

Supplementary information

Efficient reducibility of layered polysilane (SiH)_n for selective recovery of platinum ions from aqueous media

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Details of experimental procedures

Materials

The chemical reagents were purchased from Aldrich and Fujifilm Wako Pure Chemical Corporation and were used without further purification. Distilled water purified using a Millipore Milli-Q gradient system was used for all the experiments. Artificial seawater (ASW) was prepared by mixing of commercially purchased sea salt (38.1 g, MARINE ART SF-1, Osaka Yakken Co., Ltd.) with distilled water (1.0 L). The prepared ASW is an aqueous solution with pH 7.5–8.0 and contains NaCl (378 mM), MgCl₂ (48.7 mM), CaCl₂ (10.2 mM), Na₂SO₄ (27.5 mM), KCl (8.2 mM), NaHCO₃ (2.3 mM), KBr (0.81 mM), Na₂B₄O₇ (0.20 mM), SrCl₂ (82 μM), NaF (71 μM), LiCl (24 μM), KI (0.49 μM), MnCl₂ (0.0030 μM), CoCl₂ (0.0084 μM), AlCl₃ (0.033 μM), FeCl₃ (0.018 μM), Na₂WO₄ (0.0060 μM) and (NH₄)₆Mo₇O₂₄ (0.015 μM). Carbon paper with a water-repellent treatment (CP; TGP-H-060H) was purchased from Chemix. An ethanol dispersion of multi-walled carbon nanotubes (MWCNT/EtOH) was purchased from Meijo NanoCarbon Co., Ltd. A cation-exchange membrane (Nafion 117) was purchased from Aldrich and fully immersed in an electrolyte solution before the electrochemical experiments.

Recovery of Pt⁴⁺ from artificial seawater (ASW) using LpSi

LpSi (28 mg, Si-H: 0.96 mmol) suspended in ASW (3 mL) was added to an ASW solution of hexachloroplatinic acid (H₂PtCl₆) (3 mL, 0.06 mmol □ Pt⁴⁺) and stirred vigorously for 1 h at room temperature and normal pressure. The resulting suspension was filtered with a membrane filter (pore size: 0.2 μm). The recovered powder was washed with distilled water (3 mL) and dried under vacuum at room temperature overnight.

Recovering low concentrations of Pt⁴⁺ using LpSi

LpSi (50.8 mg, Si-H: 1.75 mmol) suspended in ASW (3 mL) was added to an ASW solution containing H₂PtCl₆ (17 mL, Pt⁴⁺: 1.0 μmol) and stirred vigorously for 24 h at room temperature and

ambient pressure. The resulting suspension was filtered with a membrane filter (pore size: 0.2 μm). The recovered powder was washed with distilled water (3 mL) and dried under vacuum at room temperature overnight.

Isolation of recovered Pt-NPs from Pt/LpSi

An aqueous solution of sodium hydroxide (NaOH, 1 mol/L, 5 mL) with dispersed Pt/LpSi (5 mg) was placed in a sealed Teflon vessel and heated at 65°C for 24 h. After heating, the suspension was filtered through a polytetrafluoroethylene (PTFE) membrane (0.2 μm) to collect the Pt-NPs isolated from Pt/LpSi. The obtained Pt-NPs were dispersed in distilled water and dropped onto a germanium plate to prepare a sample for SEM observation.

Fabrication of electrodes

A Pt/LpSi electrode (Pt/LpSi/CP) was fabricated by rubbing Pt/LpSi (3 mg), which was obtained from the reaction of H_2PtCl_6 (Pt^{4+} : 0.06 mmol) and LpSi (Si-H: 0.96 mmol) in ASW (6 mL), onto the centre of the CP (20×30 mm) using a spatula, and then coating it with MWCNTs/EtOH solution (0.25 wt%, 0.4 mL). For comparison with Pt/LpSi/CP, a LpSi electrode (LpSi/CP), in which LpSi (3 mg) was fixed on CP, and a MWCNTs electrode (MWCNTs/CP), in which only MWCNTs were coated on the CP surface, were also fabricated by the same procedure.

