheet. 1 mL of Pd NCs aqueous solution was diluted to 10 mL with MQ water followed by centrifuging at 14000 rpm for 10 min. The collected Pd NCs were then re-dispersed in 5 mL 4 mg/mL PS ($M_n = 20,000$ g/mol) in THF solution and kept undisturbed overnight to finish the ligand exchange process. The PS-capped Pd NCs were washed with THF for 2 times and chloroform once by centrifuge at 13500 rpm for 5 min. The final PS-capped Pd NCs in chloroform was concentrated to about 10 μ L by centrifuge. The fabrication of Pd NCs nanosheets follows the same procedure as that of Au NCs plasmene nanosheets. The substrate for Pd NCs nanosheets was ITO glass. Before being used for catalytic investigation, Pd NCs nanosheets were treated by air plasma treatment for 1 min under high radio frequency power (RF) using Harrick Plasma Cleaner PDC-002-HP to remove PS.

Fabrication of Janus plasmene nanosheets. The PS-capped plasmene nanosheets were firstly treated by air plasma for 1 min under high RF power to selectively remove PS. Once the PS was removed, the plasmene nanosheets were immediately immersed in 0.8 mL of 1 mM ice-cold H_2PdCl_4 solution to grow Pd.⁶ 1 mM H_2PdCl_4 solution was obtained by diluting 10 mM H_2PdCl_4 solution which was prepared by fully dissolving 88.6 mg $PdCl_2$ in 50 mL of 0.1 M HCl under stirring at 800 rpm in a 60 °C water bath. To fabricate Au NCs plasmene nanosheets with different Pd thicknesses, the concentration of H_2PdCl_4 solution was tuned from 0.1 mM to 1 mM. After that, 0.2 mL of 10 mM AA was added to the Pd precursor solution using syringe pump at a rate of 0.1 mL/min. Once the injection completed, the plasmene nanosheets were

immediately taken out and washed thoroughly with MQ water and dried at room temperature for further characterization.

Control samples. 100 μL of CTAB protected Au NCs solution was diluted to 1 mL by MQ water, followed by washing with MQ water once at a centrifuge speed of 7800 rpm for 10 min and finally redispersed in 1 mL MQ water. 50 μL of the washed Au NCs aqueous solution was then dropped on Si wafer and left undisturbed until the fully evaporation of water. The CTAB-capped Au NCs on Si wafer was then immersed in Pd precursor solution to grow Pd. The growing conditions of Pd are the same as that of Janus plasmene nanosheets.

Artificial tree. To build “artificial leaf”, the Au NCs-based Janus plasmene nanosheets was fabricated on the PET substrate. A tree frame was printed by Objet Eden 360 3D printer. Then, 8 pieces of Janus plasmene nanosheets on PET were assembled on the tree frame by glue.

Catalytic activity. The catalytic reduction of 4-NP to 4-AP⁷ was chosen as the model reaction to investigate the plasmon-enhanced catalytic property of Janus plasmene nanosheets. 3 mL of 0.05 M ice-cold NaBH_4 was added into a cuvette, followed with the addition of 60 μL of 5 mM 4-NP. The UV-vis spectrum of the initial solution was recorded before adding Janus plasmene nanosheets. The catalytic reaction will be triggered by adding the Janus plasmene nanosheets into the 4-NP solution. The reaction was carried out in a sunlight-permeable room at Melbourne, Australia on sunny days from 10 to 11 a.m. from July to September 2019 or driven by using different light sources: UV-365 (XL-1000 UV crosslinker, Spectrolinker), lasers with wavelength of 532 nm and NIR (800-1070 nm). The UV-vis spectrum was recorded every 5 min. For the reaction without light, the same reaction was carried out at night at room temperature. The Al foil was used to cover the cuvette to avoid any light irradiation. For the reaction with scavengers, 2 μL of MeOH was added as the hole (h^+) scavenger and 2 μL of acetone was added as the electron (e^-) scavenger. For the reaction without NaBH_4 , the 60 μL

of 4-NP was added into 3 mL MQ water. For the thermally enhanced reactions, the Al foil-covered cuvettes were put in a 40 °C or 60 °C water bath to carry out the catalytic reactions. To test the catalytic activity of “artificial tree”, 600 µL of 5 mM 4-NP was added into 30 mL of 0.05 M NaBH₄ in a glass beaker, followed with the addition of “artificial tree”. The reaction was carried out under sunlight for 45 min. Before each recycling test, the tree was washed by MQ water for 3 times and dried at room temperature.

Characterization. The morphology of plasmene nanosheets and nanoparticles was characterized by scanning electron microscope (SEM, FEI Helios Nanolab 600 focused ion beam (FIB)-SEM operating at voltage of 5 kV and current of 86 pA) and transmission electron microscope (TEM, FEI Tecnai G2 T20 TWIN LaB6 TEM operating at voltage of 200 kV). The elemental mapping of Janus structure were obtained by FEI Tecnai F20 S/TEM operating at voltage of 200 kV. X-ray photoelectron Spectroscopy (XPS) measurements were obtained using a Thermo Scientific NEXSA photoelectron spectrometer calibrated to Au 4f and equipped with a hemispherical analyser and a 128-channel position sensitive detector. The incident radiation was monochromatic Al K α X-rays (1486.6 eV) at 72 W (6 mA and 12 kV, 400 × 800 µm² spot). Survey and high-resolution scans were recorded at analyser pass energies of 150 and 50 eV, respectively. The base pressure in the analysis chamber was less than 3.0 × 10⁻⁹ mbar. Samples were mounted using copper clips and charge compensation was achieved using a dual neutralisation system comprised of low energy argon ions and an electron flood gun. Data processing was carried out using Avantage v5.9910. All photoelectron peaks were modelled using the Smart background type and energy calibration was referenced to the low binding energy component of the C 1s peak at 284.8 eV. The contact angle measurements were carried out on an optical contact angle measuring and contour analysis system (OCAH 230, Dataphysics) by applying 5 µL of MQ water for each test. The intensity of light was measured by a power meter (Model 843-R, Newport). An Agilent 8453 UV–vis spectrophotometer was

used to record the absorption spectra and a J&M MSP210 microscope spectrometry system under a 20× objective was used to record the extinction spectra of plasmene nanosheets. The acquired area for extinction spectra of plasmene nnaosheets is 6 μm×6 μm. The size and Pd thickness of nanoparticles were analysed by Image J software.

