Supporting Information

Platinum Monolayer Electrocatalyst on Silicon Electrode for Photoelectrochemical Hydrogen Evolution

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1. Measurements of Electroactive Surface Area of AuNF on n^+-Si(100) by Cu upd

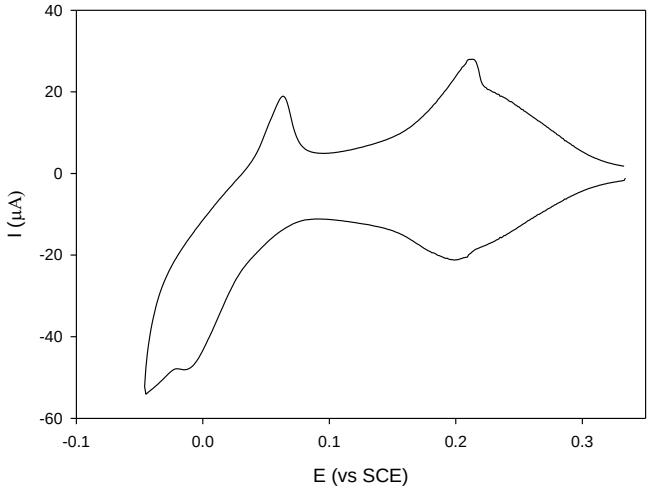

Figure S1. Cyclic voltammogram (CV) for a AuNF/n^+-Si in an aqueous solution containing 5 mM $CuSO_4$ and 0.1 M H_2SO_4 without illumination. Scan rate = 20 mV/s.

2. Photoelectrochemical H_2 evolution on Pt/AuNF/Si with the higher Pt coverage by the use of Pt^{2+}

Photoelectrochemical hydrogen generation of Pt(by Pt^{2+})/AuNF/Si was measured under illumination and without illumiatnion. FigureS2 shows current density (J)-electrode potential (E) for hydrogen generation on Pt(Pt^{2+})/AuNF/Si. Owing to the higher Pt coverage, Pt(Pt^{2+})/AuNF/Si shows the high dark current for H_2 evolution while photovoltage is very small as discussed in the manuscript.

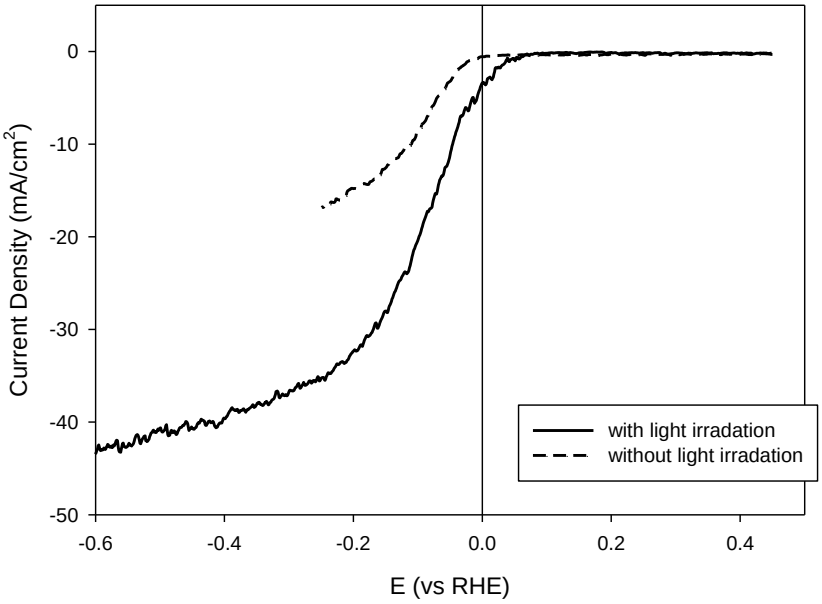

Figure S2. Electrochemical H_2 generation on Pt(Pt^{2+})/AuNF/Si with and without light illumination in a stirred solution of H_2SO_4 + 0.5 M K_2SO_4 (pH 1). Scan rate = 0.02 V/s.