Electrochemical hydrogen evolution reaction (HER)

The hydrogen evolution reaction (HER) under constant potential electrolysis was monitored by in situ measurements using an electrochemical flow cell in combination with gas chromatography (GC). The flow reactor was directly connected to a GC system (Multiple Gas Analyzer #5, SRI Instruments) equipped with an autosampler for in situ analyses with Molecular Sieve 5A and HayeSep D columns. At the start of each experiment, Ar was flowed at 10 mL/min for 20 min to saturate the electrolyte and remove air from the flow reactor system. The amount of evolved H_2 was estimated by multiplying the concentration of products determined using GC, the flow rate, and the measurement interval (20 min).

Additional experimental results

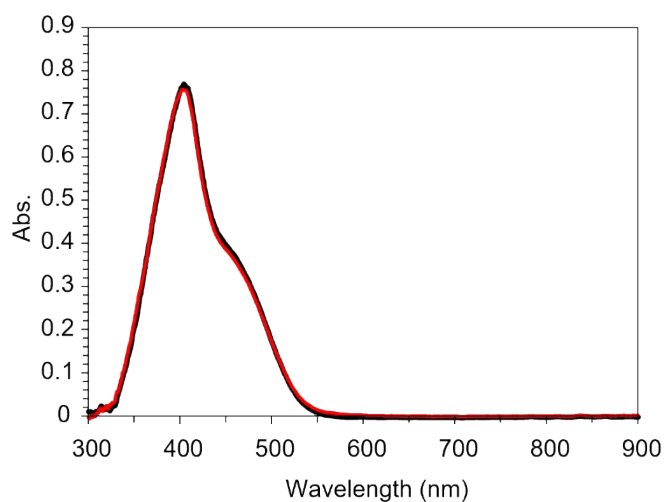


Figure S1. UV-Vis spectra of H₂PtCl₆ (0.06 mmol) dissolved in ASW (6 mL) (black line) and filtrate obtained from control reaction (red line).

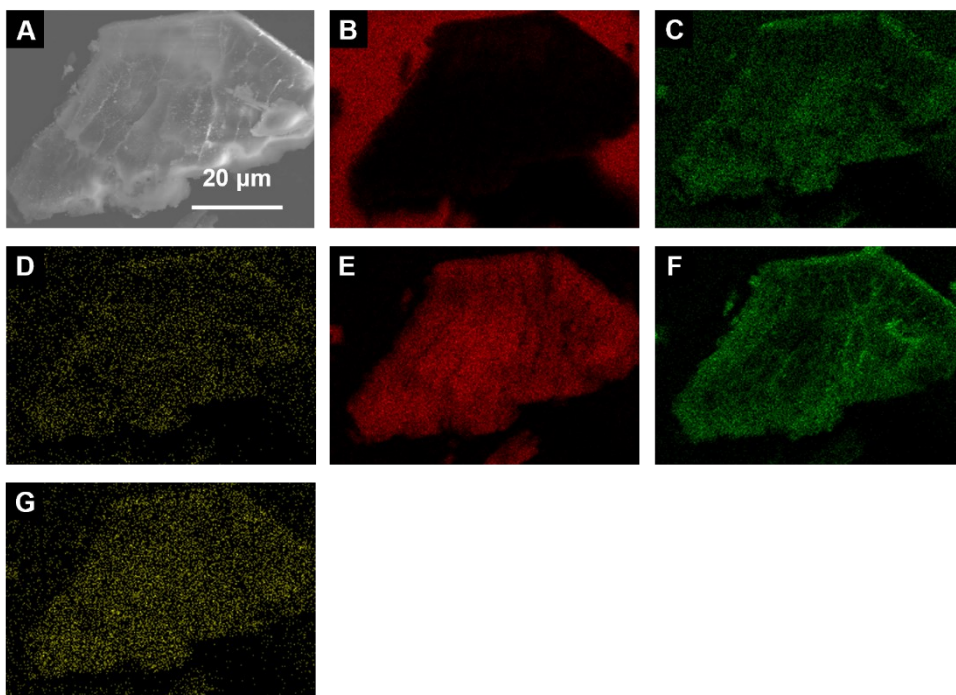


Figure S2. (A) SEM micrograph and (B–G) elemental distribution maps of Pt/LpSi; B: carbon, C: oxygen, D: sodium, E: silicon, F: platinum, and G: chlorine. Carbon was rarely found in the plate-like particles of LpSi, and it was mainly present around these particles. This is due to the carbon tape used to fix the sample to the SEM plate.

