

Electronic Supplementary Information

Three-dimensionally Patterned Ag-Pt Alloy Catalyst on Planar Si Photocathodes for Photoelectrochemical H₂ Evolution

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1. Three-dimensionally (3D) patterned Ag-Pt/*p*-Si (100) synthesis procedures.

1-1. Cross pattern of SiO_x formation on Si (100).

For fabricating an electrically insulating layer, we deposited a 50 nm-thick SiO_x film on a *p*-Si (100) substrate by plasma enhanced chemical vapor deposition (PECVD). Then, we formed a cross-shaped SiO₂ etched pattern with 400 nm in width, 550 nm in length and a 2 μm period by electron beam stepper lithography.

1-2. 3D-patterned Ag catalyst deposition.

For fabricating 3D-patterned Ag catalyst, we employed an ion-induced electrostatic focusing method using a multi-pin spark discharge generator (MSDG) and the SiO₂ pattern. When positive voltage of +4 kV is applied to the multi pins with a nitrogen gas flow of 60 lpm, positively charged Ag nanoparticles and nitrogen ions are generated by spark discharge and corona discharge, respectively. Then, we applied the negative voltage of -4 kV to the substrate located in a deposition chamber to attract oppositely charged Ag nanoparticles and ions. Through the electrostatic force and the flow of nitrogen carrier gas, Ag nanoparticles and ions are transported to the substrate. The ions with larger electrical mobility than the nanoparticles are deposited earlier at the SiO₂ surface of substrate, which induces the nanoscopic electrostatic lens. Due to the distorted equipotential surfaces resulting from the ions accumulated on the SiO₂ surface, the following Ag nanoparticles are focused only at the center of SiO₂ etched region. Then, 3D flower-shaped structures are formed by the assembly of nanoparticles under the influence of the repelling force from the SiO₂ surface and the enhanced electric field near the growing assembled nanoparticles. This fabrication process

was conducted at 25 °C and 1 atm. Lastly, the 3D-patterned Ag catalyst was sintered by the electron-beam sintering process for strengthening the structures.

1-3. Pt incorporation into the 3D Ag catalyst structure.

A Pt introduction through galvanic exchange reaction was conducted with a slight modification of previous report. The 3D Ag/Si (100) electrode was sequentially cleaned with acetone, 2-propanol, ethanol, and DI water in ultrasonic bath for 5 min in each solution. The photoelectrode was transferred to 30 mL of polyvinylpyrrolidone (0.27 g mL⁻¹, PVP, Merck, average M_w 40,000) and reacted for 30 min. Then, 30 mL of 10 mmol L⁻¹ K₂PtCl₄ (Merck, pH adjusted to 1 with 1 mol L⁻¹ HCl) was added to the PVP solutions for Pt incorporation. The optimized reaction time was 2 h to acquire 2.3 of Pt/Ag ratio (at.%). After the exchange reaction, the electrode was rinsed with ethanol and DI water.

1-4. Removal of SiO₂ pattern.

To remove the 50 nm-thick SiO₂ that was used for masking layer for Ag patterning, the 3D Ag-Pt/ Si (100) electrode was dipped into buffered oxide etch (BOE) solution (J.T. Baker, 6:1) with gentle stirring (25 min was the optimized reaction time). The photocathode was rinsed with a sufficient amount of DI water and dried with N₂ blow gun.

1-5. Electrical wiring of 3D Ag-Pt/Si (100) electrode.

The backside of Si was scratched with a diamond scribe and a few drops of 1% hydrofluoric acid (HF, Merck, 48 wt.%) was used to remove the native oxide. An electrical back contact was made with using a Gallium-Indium eutectic (Merck) and Al conductive tape. Back contact was sealed and 0.13 cm² of circular opening on the front photoelectrode area was made with 3M electroplater's tape. Then, Al conductive tape was protected with a glass tube and Hysol 9460 epoxy to make perpendicular photoelectrode configuration.

2. Patterning Pt/Ag dots on *p*-Si (100) by photolithography.

Same type of *p*-Si (100) wafers, as used for 3D Ag-Pt patterning were cleaned by a standard Radio Corporation of American (RCA) procedure. Ordered arrays of 30 or 5 nm-thick Ag and 20 nm-thick Pt were sequentially evaporated through shadow masks onto wafers by e-gun evaporation (ZZS550-2/D, Maestech). The shadow mask which has 50/50 μm as a diameter/pitch was employed. The entire process was conducted at Inter-university Semiconductor Research Center in Seoul National University.

