

Spontaneous decoration of silicon surfaces with MoO_x nanoparticles for the sunlight-assisted hydrogen evolution reaction

T.-G. Truong, C. Mériadec, B. Fabre,* J.-F. Bergamini, O. de Sagazan, S. Ababou-Girard, G. Loget*

Experimental section

Reagents

Acetone (MOS electronic grade, Erbatron from Carlo Erba) and anhydrous ethanol (RSE electronic grade, Erbatron from Carlo Erba) were used without further purification. The chemicals used for the cleaning and etching of silicon wafer pieces (30% H₂O₂, 96-97% H₂SO₄ and 50% HF solutions) were of VLSI (H₂O₂, from Sigma-Aldrich) and MOS (H₂SO₄ from BASF and HF from Sigma-Aldrich) semiconductor grade. Isopropanol (HPLC grade) was purchased from VWR. KOH (> 85 %, Reag. Ph. Eur.) was purchased from Sigma Aldrich. Anhydrous Na₂SO₄ was purchased from Carlo Erba. (NH₄)₂MoS₄ (99.99 %, Puratrem) was obtained from Strem. K₂MoO₄ (99.8%) was purchased from Alfa Aesar.

Surface preparation

All Teflon vials and tweezers used for cleaning of silicon were previously decontaminated in 3/1 v/v concentrated H₂SO₄/30% H₂O₂ at 100 °C for 30 min, followed by copious rinsing with ultrapure water. **Caution:** the concentrated aqueous H₂SO₄/H₂O₂ (piranha) solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully. The *p-type* (1-5 Ω cm resistivity, boron doped, double side polished, 250-275 μm thickness) and *n-type* (1-5 Ω cm resistivity, phosphorus doped, double polished, 250-275 μm thickness, Siltronix) (100) silicon wafers were purchased from Siltronix. The wafers were cut in 1 x 1 cm² squares and degreased by sonication (10 min) in acetone, ethanol, and ultrapure water (resistivity: 18.2 MΩ cm, Purelab Classic UV). The surfaces were then cleaned in 3/1 v/v concentrated H₂SO₄ /30% H₂O₂ at 100 °C for 45 min, followed by copious rinsing with ultrapure water.

The Si micro-pyramids (SimPy) arrays were made as follows: after the cleaning treatment described above, the surface was first etched in 5/1 v/v ultrapure water/50% aq. HF for 2 min in order to remove the oxide layer and rapidly dried under an argon stream. The surface was then immersed for 50 min in a 0.42 M KOH aqueous

solution containing 5 vol% of isopropanol that was heated at 100 °C. After etching, the silicon wafers were copiously rinsed with ultrapure water and dried under an argon flow.

For electrochemical experiments, the decontaminated flat or SimPy surfaces were further processed to fabricate electrodes. An ohmic contact was established on the backside Si surface with a metal wire by first scrubbing the surface with sand paper and a diamond glass cutter and then applying a droplet of InGa eutectic (99.99%, Alfa Aesar). A layer of silver paste (Electron Microscopy Sciences) was then deposited on the contact. After drying of the silver paste, the metal wire was inserted in a glass capillary, and the electrode area (~ 0.45 cm² for the LSV and ~ 0.9 cm² for the preparative electrolysis) was defined with an epoxy-based resin (Loctite 9460, Henkel) that covered all the back of the Si surface as well as the silver paste.

In the case of the patterning experiment depicted in Figure S6, a SPR 220 (Microchem) thick photoresist layer (6 μ m) was spin coated on a piranha -oxidized Si surface. The photoresist was then flashed through a photomask with a standard 405 nm UV lamp and developed with MFCD-26 (Microchem) in order to create photoresist lines on the SiO₂.

Surface modification

The (NH₄)₂MoS₄ solution was prepared by dissolving 30 mg of (NH₄)₂MoS₄ in 15 mL of ultrapure water. In order to ensure a good solubility of the product, the solution was heated at 80 °C for 30 min and filtered through a 100 nm filter (Millex VV, Millipore). Measurement of the weight of the remaining powder after water evaporation allowed determining a final concentration of salt of 3.6 mM. For the XPS control experiment with MoO₄²⁻, the K₂MoO₄ solution was prepared by dissolving 13 mg in 15 mL of ultrapure water.

After preparation, the solution was maintained at 80 °C. The decontaminated and oxidized Si surface (flat Si, SimPy or Si electrodes) was freshly hydrogenated by dipping it for 2 min in a 5/1 v/v ultrapure water/50% aq. HF, quickly dried under an Ar flow and dipped for 5 min in the Mo⁶⁺ solution under stirring in a dark environment. The surface was then copiously rinsed with ultrapure water and dried under an Ar stream.

For the modification of the Si/SiO₂ arrays, the surface patterned with the PR layer was dipped for 30 s in a 5/1 v/v ultrapure water/50% aq. HF in order to generate Si-H on the unprotected areas, the PR lines (protecting the

underlying SiO₂) were then dissolved by washing with acetone. After this step, the surface was dipped for 5 min in the Mo⁶⁺ solution under stirring in a dark environment. The surface was then copiously rinsed with ultrapure water and dried under an Ar stream.

We noticed that the filtering step was very important for decoration with (NH₄)₂MoS₄ NPs. Indeed, without filtering the solution, AFM and SEM revealed that Si-H surfaces were modified with particle aggregates (see Figure S13) that contained sulfur (see the XPS spectra of Figure S13c). Therefore, in this case, the modification was likely due to adsorption of undissolved (NH₄)₂MoS₄ compound. As K₂MoO₄ is totally soluble, filtration was unnecessary when using this salt.