Table S1. Elemental composition ratio for Pt/LpSi by SEM/EDS analysis

Element	Wt%	At%
C (K)	70.97	86.21
O (K)	8.30	7.57
F (K)	0.13	0.10
Na (K)	0.11	0.07
Si (K)	9.80	5.09
Pt (M)	10.22	0.76
Cl (K)	0.48	0.20

Na and Cl are considered to be loaded on LpSi as salts, i.e., NaCl; however, the amount of Cl detected was approximately 2.8 times higher than that of Na. This is thought to be due to adsorption of Cl ions onto the cationic Si framework formed after the Pt ion reduction reaction.

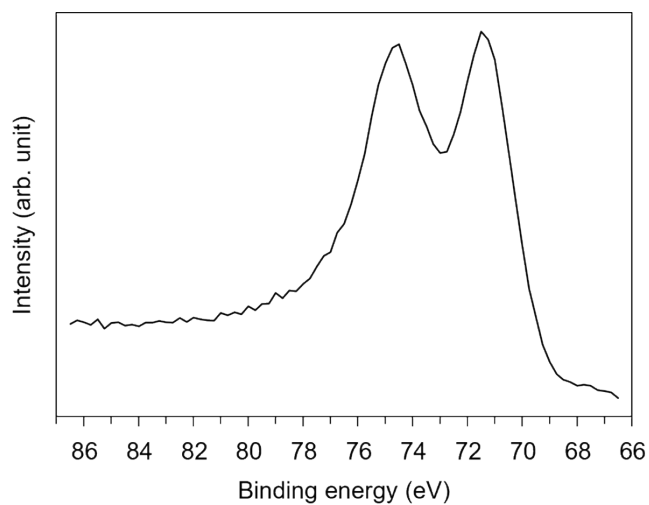


Figure S3. XPS Pt 4f spectrum of Pt/LpSi.

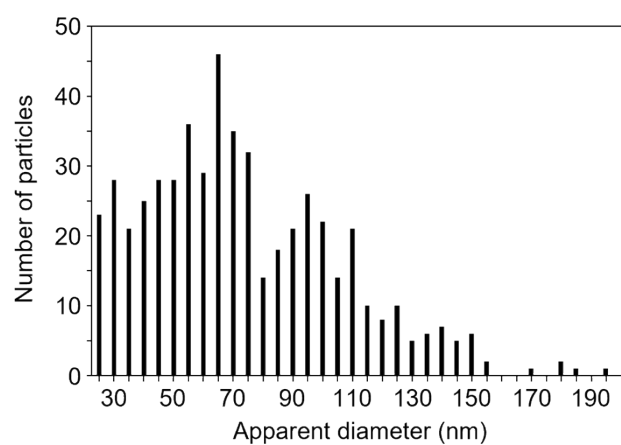


Figure S4. Size distribution of Pt-NPs observed in the HAADF-STEM image in Figure 4a.