3. Morphology of PtNP/Si

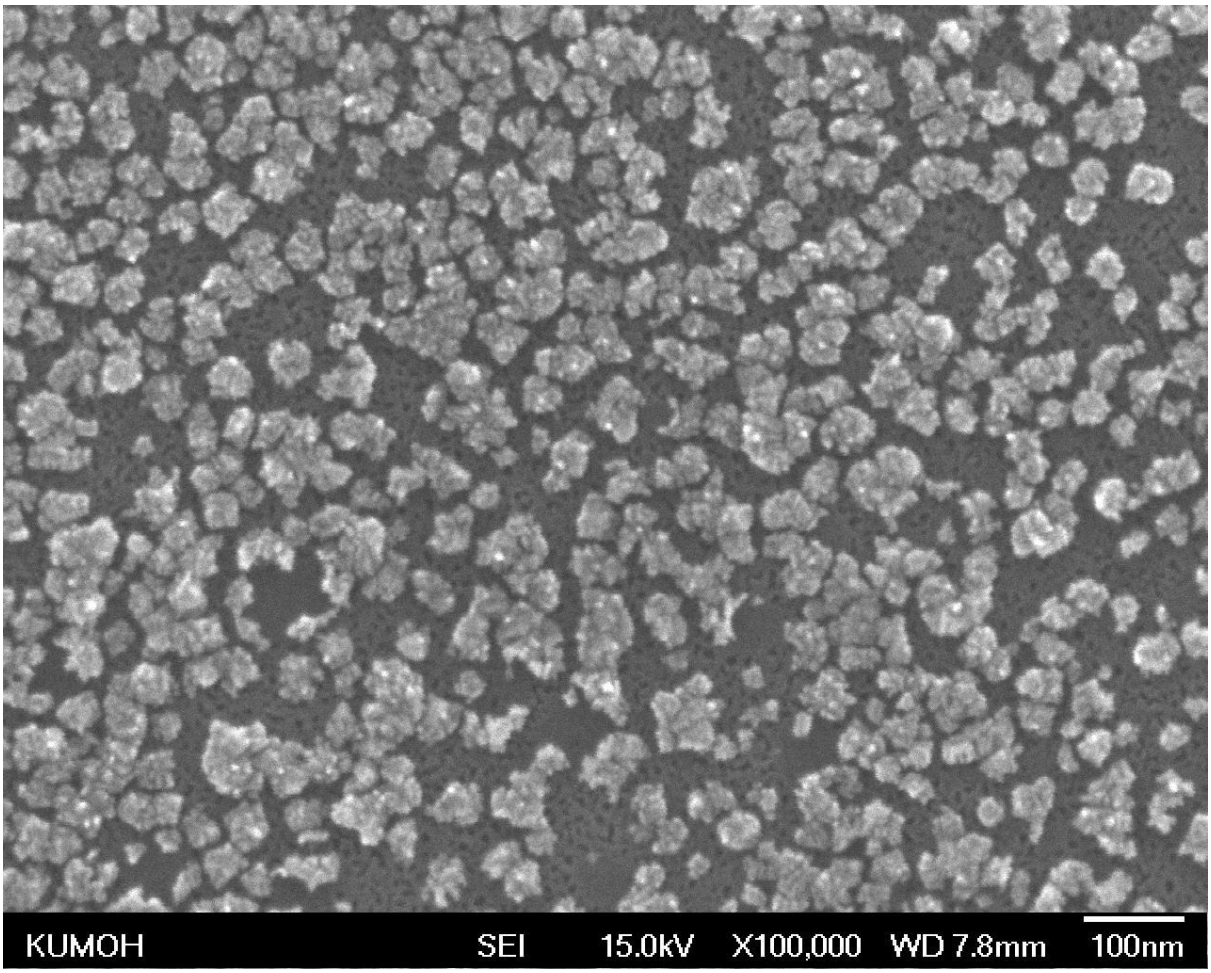

Figure S3. SEM image of PtNP/Si which is deposited by immersion of planar Si into a solution of 0.5M HF for 3min with 1mM K_2PtCl_6.

4. XPS of Pt/AuNF and Cu/AuNF on p-Si(100)

The X-ray photoelectron spectroscopy was conducted to observe the complete exchange of Cu with Pt and to check the thickness of Pt. The exchange of Cu monolayer was confirmed by the disappearance of Cu2p peaks and the appearance of Pt4f peaks on Pt/AuNF/Si as shown in Figure S4. Then, the Cu and Pt contents on AuNF are estimated by Cu:Au and Pt:Au ratio using Cu $2P_{3/2}$,Pt 4f, and Au 4f peak areas and relative sensitivity factors. Average compositions of ~0.14 (Cu:Au) and ~0.08 (Pt:Au) are determined, indicating that the Pt content is about half the Cu content as expected for stoichiometry of galvanic exchange ($2Cu_{upd} + Pt^{4+} \rightarrow 2Cu^{2+} + Pt$). In addition, the ratio is in good accordance with ESA_{Au} and $ESA_{Pt,Pt4+}$ in Table 1 in the manuscript demonstrating that most of Pt is not buried but exposed on the surface. Thus, it is reasonable that monolayer of Cu upd is exchanged to monolayer Pt by galvanic exchange. The low Pt:Au ratio also shows that Pt layer is quantitatively down to monolayer considering the mean free path of electrons.