Photoelectrochemical measurements

The linear sweep voltammograms (LSVs) were performed in a homemade three-neck cell comprising a quartz window in which were inserted a KCl saturated calomel reference electrode (SCE) and a Pt counter electrode (the counter electrode was separated from the rest of the cell by a glass frit). The cell was filled with a 0.5 M Na₂SO₄ solution (pH adjusted to 1 with H₂SO₄) and was deaerated by bubbling Ar for at least 30 min prior to experiments. The Si surface sealed in epoxy (hydrogen-terminated or freshly decorated with MoO_x NPs using the protocol described above) was disposed in front of the quartz window and used as a working electrode. The light was provided by a solar simulator with a fluence of 100 mW cm⁻² (LS0106, LOT Quantum Design) equipped with a AM 1.5G filter. Electrochemical measurements were performed with a potentiostat/galvanostat Autolab PGSTAT 302N (Eco Chemie BV) equipped with the GPES and FRA softwares. LSVs were recorded at 20 mV/s. All the LSVs and the reported potentials were corrected by the ohmic drop that was determined by measuring the impedance of the system at 100 kHz. The geometrical areas of the electrodes used for LSVs were around 0.4 cm² and their exact value was measured using the imageJ software in order to calculate the current densities. Potentials vs SCE were converted into potential vs reversible hydrogen electrode (RHE) using the equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.24 + 0.059 \cdot \text{pH}$ (that was experimentally verified in our operating conditions, as shown in Figure 5a). The preparative-scale electrolysis was performed in a Hoffman cell comprising a quartz window and two closed graduated cylinders above the working electrode and the

counter electrode. The volumes of H₂ and O₂ gases were measured in-situ during the electrolysis, more details can be found in the following reference (Loget et al. Int. J. Hydrogen Energy, 34, 84, 2009). The geometrical area of the MoO_x-NPs decorated SimPy used for the electrolysis shown in Figure 5 was 0.93 cm², as determined by the ImageJ software. For the determination of the faradaic yield, the theoretical volume of produced H₂ ($V_{H_2}^T$) was calculated using the electrical charge used during the electrolysis using the following equation:

$$V_{H_2}^T = \left(\frac{Q}{2F}\right) \times \left(\frac{RT}{P}\right)$$

with Q being the charge passed during the electrolysis, F the Faraday constant, R the gas constant, T the ambient temperature and P the atmospheric pressure.

The setup was tested with a platinum working electrode having an area of 1 cm² at a potential of -240 mV vs RHE. The resulting chronoamperogram is shown in Figure S14. The resulting charge and the measured volume of H₂ allowed to determine a faradaic efficiency of 94 %.

Surface characterization

Reflectance spectra were acquired on a Cary 100 (Varian) spectrophotometer, equipped with an integrating sphere (DRA-CA- 301, Labsphere) referenced with a Spectralon standard (Labsphere). The total reflectance was measured with the surface tilted to include the specular reflectance component. Scanning electron microscopy (SEM) was performed using a JSM 7100F (JEOL). SEM picture analysis was performed using ImageJ software.

XPS measurements were performed with a Mg K_{alpha} (hν) 1254 eV X-ray source, using a VSW HA100 photoelectron spectrometer with a hemispherical photoelectron analyzer, working at an energy pass of 20 eV for survey and resolved spectra. The experimental resolution was then 1.0 eV. The binding energy for the main C-C peak has been taken at 285.0 eV as an internal reference level for all measurements. Spectral analysis included a Shirley background subtraction and peak separation using mixed Gaussian-Lorentzian functions. AFM images were acquired on a NT-MDT Ntegra microscope in semi-contact mode with FM tips (resonance frequency around 60 kHz). The images were treated and analysed with the open-source Gwyddion software.