Figures

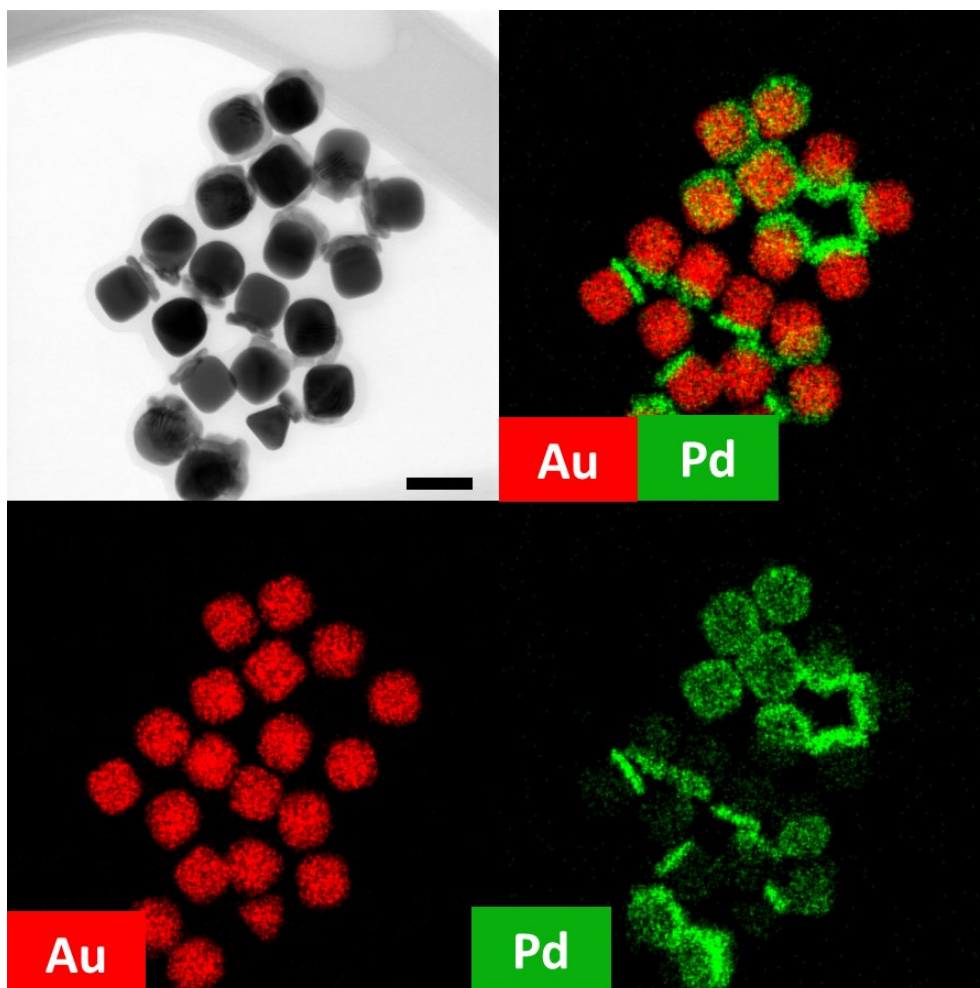


Figure S1. Dark-field TEM images and corresponding EDX elemental mapping images of individual Janus NPs. (Scale bar: 50 nm)

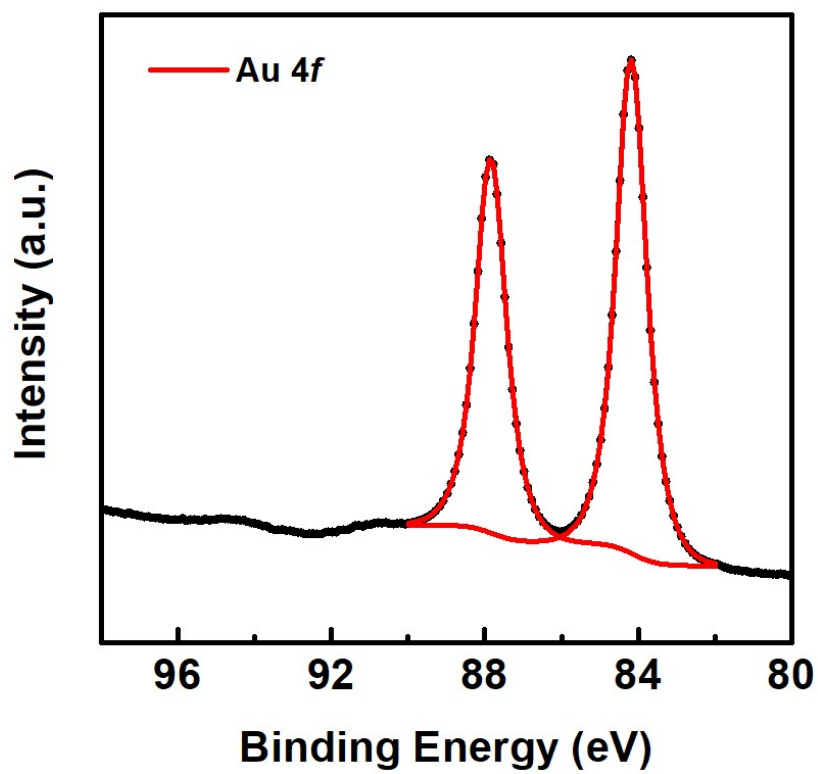


Figure S2. High-resolution XPS spectra of PS-capped plasmene nanosheet (the one shown in Figure 1a-c).

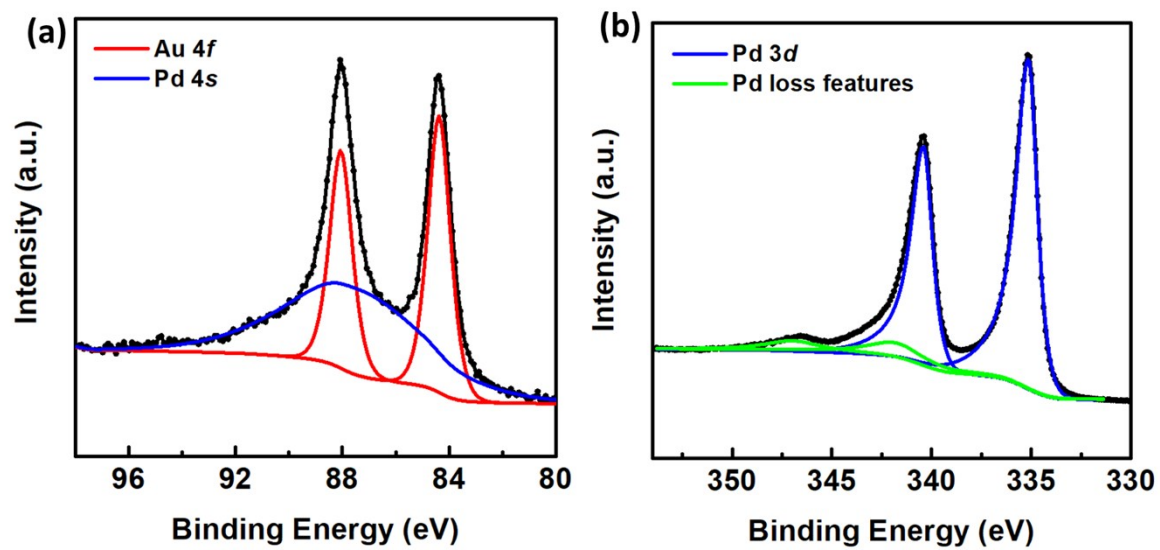


Figure S3. High-resolution XPS spectra of Pd-Au Janus plasmene nanosheet (the one shown in Figure 1g-i).