3. Inductively coupled plasma – mass spectrometry (ICP-MS).

To calculate the Pt and Ag metal loading amounts as a catalyst layer, the 3D Ag-Pt/*p*-Si (100) photoelectrodes were immersed into 10 mL of aqua regia for 12 h to dissolve Pt and Ag into the solution. Then 10 mL of deionized water was added for dilution and analyzed by an ICP-MS spectrometer (nexION 350 D, PerkinElmer Inc.) installed at National Center for Inter-university Research Facilities (NCIRF) at Seoul National University. The amounts of Pt and Ag from optimized photoelectrode was 161.5 (± 11.9) and 34.49 (± 5.24) ppb, respectively.

4. Electromagnetic simulations.

In order to analyze the optical responses of the Ag-Pt catalyst structures, we numerically solved the time-dependent Maxwell's equations using the finite-difference time-domain (FDTD) method. Assuming that the Ag and Pt are evenly distributed in the Ag-Pt alloy, the complex relative permittivity of the alloy was estimated by using the weighted average method^{1,2} as follows.

$$\epsilon_{Ag-Pt} = x\epsilon_{Ag} + (1-x)\epsilon_{Pt},$$

where $x = 0.279$ is the volume fraction of Ag in Ag-Pt alloy and the dielectric functions of Ag and Pt were adopted from Palik.³ The resulting permittivity of Ag-Pt is plotted in Figure S11. In our electromagnetic simulations, the complex three dimensional geometries of the Ag-Pt catalysts were modeled by mimicking the SEM images of the real structures (Figure S1) and shown in Figure S12. The overall optical absorption of the device was calculated by $1 - \text{reflectance}$ of the device, and the absorption in the metallic catalyst was calculated by integrating the absorption profile $P_{\text{abs}} = -\text{Im}\{\epsilon\}\omega|E|^2/2$ over the volume of the catalyst structure and dividing it by the incident power. The absorption in Si substrate was then obtained by subtracting the absorption in metal from the overall absorption.

Figure S13 compare the optical response of the 3D patterned Ag-Pt catalyst structure with the responses of several basic structures including cylinders, squares, and crosses. For fair comparison, we set the area coverage and the height of the structures are identical for all structures.

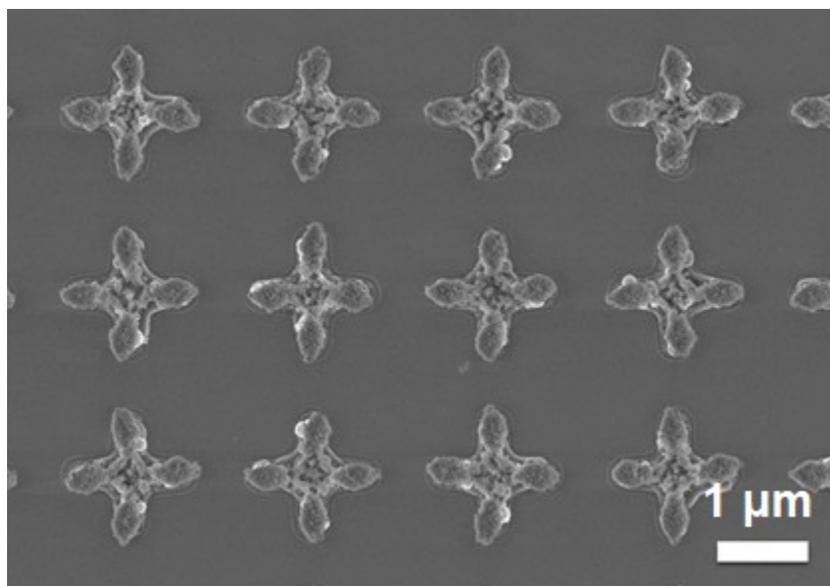


Fig. S1 Top view of FE-SEM image of 3D Ag-Pt/*p*-Si (100) after Pt incorporation into 3D Ag/*p*-Si (100) through galvanic exchange.