Supplementary figures

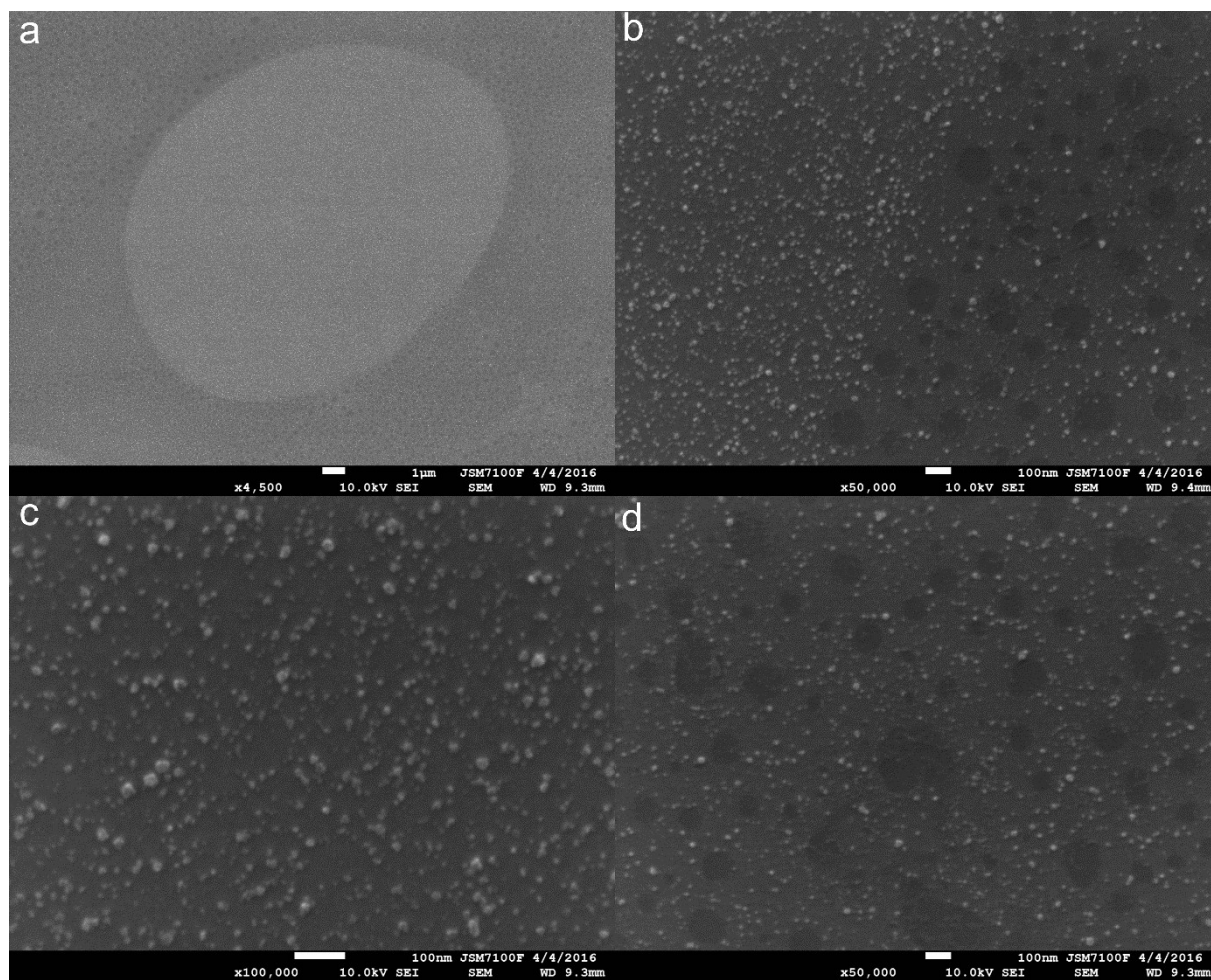


Figure S1. SEM pictures showing: a) a micro-island, b) the boundary between a micro-island and the rest of the surface, c) the inner area of a micro-island and d) the outer area of a micro-island. These pictures were obtained for a HF-treated *p*-type Si (100) surface immersed in a stirred and filtered MoS_4^{2-} aqueous solution for 5 min at 80 °C.

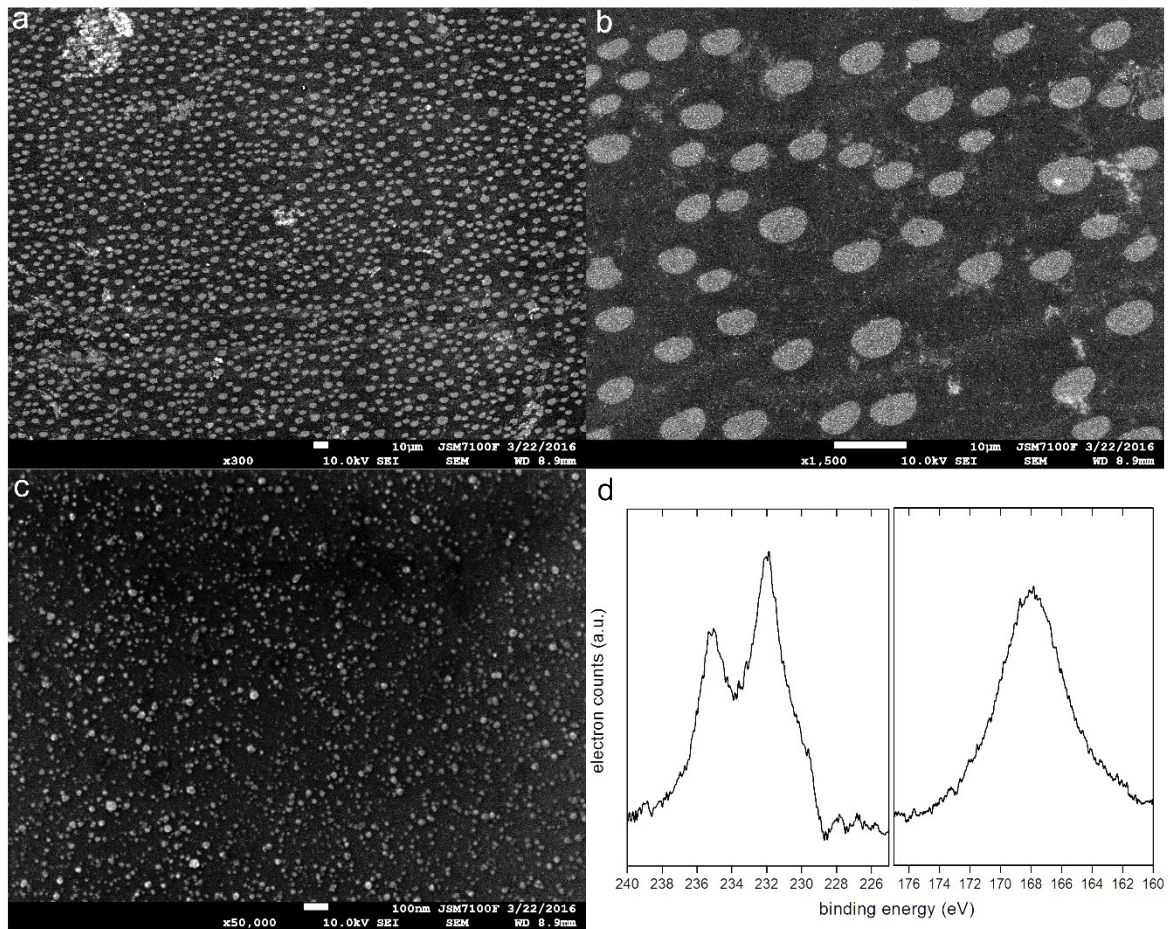


Figure S2. a-c) SEM pictures showing: a) a low-magnification view, b) micro-islands and c) the inner area of a micro-island. d) XPS spectra of this modified surface for the Mo (left) and the Si plasmon (right) regions. These data were obtained for a HF-treated *p*-type Si (100) surface immersed in a stirred and filtered MoS_4^{2-} solution for 30 s at 80 °C.