Analysis of the X-ray photoelectron spectra was performed on an ESCALAB 250 XPS system (Thermo Fisher Scientific, U. K.) using Al Kα X-ray radiation as the exciting source.

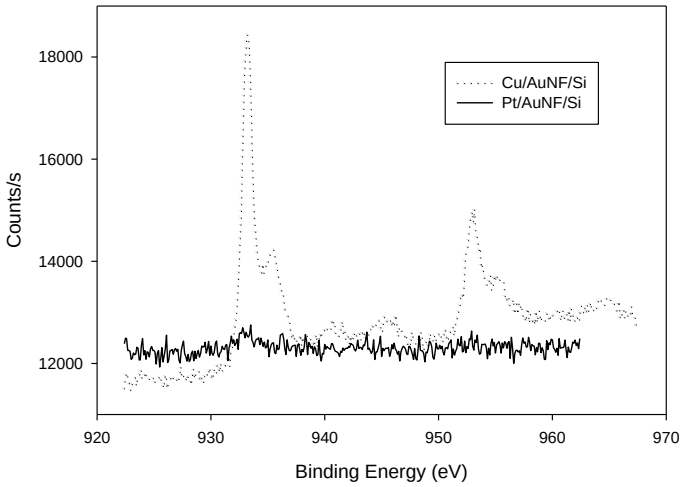

Figure S4. Narrow-scan XPS spectra of Cu2p region acquired from Cu/AuNF/Si (dotted line) and Pt/AuNF/Si (solid line).

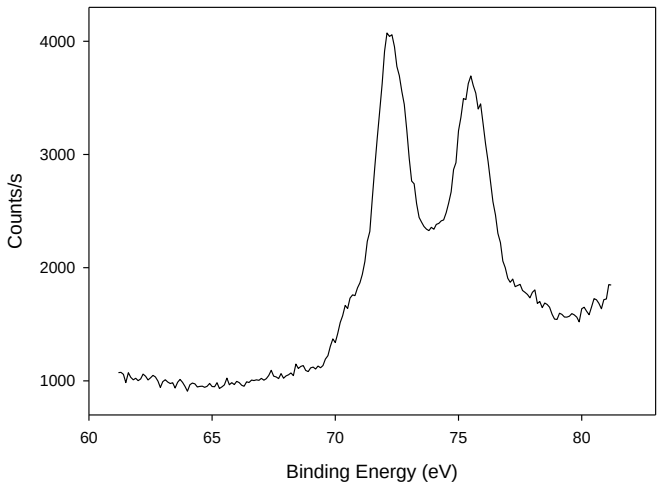

Figure S5. Narrow-scan XPS spectrum of Pt4f region acquired from Pt/AuNF/Si.

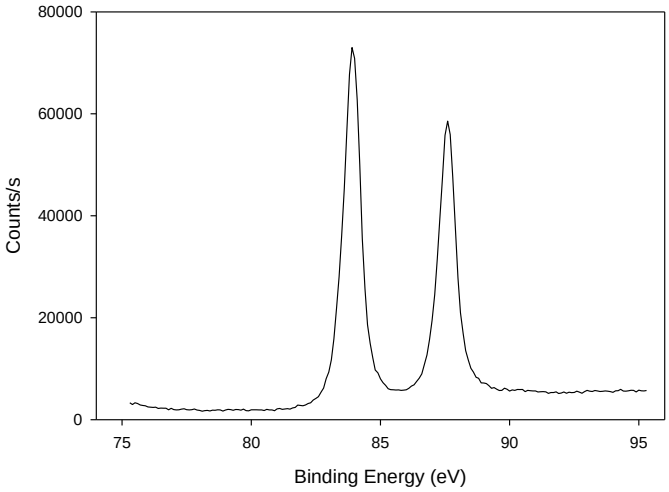

Figure S6. Narrow-scan XPS spectrum of Au 4f region acquired from Pt/AuNF/Si.