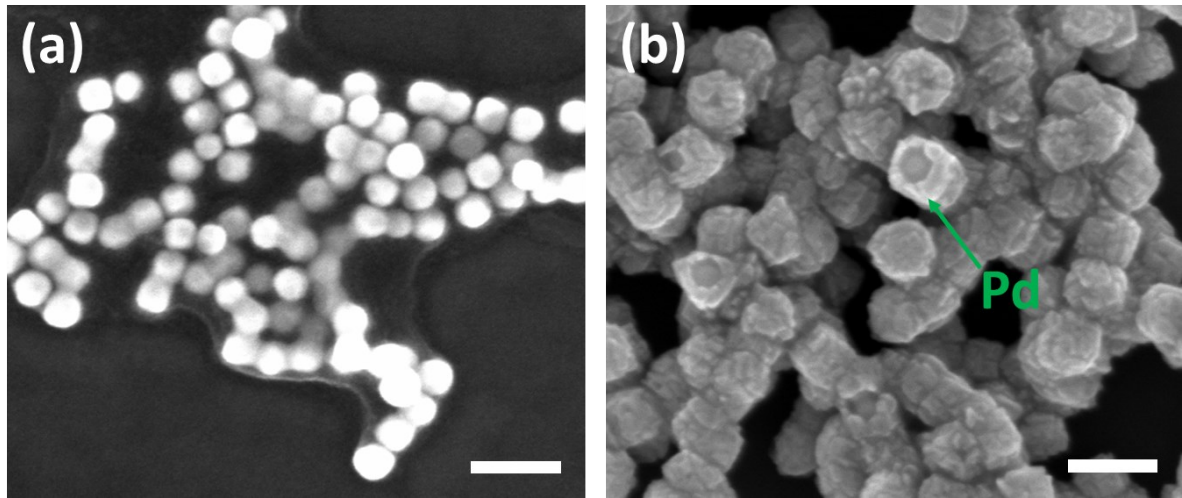


Figure S4. SEM images of CTAB-capped Au NCs (a) before and (b) after the deposition of Pd. (Scale bar: 100nm)

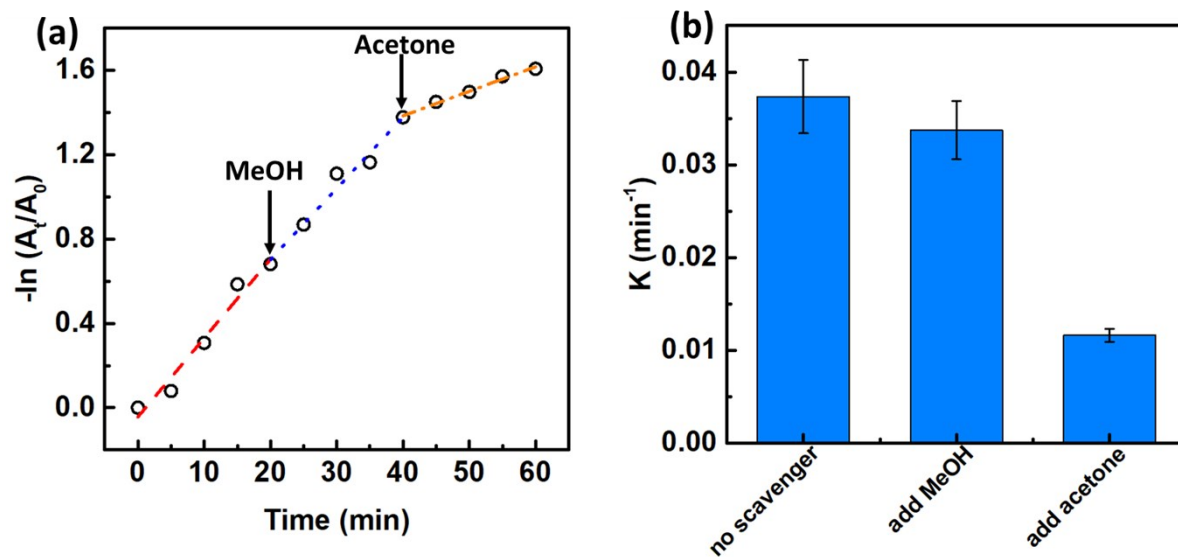


Figure S5. Catalytic kinetics (a) and rates (b) of Janus plasmene nanosheet (the one shown in Figure 1g-i) by adding methanol (MeOH) as hole scavenger and acetone as electron scavenger.

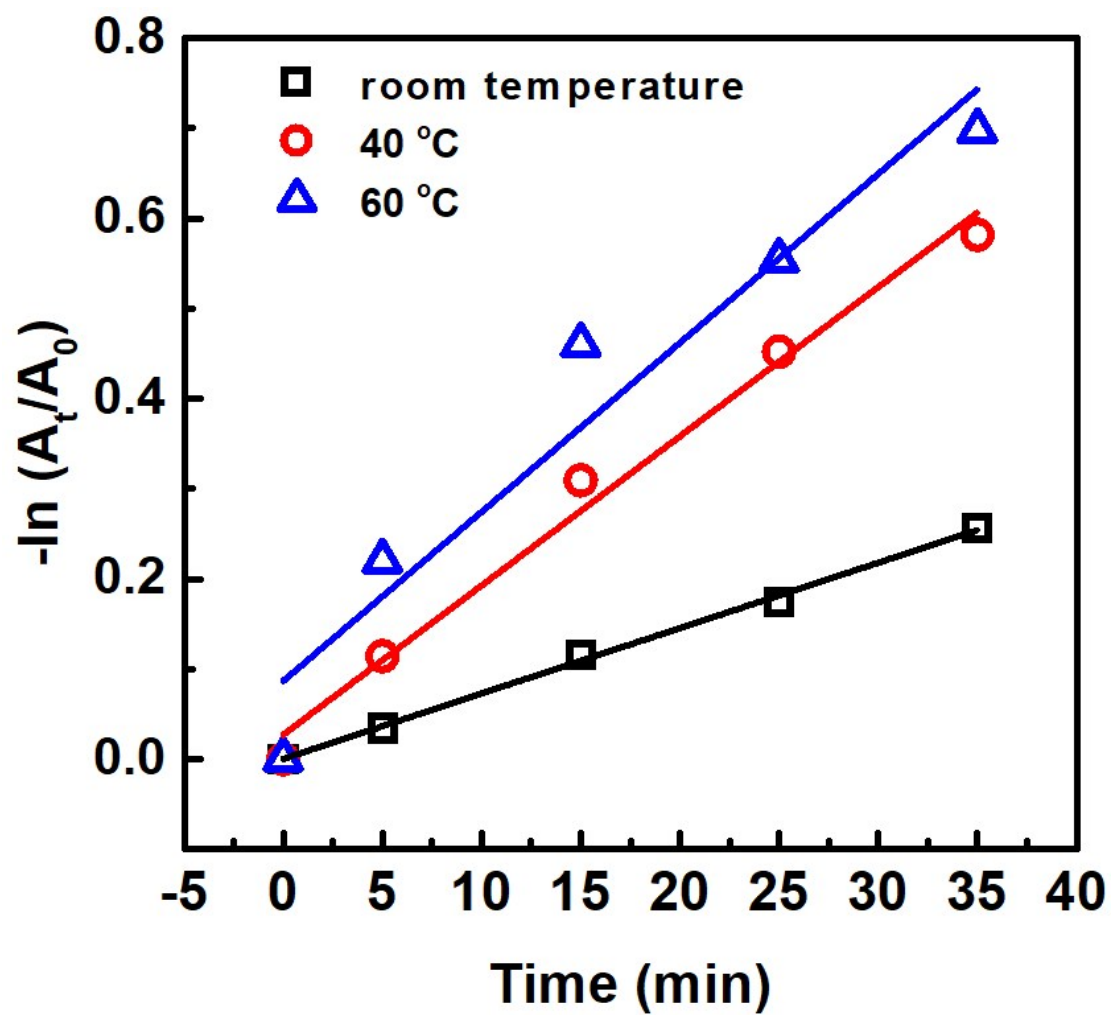


Figure S6. Kinetic curves of reduction reaction of 4-NP by Janus plasmene nanosheet (the one shown in Figure 1g-i) under different temperatures: room temperature, 40 °C and 60 °C without sunlight irradiation.