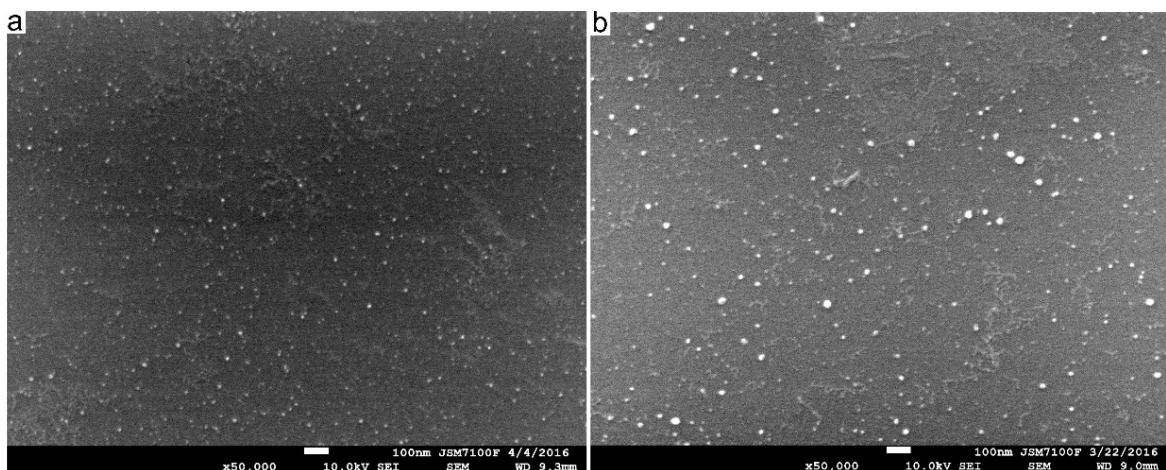


Figure S3. a) SEM picture showing a HF-treated *n*-doped Si (100) surface decorated with NPs obtained by immersing a Si-H surface in a stirred and filtered MoS_4^{2-} aqueous solution, at 80°C for 30 s. b) SEM picture showing a *p*-type Si (100) surface decorated with NPs obtained by immersing a Si-H surface in a stirred and filtered MoS_4^{2-} aqueous solution, at room temperature for 30 s.

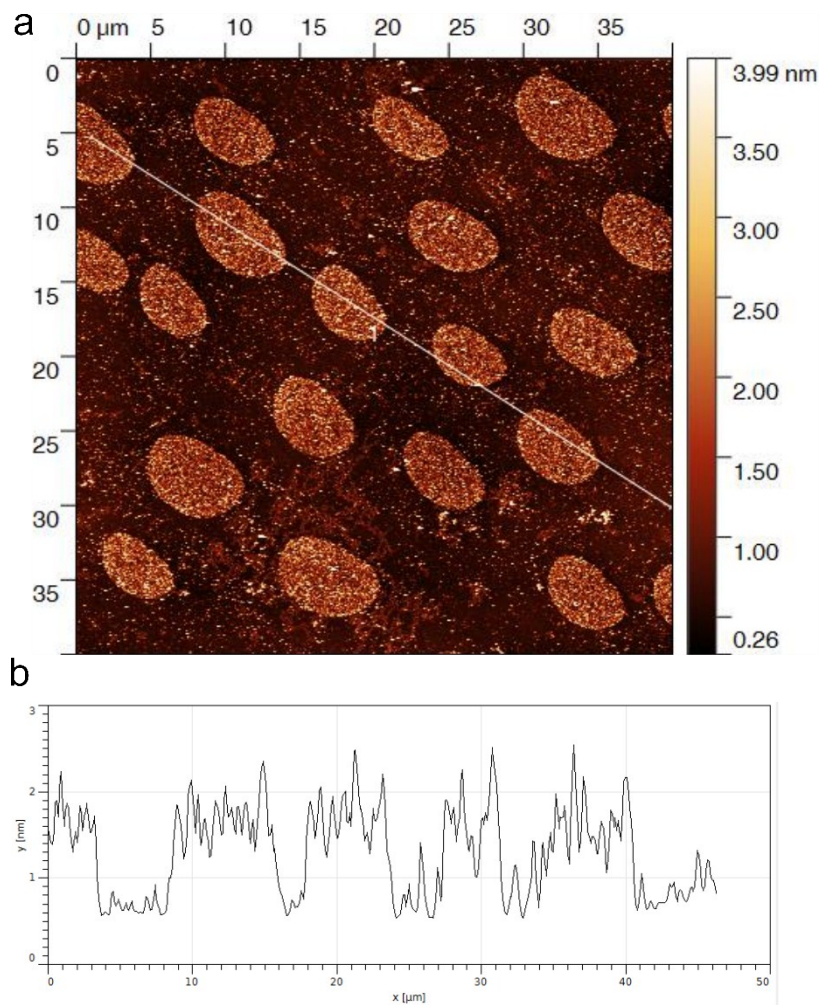


Figure S4. a) AFM image showing a HF-treated *p*-type Si (100) surface decorated with NPs obtained by immersing a Si-H surface in a stirred and filtered MoS_4^{2-} aqueous solution, at 80 °C for 30 s. b) Height profile corresponding to the white line in Figure S4a.