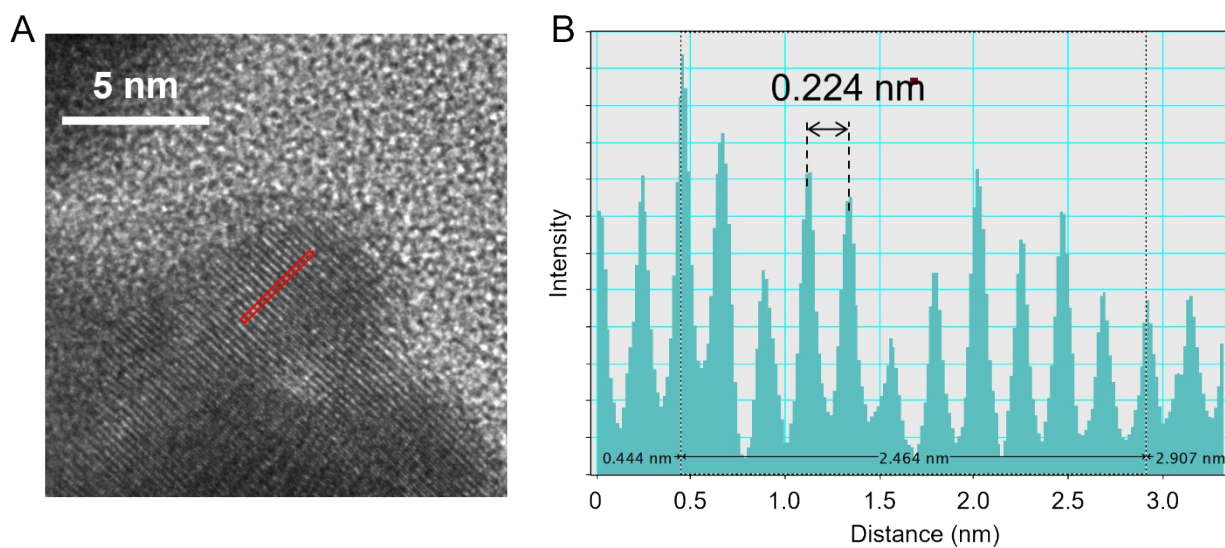


Figure S5. (A) HRTEM image of Pt-NPs on LpSi. (B) Line-scanning intensity profile analysis of diffraction fringes in red rectangular area indicated in image (A).

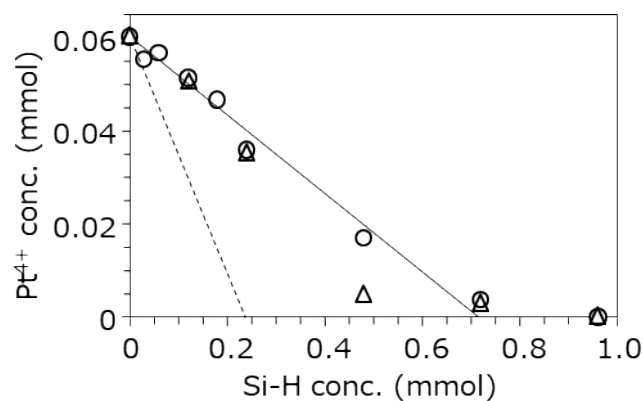


Figure S6. Stoichiometric relationship for reduction of Pt^{4+} with LpSi in ASW (\circ) and distilled water (\triangle). The lines show the decrease for the stoichiometric reaction (dashed line) and the actual experimental results (solid line).

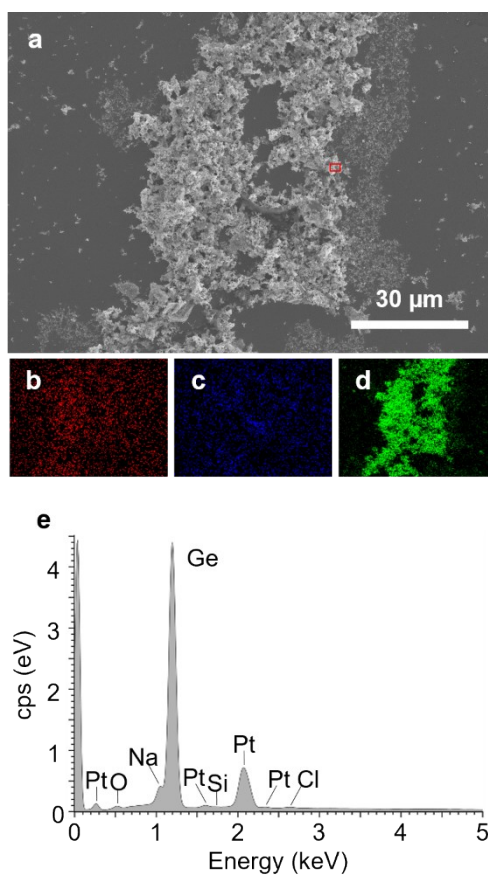


Figure S7. SEM/EDS analysis of isolated Pt-NPs. SEM images (a), elemental mapping images of Si (b), O (c) and Pt (d) and EDS spectra of SEM observation field (e). The observation position shown in Fig. 4 is the area circled in red line on the SEM image. Ge detected in the EDS spectrum is due to the SEM plate used to load the observation sample.

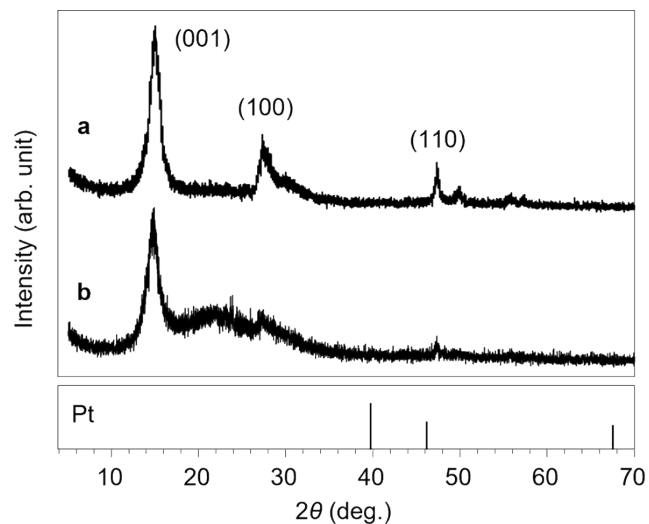


Figure S8. XRD patterns for (a) LpSi and (b) Low-Pt/LpSi. The XRD pattern for standard Pt was obtained from the JCPDS files (JCPDS No. 65-2868).