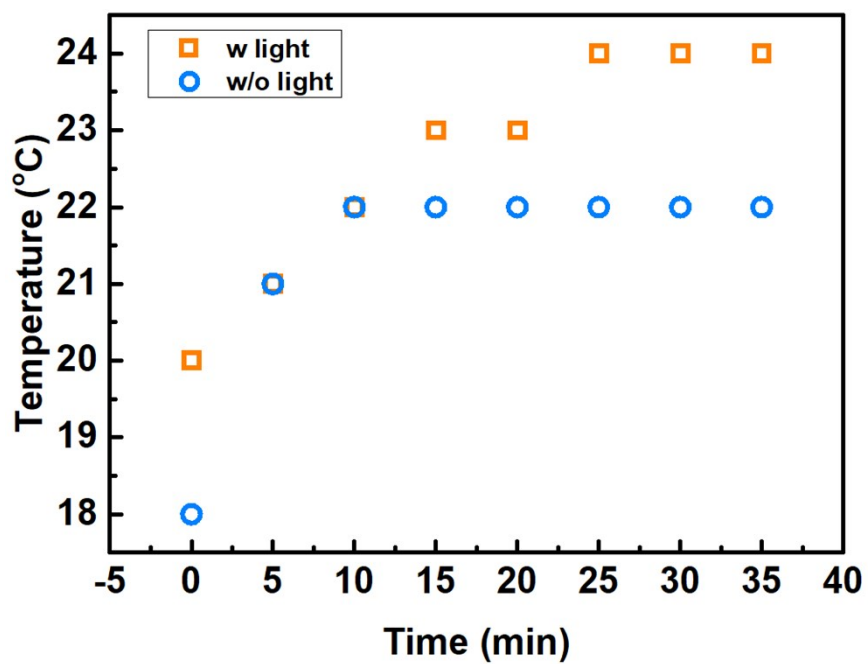


Figure S7. Temperature change of the 4-NP solution during the catalytic reaction by using Janus plasmene nanosheet (the one shown in Figure 1g-i).

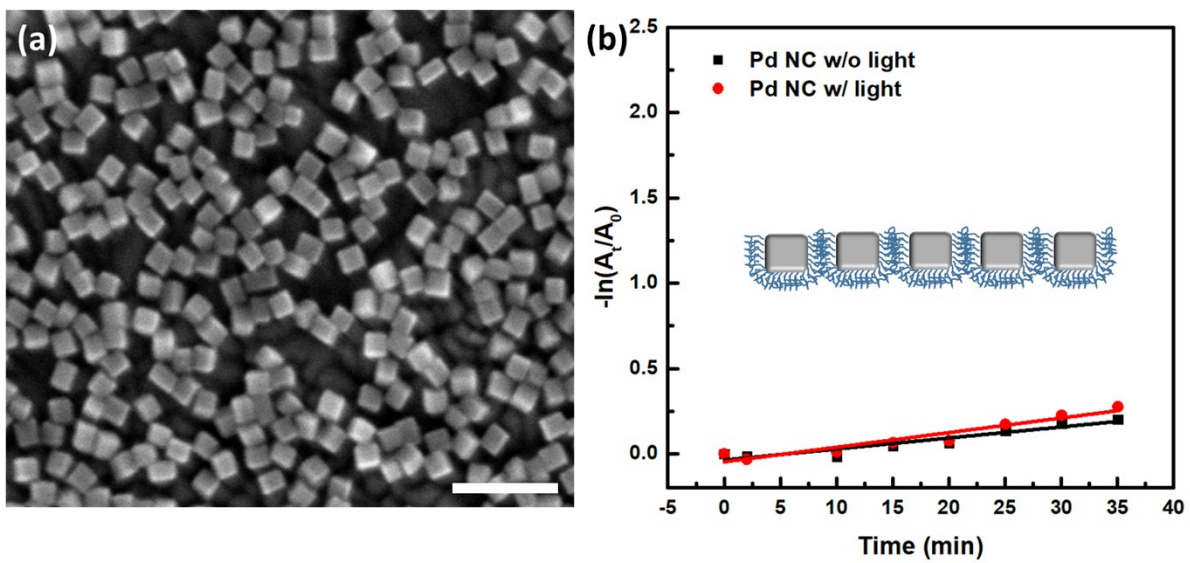


Figure S8. (a) SEM image of Pd NC nanosheets. (b) Catalytic property of Pd NC nanosheet for the reduction of 4-NP w/ (red curve) and w/o light (black curve). (Scale bar: 100 nm)

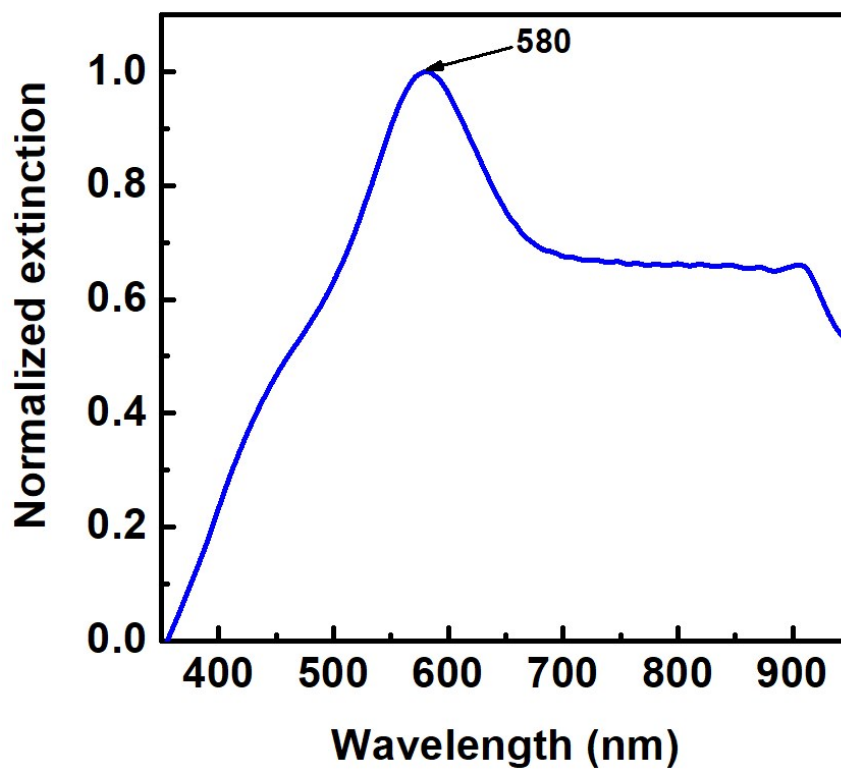


Figure S9. Extinction spectrum of Janus plasmene nanosheet (the one shown in Figure 1g-i).