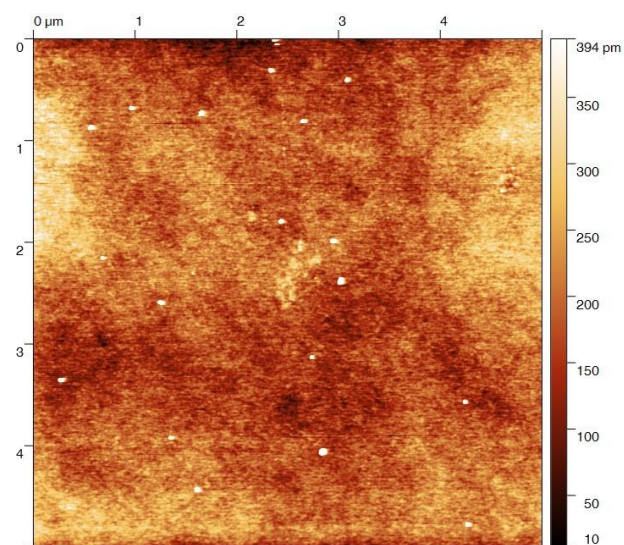


Figure S5. AFM picture showing an oxidized *p*-type Si surface (that was not treated with HF) after immersion in a filtered and stirred MoS_4^{2-} aqueous solution, at 80 °C for 5 min.

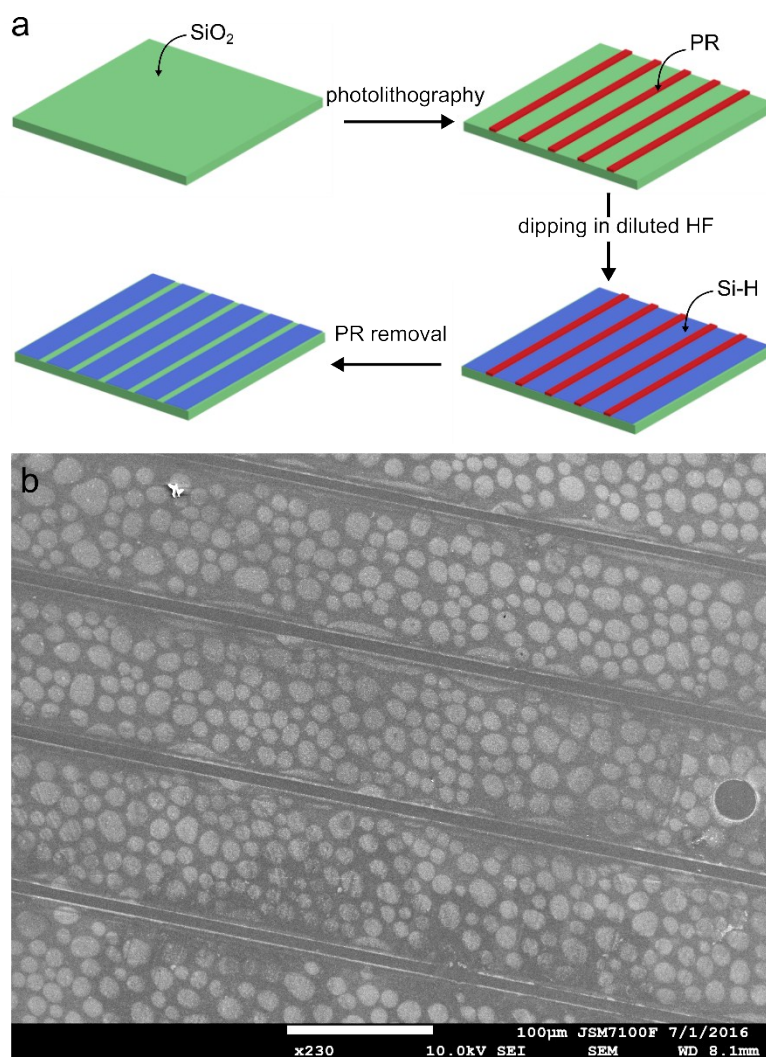


Figure S6. a) Scheme showing the treatments performed on a *p*-type Si (100) surface to create SiO₂ stripes. b) SEM picture showing the surface after immersion in a filtered and stirred MoS₄²⁻ aqueous solution, at 80 °C, for 5 min.