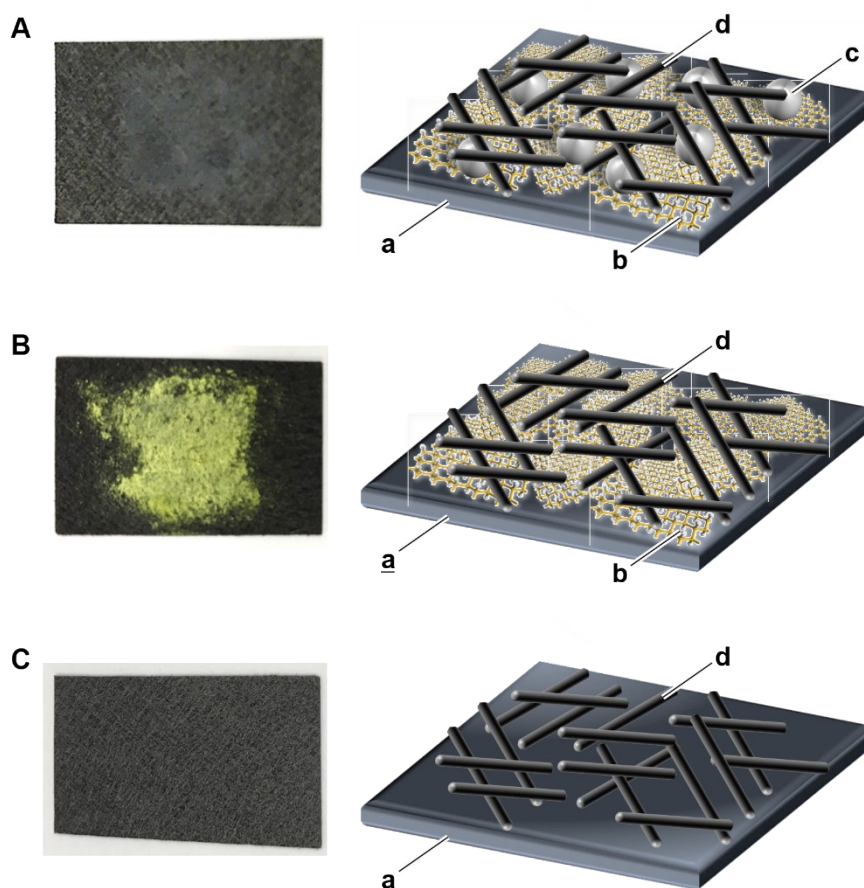


Figure S9. Digital camera images of fabricated electrodes, and schematic illustrations of electrode configurations. (A) Pt/LpSi electrode, (B) LpSi electrode and (C) MWCNTs electrode. (a) CP, (b) LpSi, (c) Pt-NPs and (d) MWCNTs

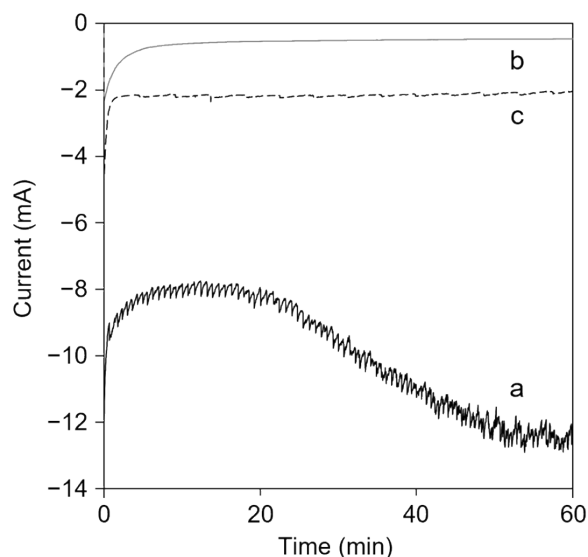


Figure S10. Time dependence of cathodic current during potentiostatic electrolysis at -1.5 V vs. Ag/AgCl (-0.94 V vs. RHE) for each electrode; (a) Pt/LpSi, (b) LpSi and (c) MWCNTs. The current values express the cathodic current as negative.

