Supporting Information

Enhanced electrocatalytic hydrogen evolution on a plasmonic electrode: the importance of the Ti/TiO_2 adhesion layer

Liuqing Pang, [a] Alexandre Barras,[a] Vladyslav Mishyn,[a] Georgiana Sandu,[b] Sorin Melinte,[b] Palaniappan Subramanian,[c] Rabah Boukherroub,[a] Sabine Szunerits[a*]

[a] *Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 - IEMN, F-59000 Lille, France*

[b] *Institute of Information and Communication Technologies, Electronics and Applied Mathematics, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium*

[c] *Department of Materials Engineering, KU Leuven, Kateelpark Arenberg, Heverlee - 3001, Belgium*

Figure S1. SEM images of the investigated electrodes. The scale bar is 2 µm. Cyclic voltammograms of the different surfaces. S1: K/Au NHs (50 nm) (black), S2: K/Ti/TiO_2/Au NHs (50 nm) (red), S3: K/Ti/TiO_2 (30 nm) (grey) in ferrocenemethanol (1 mM)/KCl (0.1 M). The scan rate is 50 mV s^{-1}.

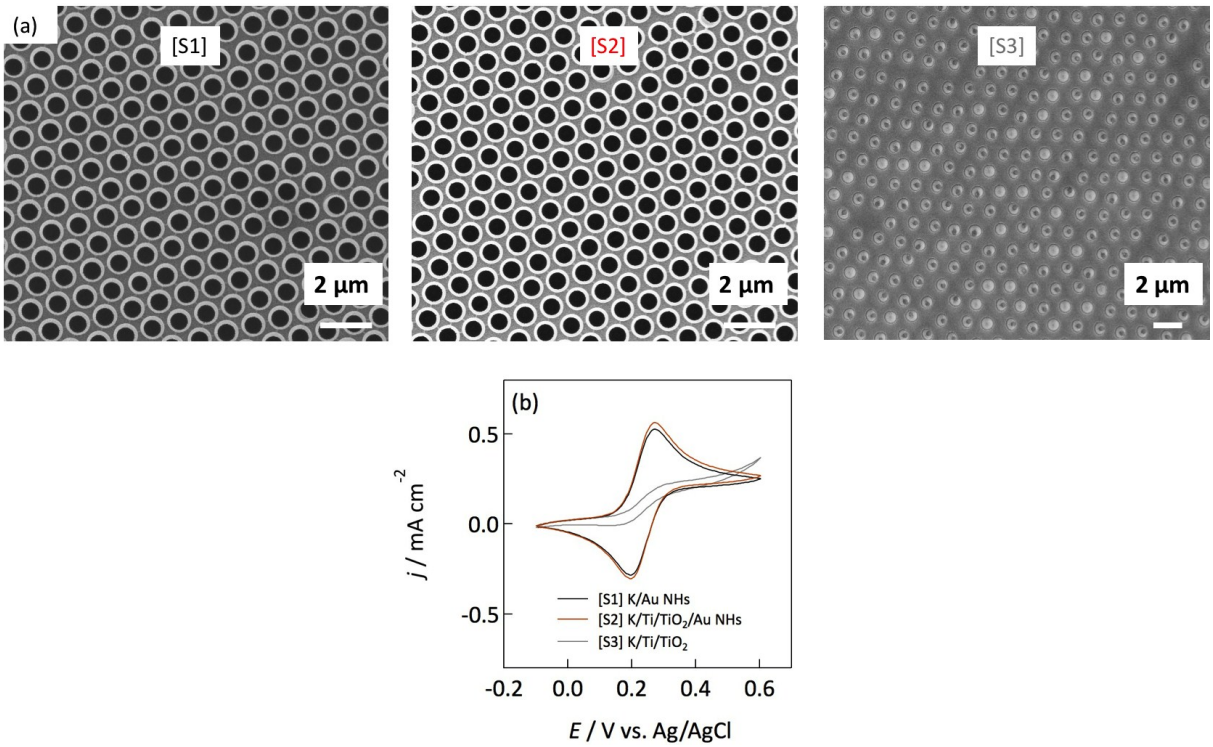

Figure S2. Nyquist plots of S1 (a) and S2 (b) under illumination at 980 nm for 10 minutes at 2 W cm^{-2} (black and red) and without illumination (grey and valentine) over the frequency range of 100 kHz to 0.01 Hz. Points are experimental data and curves are fits to the data. The equivalent circuit used for analysis is shown in the inset of panel (a).