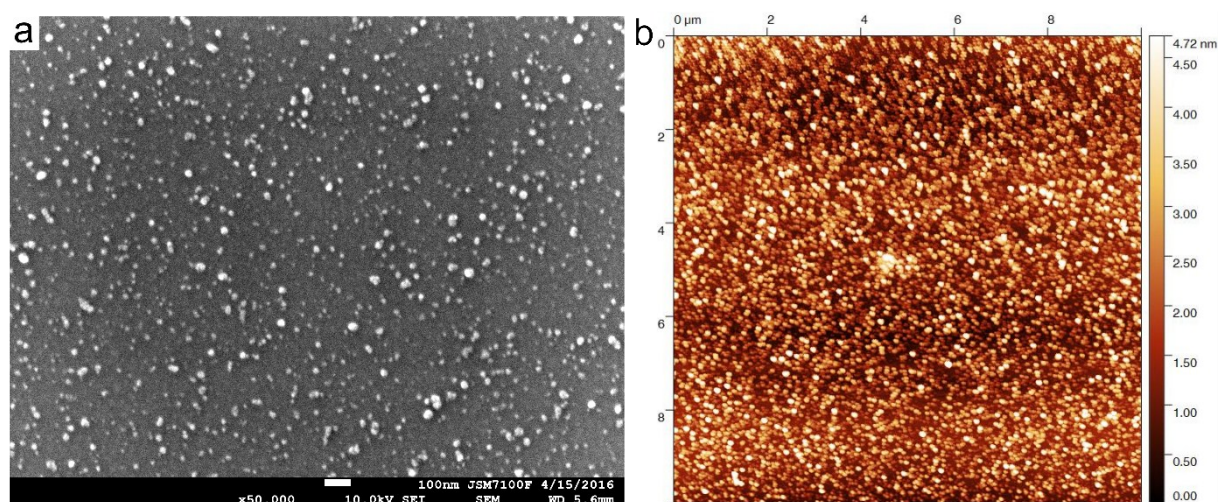


Figure S7. a) SEM and b) AFM pictures showing a *p*-type Si (100) surface decorated with MoO_x NPs obtained by immersing a Si-H surface in a stirred MoO₄²⁻ aqueous solution, at 80°C for 5 min.

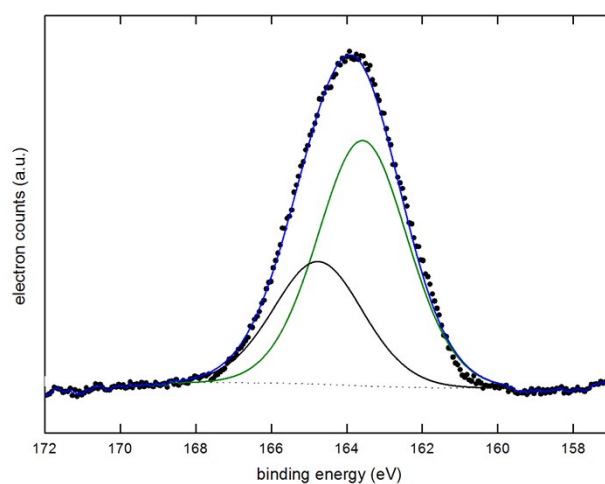


Figure S8. XPS spectra showing the S 2p region for $(\text{NH}_4)_2\text{MoS}_4$; experimental data (dots) and fits for S^{2-} S $2p_{1/2}$ (black solid line), S^{2-} S $2p_{3/2}$ (green solid line) as well as the fitting envelope (blue solid line).

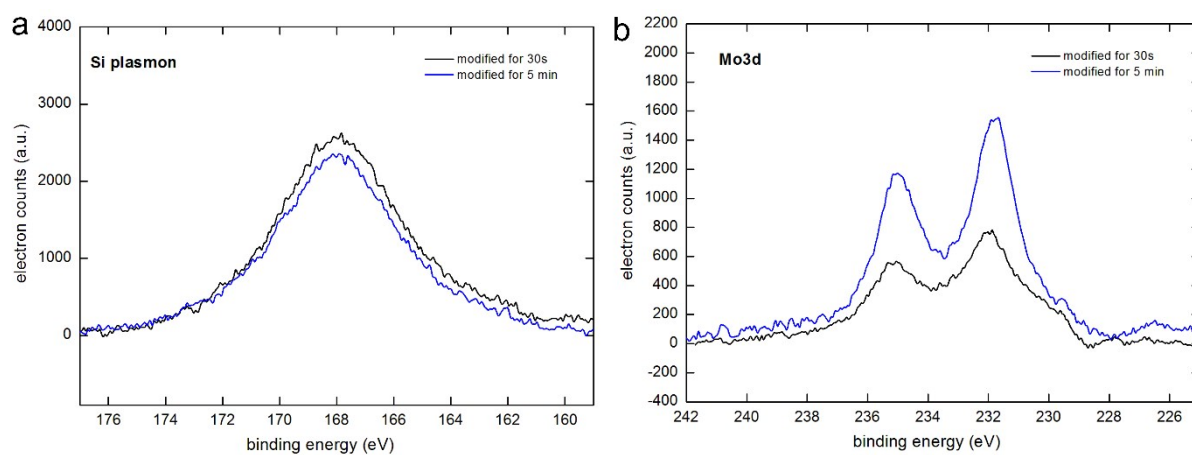


Figure S9. XPS spectra showing a) the Si plasmon region and b) the Mo 3d region for *p*-type Si surfaces after immersion in a filtered and stirred MoS_4^{2-} aqueous solution, at 80 °C for 5 min (blue) and 30 s (black).