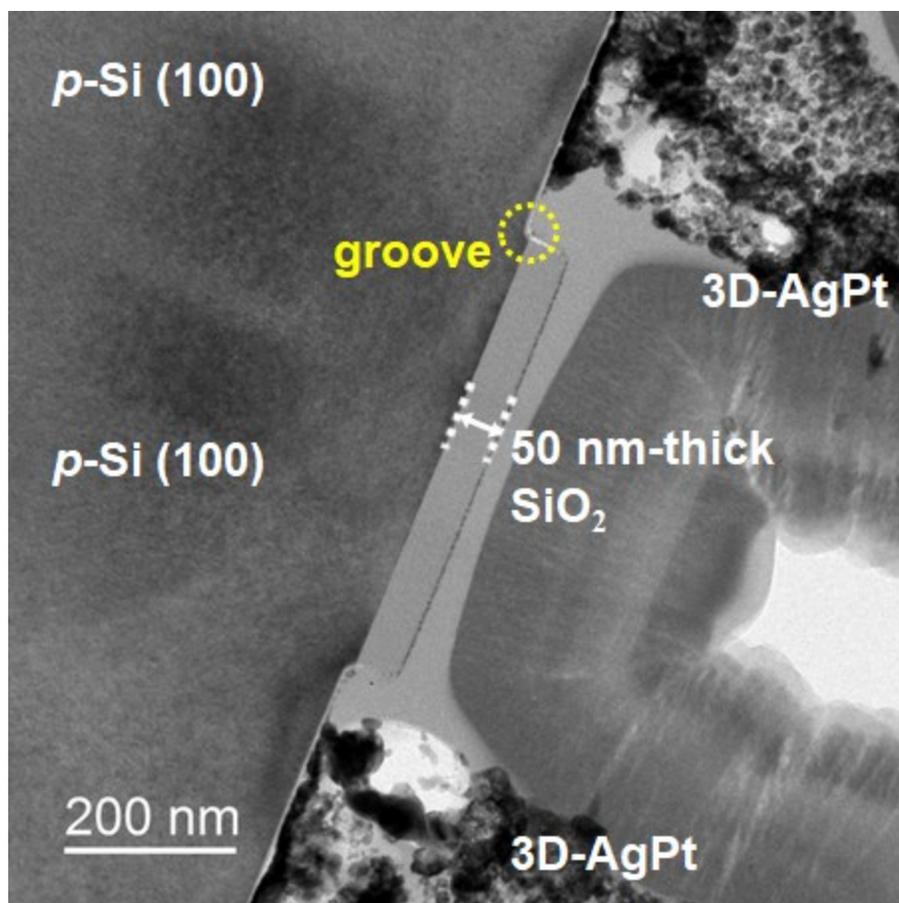


Fig. S2 Cross-sectional HRTEM image of 3D Ag-Pt/*p*-Si (100) with having ~ 15 nm deep groove and 50 nm-thick SiO₂ layer deposited for pre-patterning of Ag catalyst.