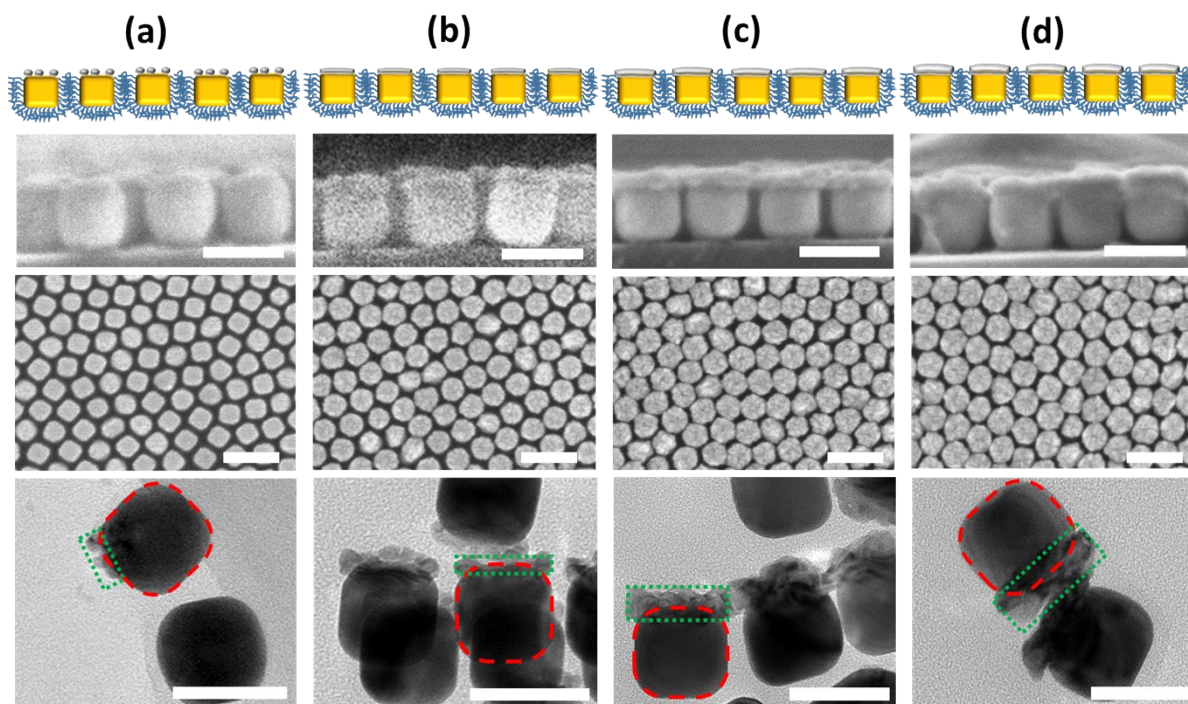


Figure S10. The control of Pd thickness by tuning concentration of H_2PdCl_4 . Cross-section schemes (top panel) and SEM images (2nd panel) and top view SEM images (3rd panel) of Janus plasmene nanosheets prepared by adding (a) 0.1 mM, (b) 0.3 mM, (c) 0.5 mM and (d) 0.7 mM H_2PdCl_4 . The 4th panel is the corresponding TEM images of individual Janus NPs. (Scale bar for top and 3rd panel: 50 nm; 2nd panel: 100 nm)

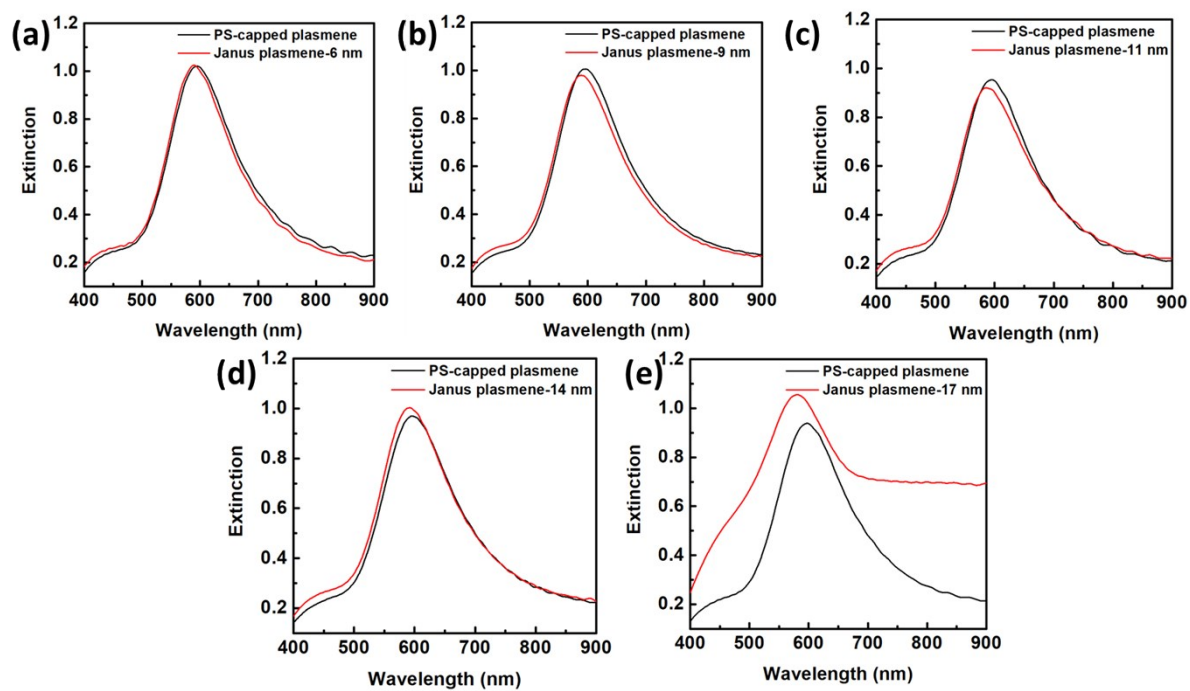


Figure S11. Representative extinction spectra of PS-capped (black), air plasma treated (red) and Janus (blue) plasmene nanosheets with different Pd thicknesses: (a) 6 nm, (b) 9 nm, (c) 11 nm, (d) 14 nm and (e) 17 nm.