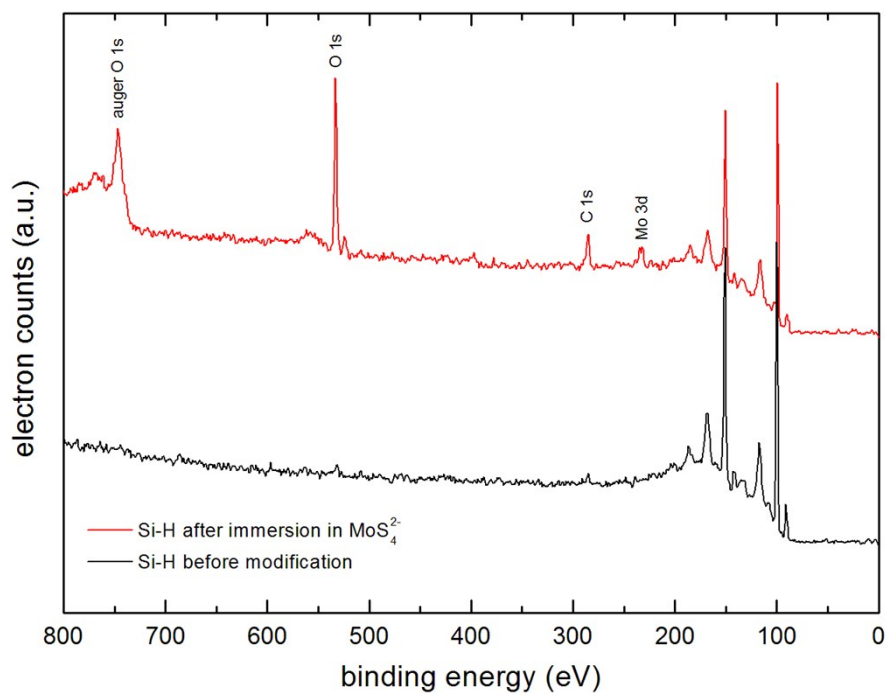


Figure S10. Survey XPS spectra recorded for a HF-treated *p*-type Si-H surface before (black) and after (red) immersion in a filtered and stirred MoS₄²⁻ aqueous solution, at 80 °C for 5 min.

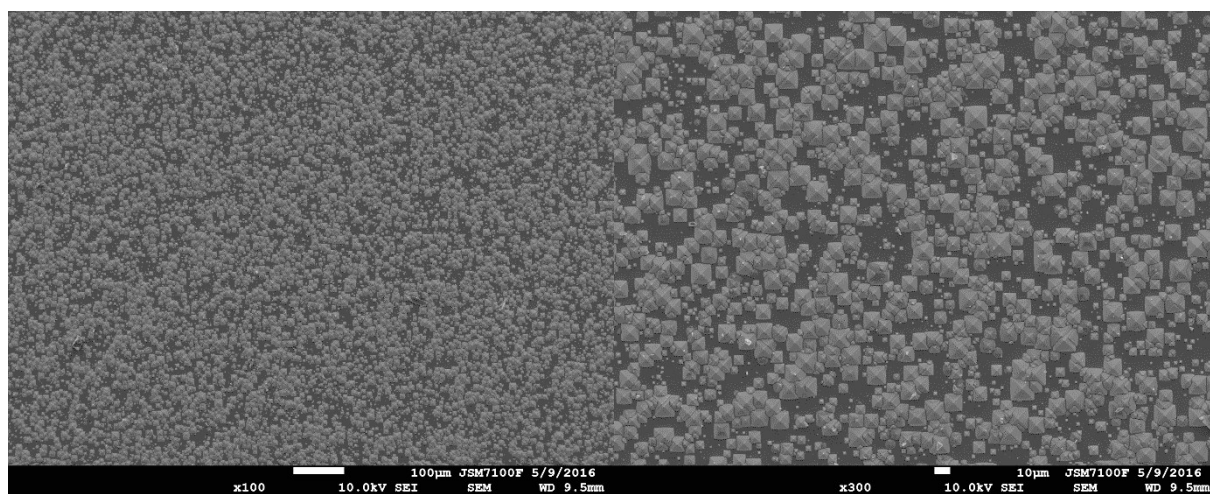


Figure S11. SEM pictures showing low magnification top views of the SimPy surfaces.

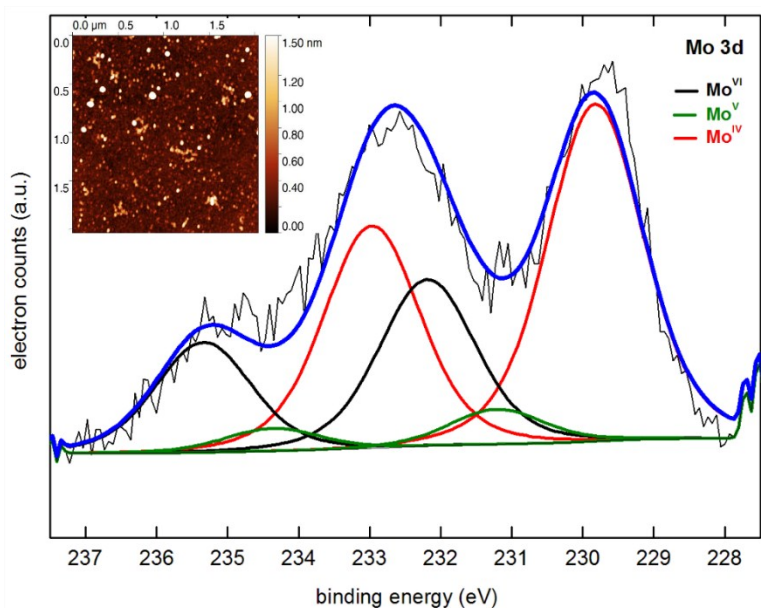


Figure S12. XPS spectrum showing the Mo 3d region for Si-H decorated with MoO_x NPs (from MoS₄²⁻ aqueous solution at 80 °C for 5 min) and immersed for 1 h in an acidic solution containing Na₂SO₄ 0.5 M (pH adjusted to 1 with H₂SO₄); experimental data (black thin line) and fits for Mo^{VI} (black thick line), Mo^V (green) and Mo^{IV} (red) as well as the fitting envelope (blue). Inset: AFM picture of the decorated surface after immersion in the acidic solution.