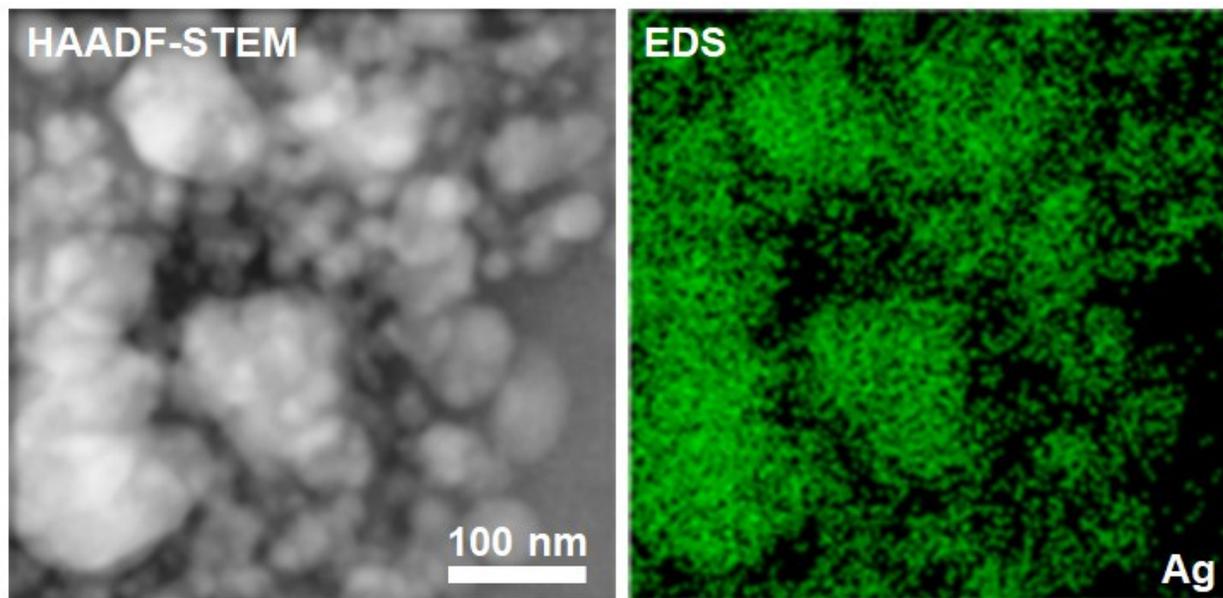


Fig. S3 HAADF-STEM image and Ag element mapping image from EDS of Ag catalyst from photocathode before Pt incorporation.