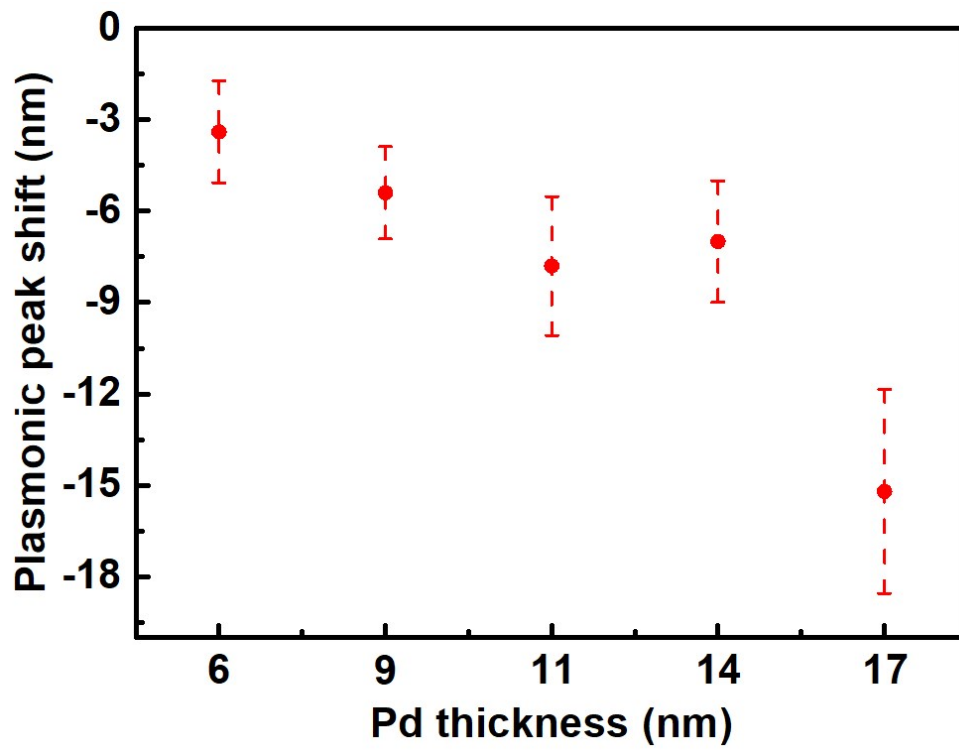


Figure S12. Plasmonic resonance peak shift of Janus plasmene with Pd thickness changing from 6 nm to 17 nm in comparison to that of PS-capped plasmene.

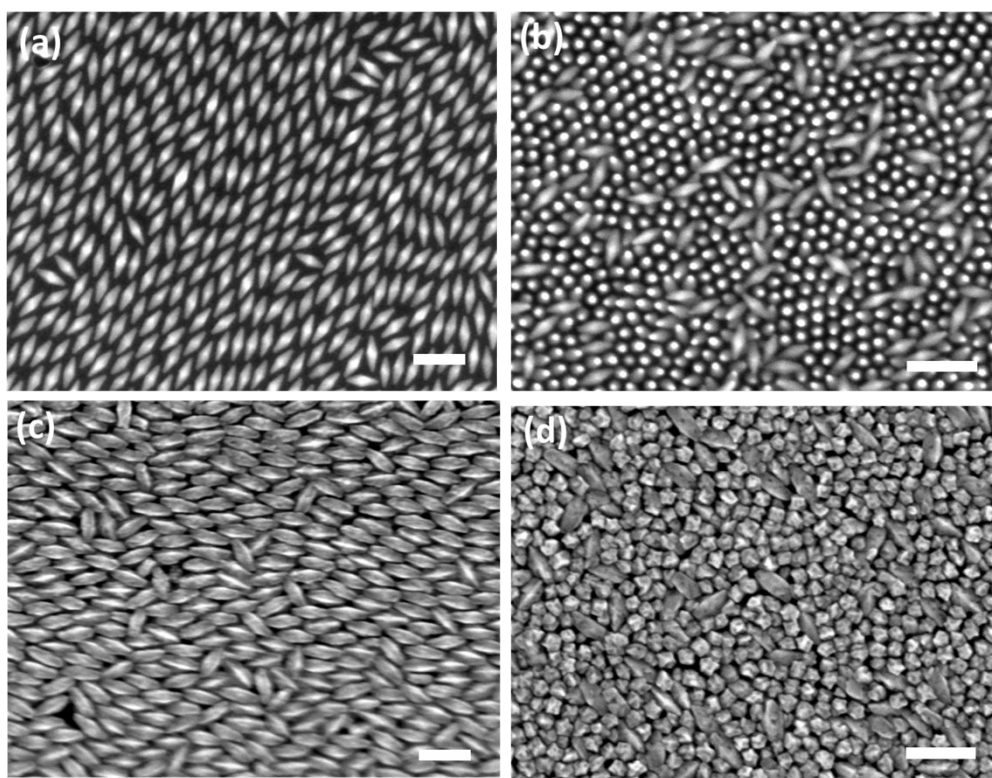


Figure S13. SEM images of (a) H-NBP, (b) V-NBP plasmene nanosheets and (c) H-NBP, (d) V-NBP Janus plasmene nanosheets. (Scale bar: 100 nm)

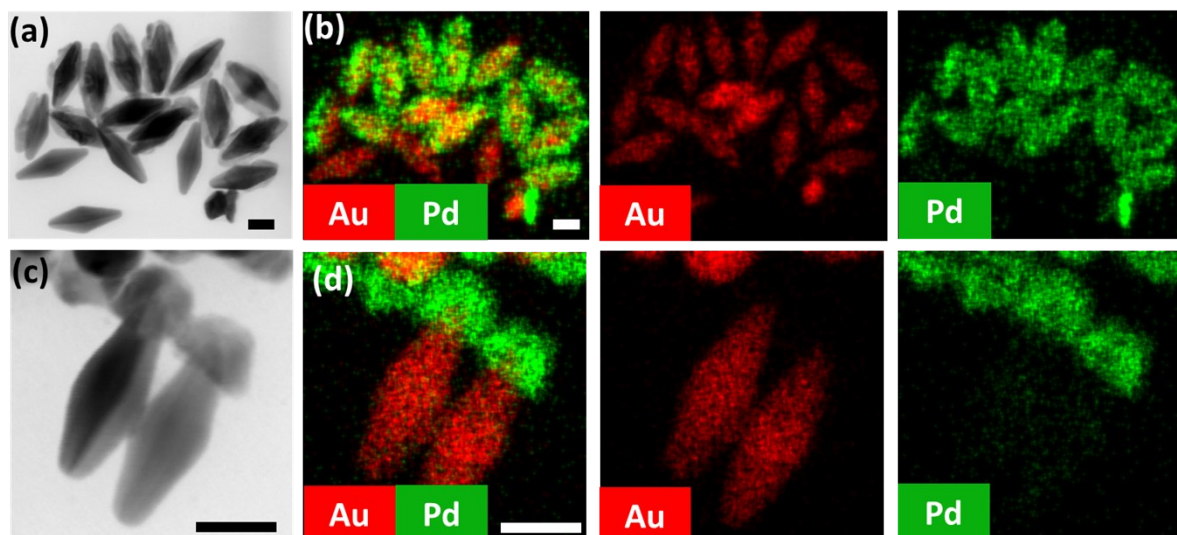


Figure S14. Dark-field TEM images of (a) Pd-tipped and (c) Pd-sided Au NBPs. (b, d) corresponding elemental mapping images of individual Janus NPs. (Scale bar: 20 nm)