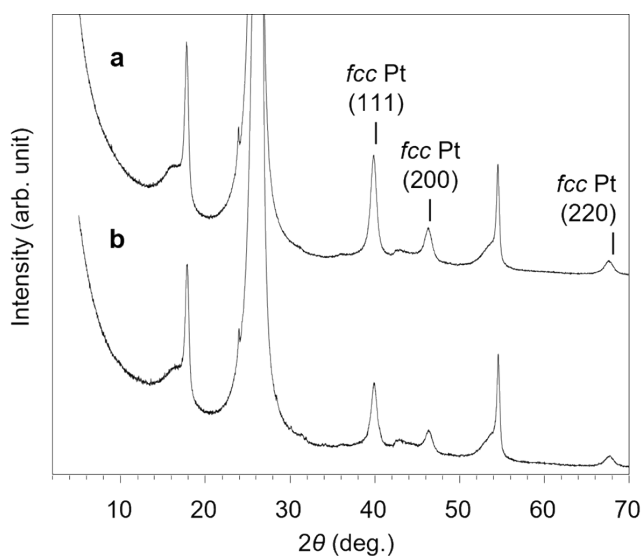


Figure S11. XRD patterns for Pt/LpSi electrode (a) before and (b) after HER evaluation. Diffraction peaks observed at 17.56° , 26.38° and 54.66° are attributed to CP.

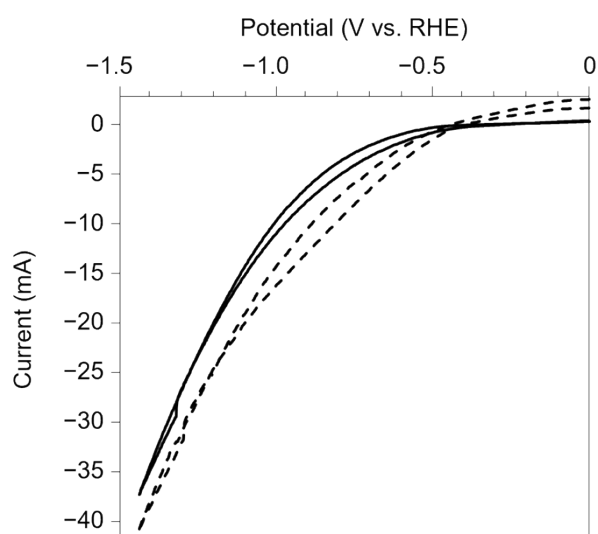


Figure S12. Cyclic voltammograms of Pt/LpSi before (solid line) and after (dashed line) HER evaluation.

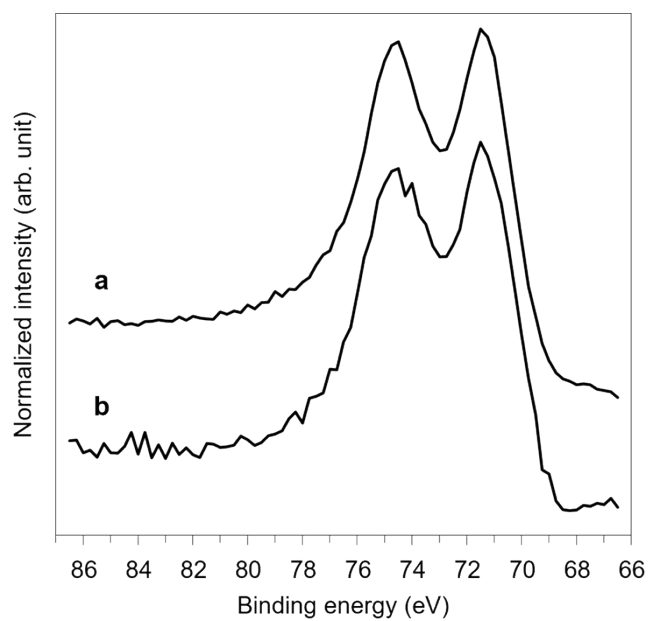


Figure S13. XPS Pt 4f spectra of Pt/LpSi electrode (a) before and (b) after HER evaluation.