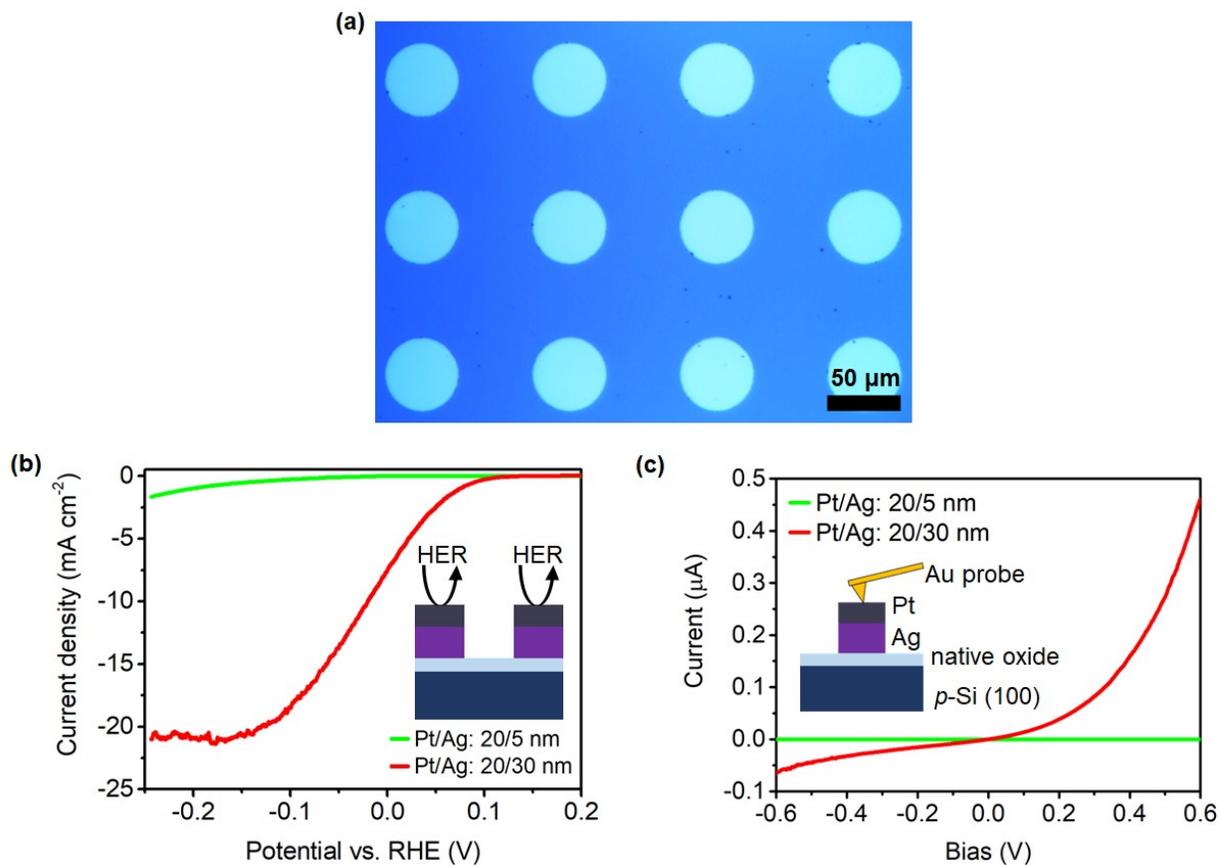


Fig. S4 (a) Optical image of 20/30 nm Pt/Ag catalysts pattern (50/50 μm diameter/pitch) on *p*-Si (100). (b) Linear sweep voltammograms for 20/30 vs. 20/5 nm-thick Pt/Ag catalyst in H_2 -purged 0.5 M H_2SO_4 at 10 mV s^{-1} (light intensity: 100 mW cm^{-2}). (c) Solid state current-voltage response of one Pt/Ag pattern on *p*-Si (100) at a 10 mV s^{-1} under dark condition.

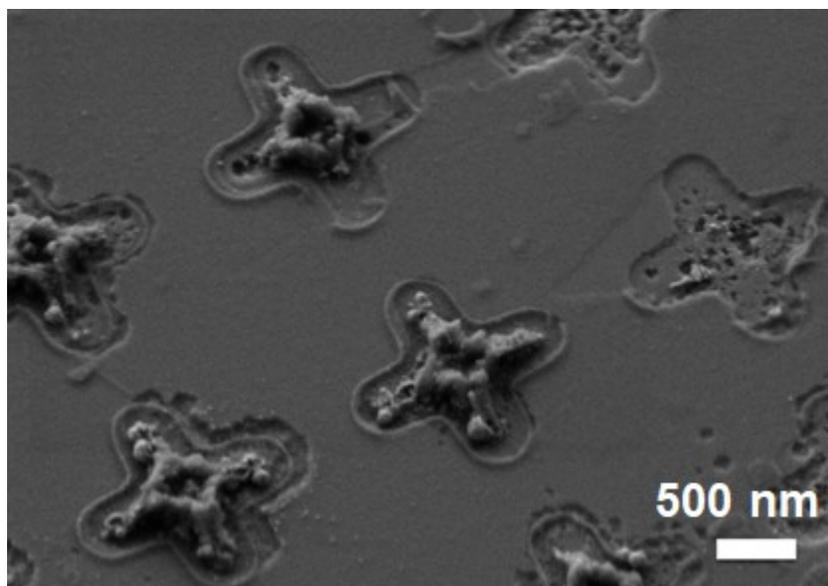


Fig. S5 Tilted FE-SEM image of 3D Ag-Pt/*p*-Si (100) photocathode after 40 min SiO_x etching.

	V_{OC} (V vs. RHE)	V_{onset} (V vs. RHE)	J_{0V} (mA cm ⁻²)	J_{SC} (mA cm ⁻²)	Mass activity at 0 V (A mg _{Pt} ⁻¹)
3D-Ag/p-Si(100)	0.360	-0.102	-0.153	-36.1	N/A
3D-AgPt/p-Si(100)	0.356	0.306	-28.1	-36.3	1.09

Fig. S6 Performance parameters for our platinumized Si-based photocathodes under AM 1.5 illumination.

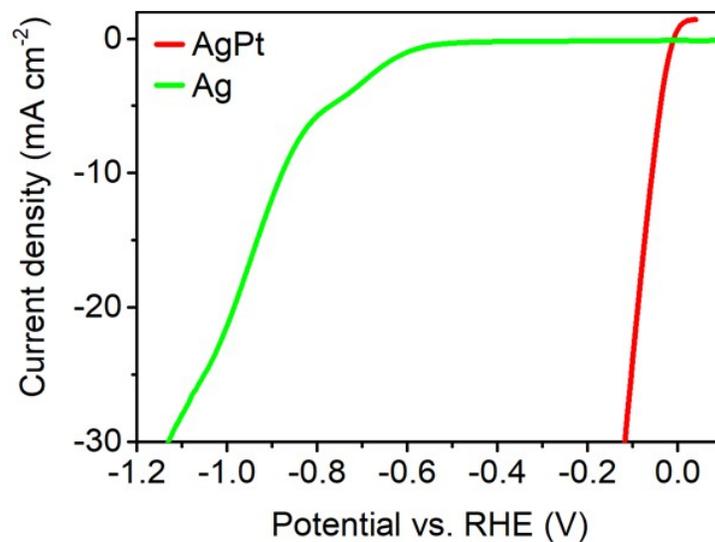


Fig. S7 Linear sweep voltammograms at 3D Ag (green line) and 3D Ag-Pt (red line) patterned catalyst on n^+ -Si (100) in H₂-purged 0.5 M H₂SO₄ under dark condition (scan rate: 10 mV s⁻¹).