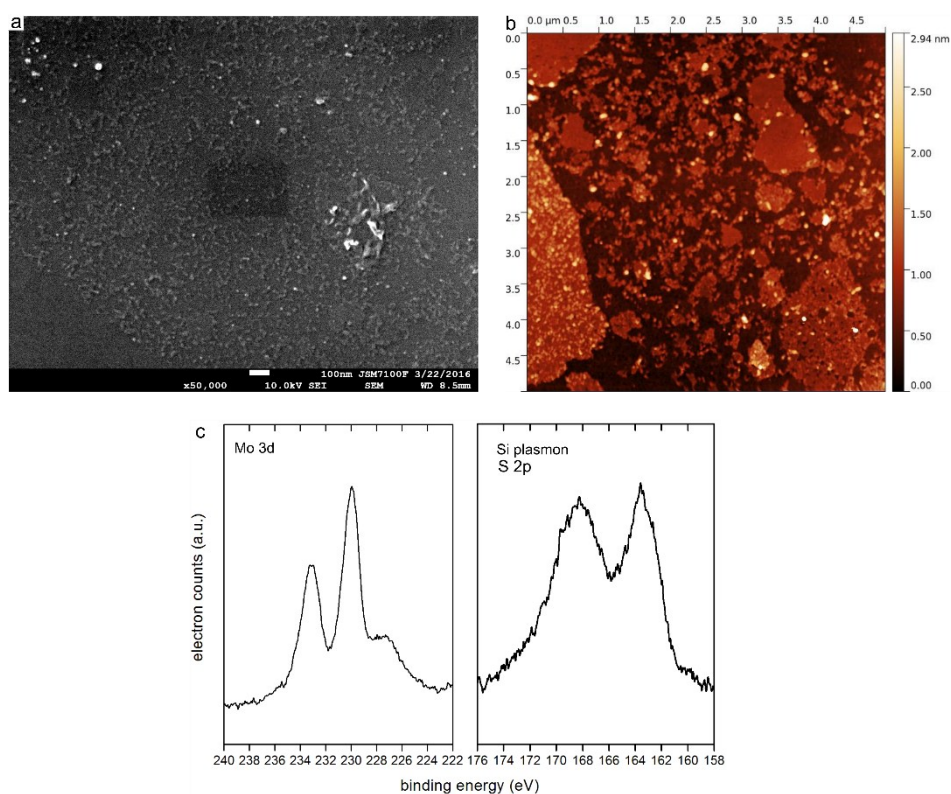


Figure S13. a) SEM and b) AFM pictures showing a HF-treated *p*-type Si (100) surface decorated with NPs obtained by immersing a Si-H surface in a stirred and not filtered MoS₄²⁻ aqueous solution, at 80°C for 30 s. c) XPS spectra showing the Mo 3d region (left) and the Si plasmon and the S 2p regions (right) for *p*-type Si surfaces after immersion of the surface in a stirred and not filtered MoS₄²⁻ unfiltered aqueous solution, at 80°C for 30 s.

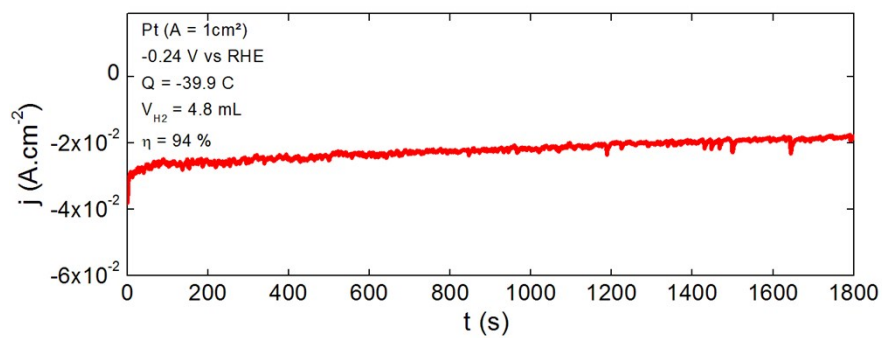


Figure S14. Chronoamperometry and data measured for a Pt electrode at -0.24 V vs RHE in 0.5 M Na₂SO₄ (pH adjusted to 1 with H₂SO₄).

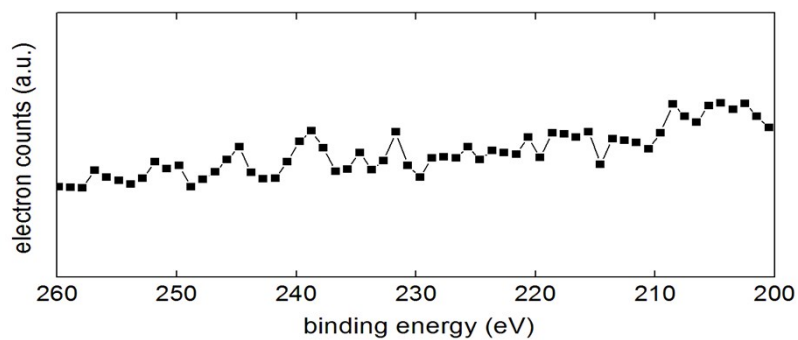


Figure S15. XPS spectrum showing the Mo 3d region for Si-H decorated with MoO_x NPs (from MoS₄²⁻ aqueous solution at 80 °C for 5 min) and used for 1 h as a photocathode in an acidic solution containing Na₂SO₄ 0.5 M (pH adjusted to 1 with H₂SO₄).