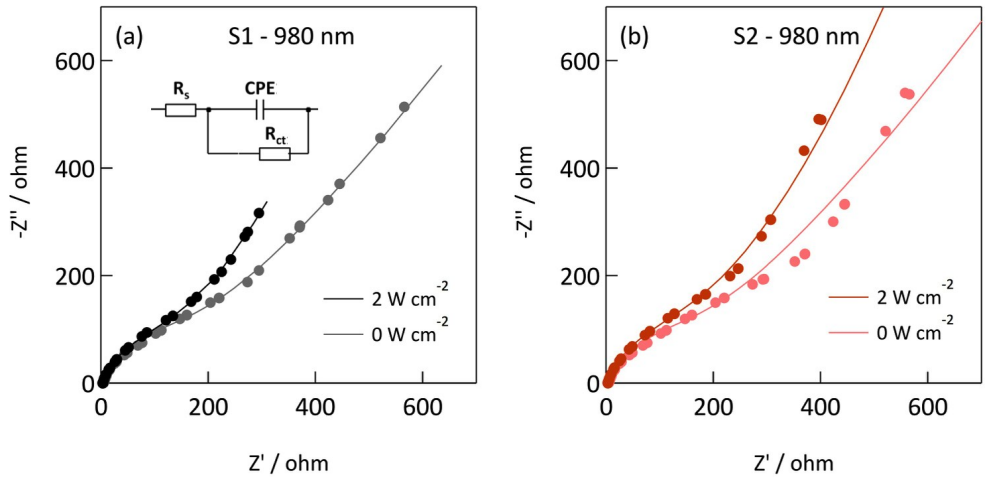

Figure S3. (a) Photothermal heating curves of S1 immersed in 0.1 M H_2SO_4 upon laser light irradiation at 980 nm (full curve) and 808 nm (dashed curve) for 10 minutes at 2 W cm^{-2}. (b) Photothermal heating curves of S2 immersed in 0.1 M H_2SO_4 and exposed to laser light of 980 nm (full curve) and 808 nm (dashed curve) for 10 minutes at 2 W cm^{-2}. (c) HER polarization curves at 24 °C, 45 °C, 65 °C and 80 °C in 0.1 M H_2SO_4 solution for S1. (d) HER polarization curves at 24 °C, 45 °C, 65 °C and 80 °C in 0.1 M H_2SO_4 solution for S2.

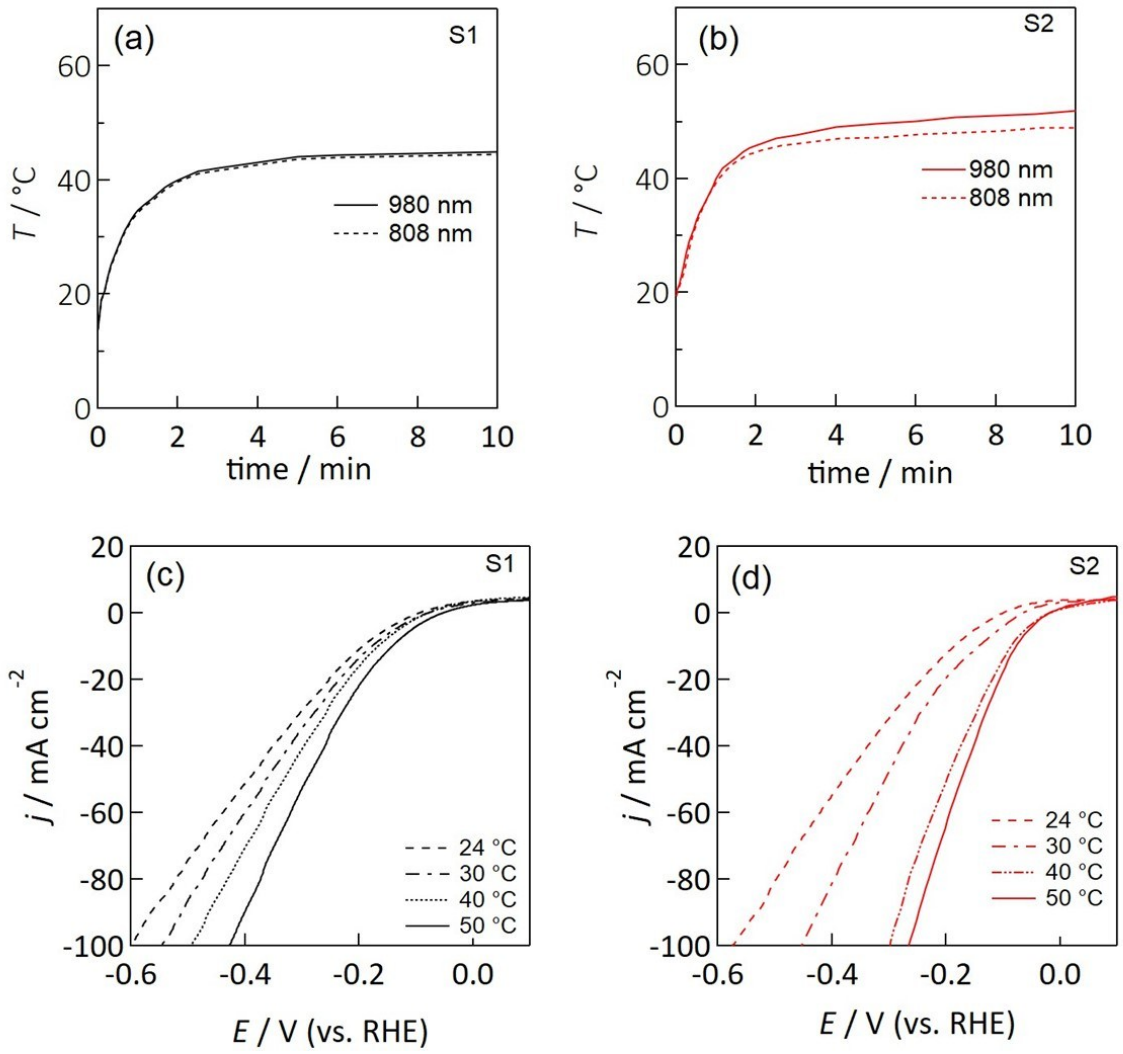

Figure S4. Arrhenius plots of the current density obtained for S1 (a) in the dark and (b) under light illumination at 980 nm for 10 minutes at 2 W cm^{-2} and overpotentials of -0.20, -0.25 and -0.30 V. Arrhenius plots of the current density obtained for S2 (c) in the dark and (d) under light illumination at 980 nm for 10 minutes at 2 W cm^{-2} and overpotentials of -0.20, -0.25 and -0.30 V. The activation energy (E_a) was determined from the slope of the Arrhenius plots according to $j \propto \exp(-E_a/RT)$, with R being the universal gas constant (8.314 J mol^{-1}) and T the temperature (K).