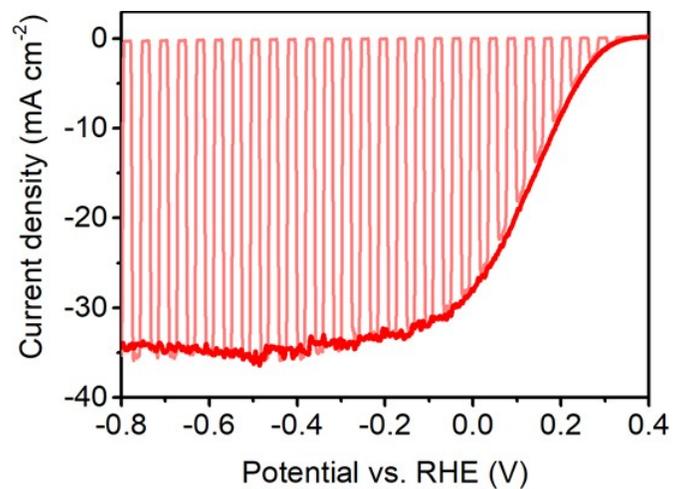


Fig. S8 Linear sweep voltammograms for 3D Ag-Pt/*p*-Si (100) under constant (scan rate: 10 mV s⁻¹) and chopped (scan rate: 50 mV s⁻¹) illumination in H₂-purged 0.5 M H₂SO₄ (Light intensity: 100 mW cm⁻²). The light chopping frequency was 1.5 Hz.

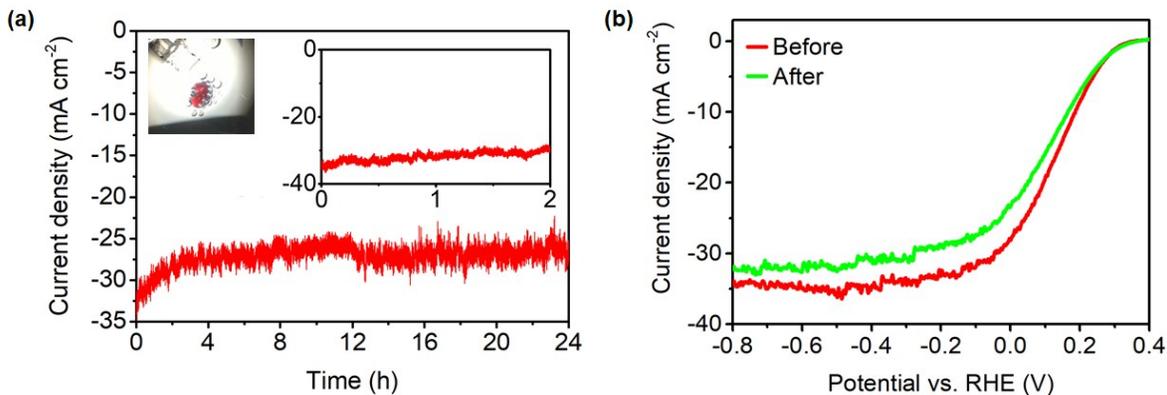


Fig. S9 (a) Long-term durability test of 3D Ag-Pt/*p*-Si (100) under constant -0.2 V (vs. RHE) in H_2 -purged 0.5 M H_2SO_4 for 24 h under AM 1.5 G illumination. Inset shows the magnified i - t curve during initial 2 h. Optical image of photocathode for HER is taken during durability test. (b) Linear sweep voltammograms taken before and after the 24 h stability test.