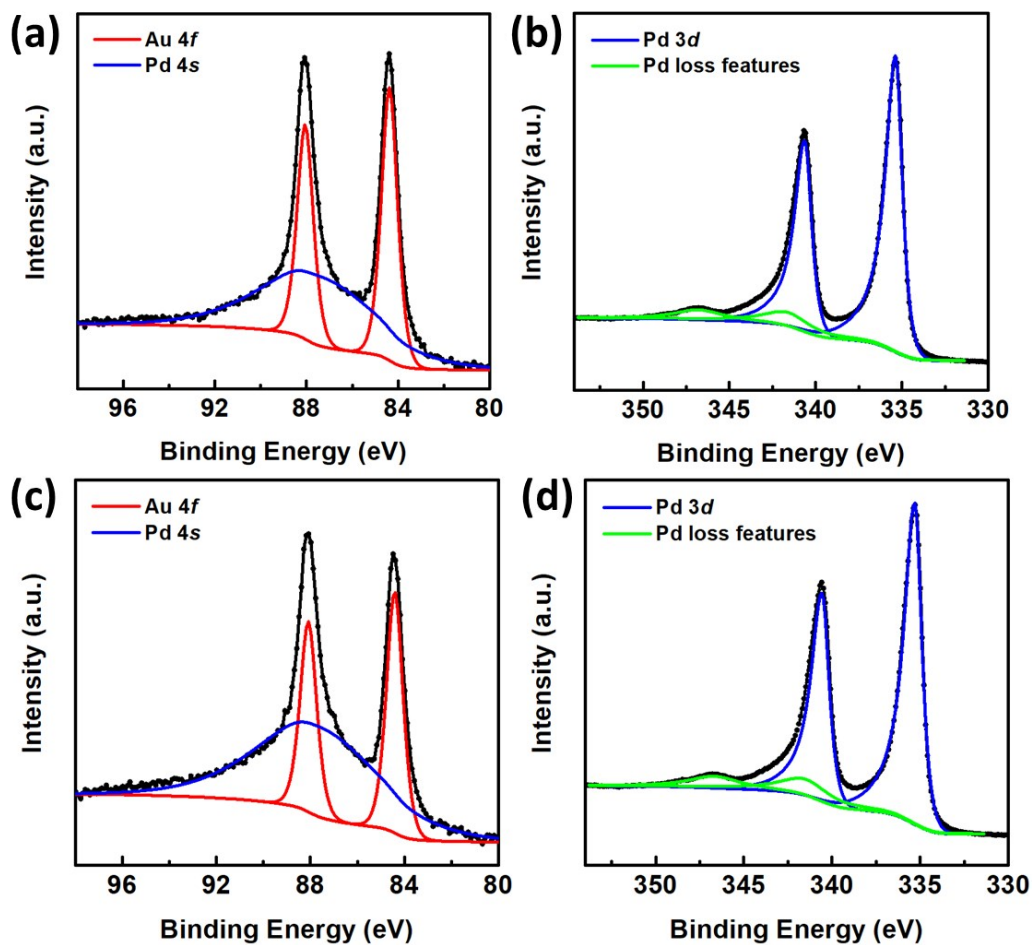


Figure S15. High-resolution XPS spectra of (a,b) H-NBP Janus plasmene nanosheet (the one shown in Figure 4a), (c,d) V-NBP Janus plasmene nanosheet (the one shown in Figure 4b).

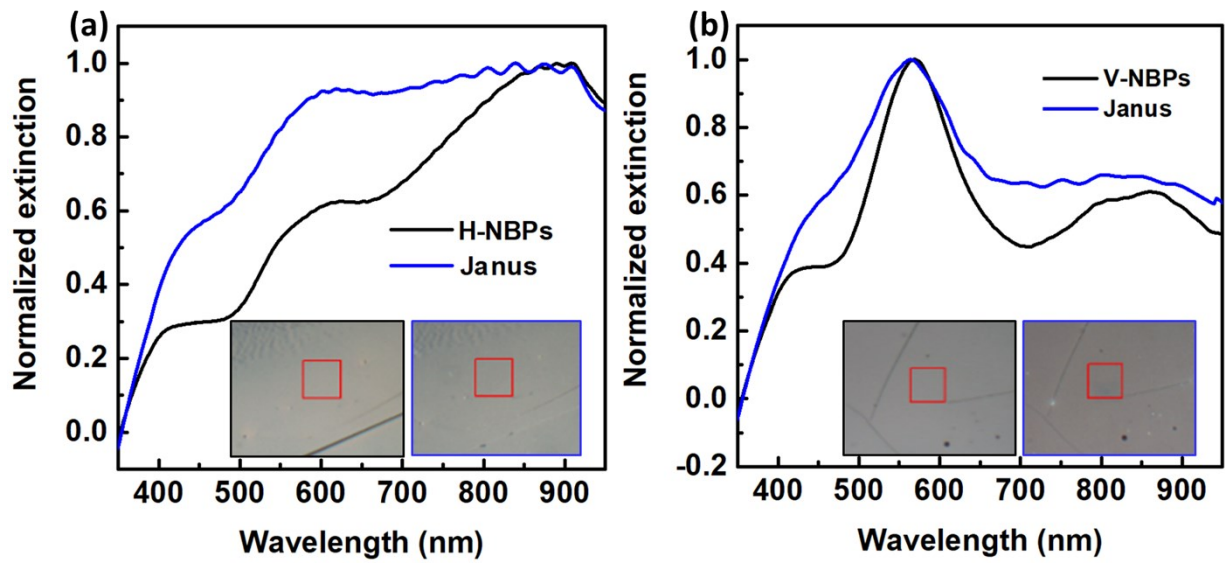


Figure S16. Extinction spectra of H-NBP (a) and V-NBP (b) plasmene nanosheets. Inserts are optical microscope images of Au NBP plasmene nanosheets before (black) and after (blue) deposition of Pd (red square is where the spectrum was acquired, 6 mm \times 6 mm).

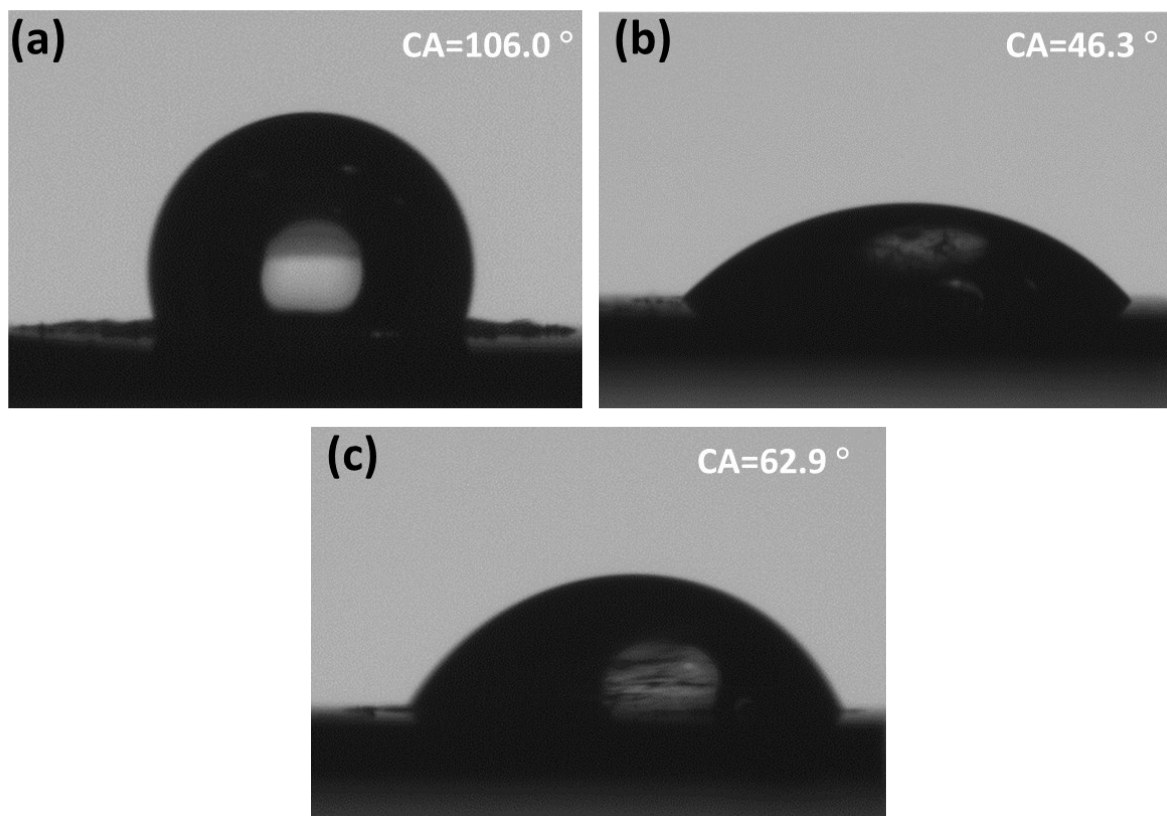


Figure S17. Contact angle (CA) of (a) PS-capped, (b) partially PS-capped and (c) Janus plasmene nanosheets.