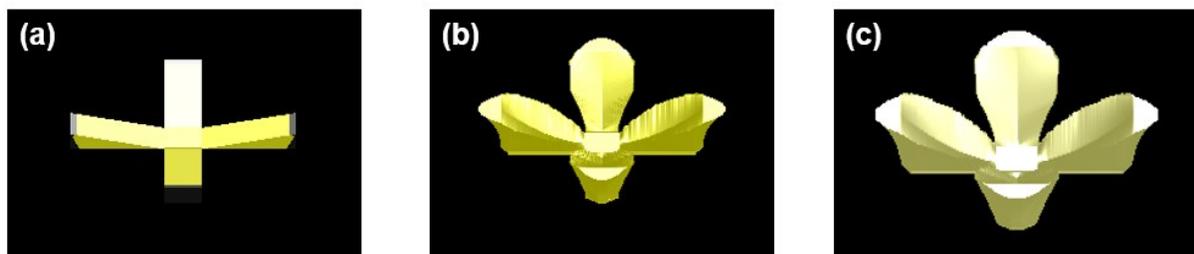


Fig. S10 The perspective view of the Ag-Pt catalyst structures used in FDTD electromagnetic simulations: (a) structure #1, (b) structure #2 and (c) structure #3. The heights of the structures are 200 nm, 500 nm, and 570 nm, respectively.

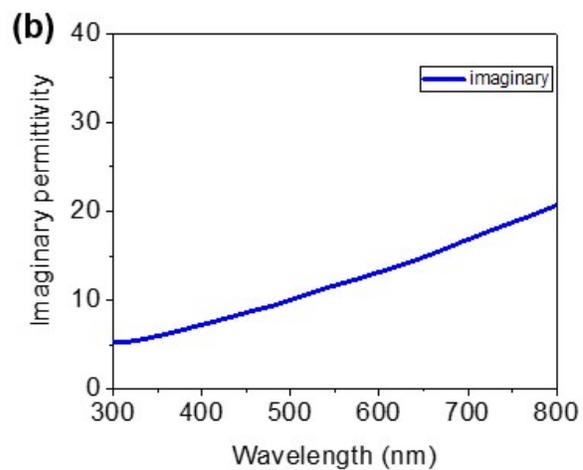
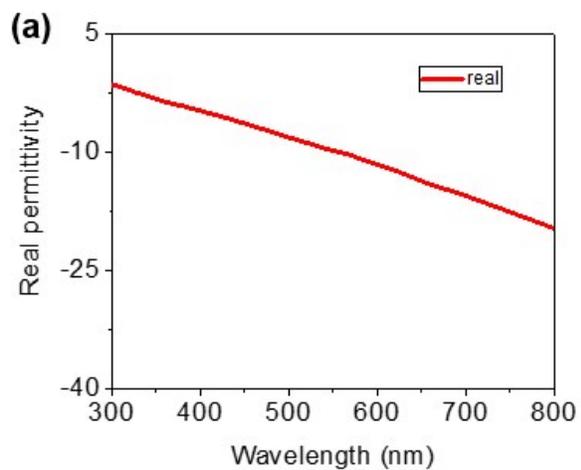


Fig. S11 Calculated (a) real permittivity and (b) imaginary permittivity of the Ag-Pt alloy.

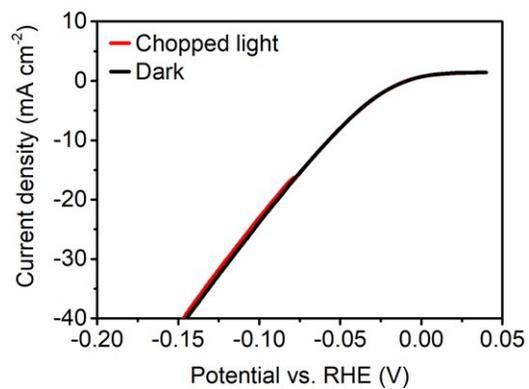


Fig. S12 Linear sweep voltammetry of 3D Ag-Pt/ n^+ -Si (100) comparing under the dark (black line) and the chopped light (red line) (100 mW cm^{-2} at 1.5 Hz). The electrolyte was H_2 -purged 0.5 M H_2SO_4 and the scan rate was 10 mV s^{-1} .

6. References.

- (1) N. E. Motl, E. Ewusi-Annan, I. T. Sines, L. Jensen, R. E. Schaak, *J. Phys. Chem. C*, **2010**, *114*, 19263-19269.
- (2) S. W. Verbruggen, M. Keulemans, J. A. Martens, S. Lenaerts, *J. Phys. Chem. C*, **2013**, *117*, 19142-19145.
- (3) Palik, E. D., *Handbook of Optical Constants of Solids*, Academic Press, New York, 1997.