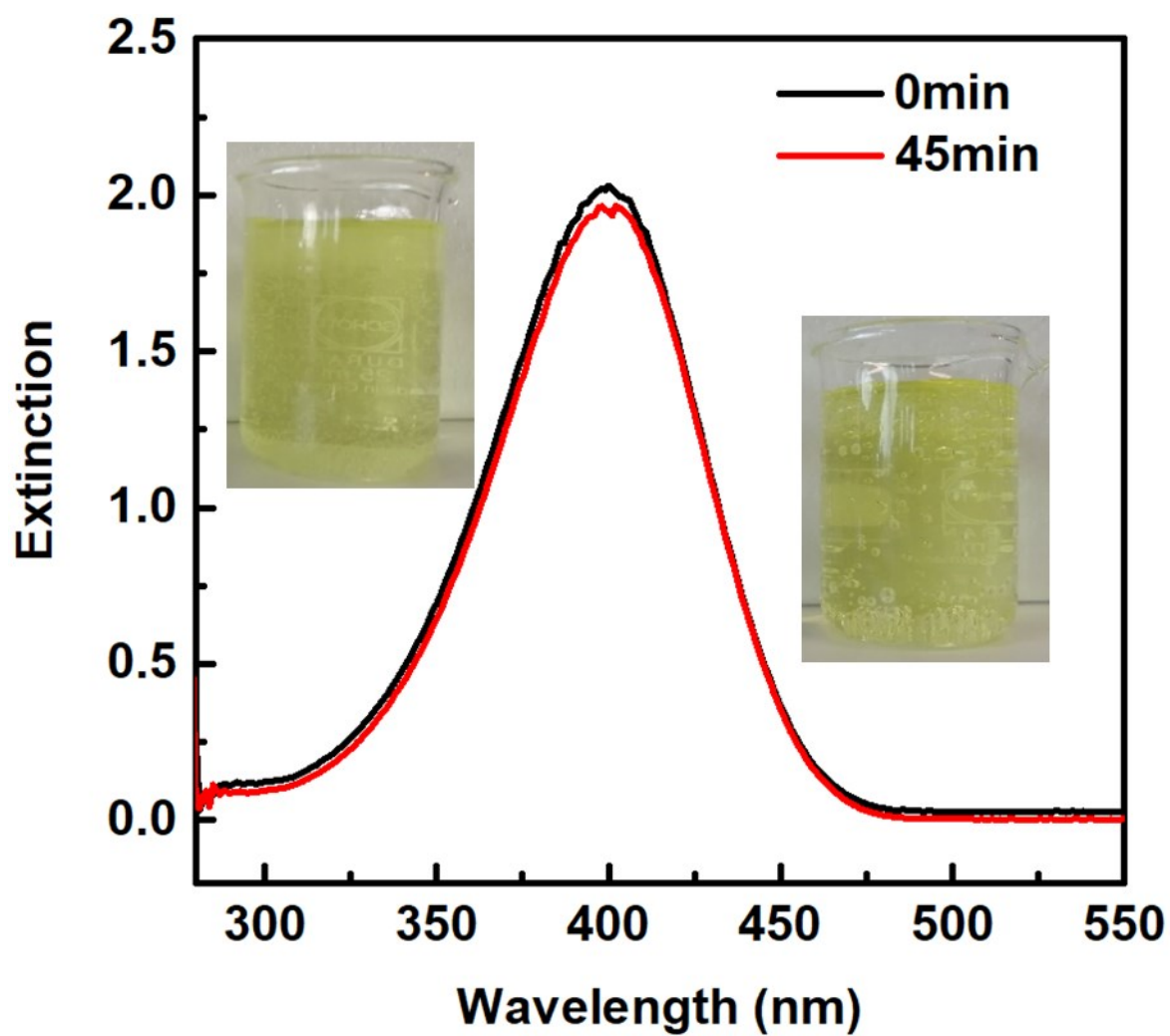


Figure S18. Absorption spectra of 4-NP solution without artificial tree (inserts are the photos of 4-NP solution).

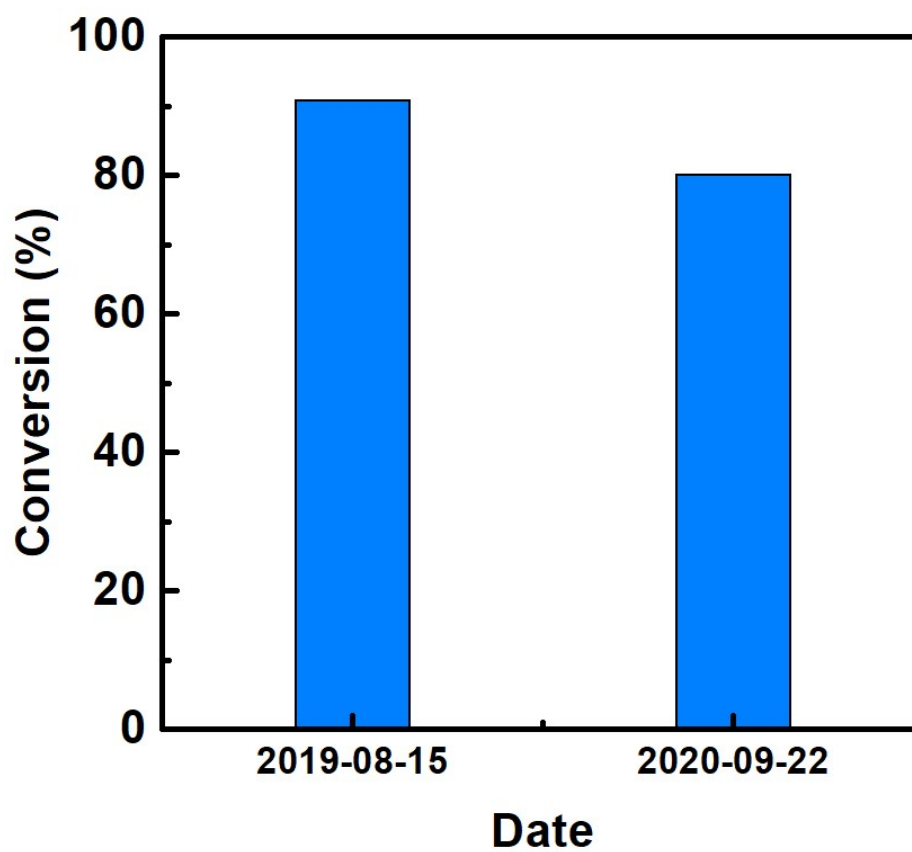


Figure S19. The conversion of 4-NP by artificial tree after storage under ambient conditions after more than a year.

References

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