Supporting Information

Photoelectrochemical water splitting

employing a tapered silicon nanohole array

Jin-Young Jung,^a Mi Jin Choi,^{b,c} Keya Zhou,^a Xiaopeng Li,^{d,e} Sang-Won Jee,^a Han-Don Um,^a Min-Joon Park,^a Kwang-Tae Park,^a Jin Ho Bang,^{*b,c} and Jung-Ho Lee^{*a}

^aDepartments of Chemical Engineering, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Kyeonggi-do 426-791, Republic of Korea

^bDepartment of Bionano Engineering, and ^cDepartment of Chemistry and Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Kyeonggi-do 426-791, Republic of Korea

^dMax-Planck Institute of Microstructure Physics Weinberg 2, D-06120 Halle, Germany Institute of Physics, ^eMartin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

Email: jungho@hanyang.ac.kr (Lee), jbang@hanyang.ac.kr (Bang)



Figure S1. SEM images of tapered SiNH arrays obtained with Ag deposition times of (a) 1 s, (b) 5s, (c) 10s, and (d) 30s, which determined the bottom filling of 65%, 45%, 38%, and 29%, respectively. All scale bars are 200 nm.



Figure S2. Diffuse reflectance spectra of tapered SiNH with varying (a) the Ag deposition time (the filling ratio) of 1s (29%), 5s (38%), 10s (45%) and 30s (65%) and (b) the depth of 70–1600 nm. Specular reflection spectra of tapered SiNH with varying the Ag deposition time (the filling ratio) of 1s (29%), 5s (38%), 10s (45%) and 30s (65%) at (c) 200 nm and (d) 400 nm depth.



Figure S3. Average reflection of tapered SiNH arrays obtained with different Ag deposition times of 1s (black), 5s (red), 10s (blue), and 30s (green), plotted in an extended range of NH depth (70–1600 nm) compared to Figure 4.



Figure S4. (a) Dark current densities versus potential with (a) various Ag deposition times and (b) depths.



Figure S5. (a) Minority carrier lifetimes and (b) the effetive surface recombination velocity in comparison to tapered SiNHs with different depths.



Figure S6. I-V curve for planar Si and SiNH with 200-nm-depth. Compared to Figure 6(a), the I-V behavior around the onset voltage is clearly seen.



Figure S7. (a) Schematic illustration of SiNH photocathode/electrolyte interface and its equivalent circuit for impedance modeling. In our SiNH based PEC system, to obtain the best fitting, values of capacitance and resistance from surface (C_{ss} and R_{ss}) in parallel to values of C_{SC} and R_{SC} need to be considered because of surface defects and surface chemisoprtion (ref 40 in manuscript). (b) Bode plots of EIS data from SiNHs with different depths: 70 nm (red), 200 nm (blue), and 400 nm (cyan).

Table S1. Electrochemical impedance spectroscopy results of tapered SiNHs photocathodes with different depths.

	R _S	R_{SC} (×10 ³)	C _{SC} (×10 ⁻⁶)	R _{SS}	C_{SS} (×10 ⁻⁶)
0 nm (Planar Si)	39.74	36	2.38	265	2.14
70 nm	39.28	10	3.48	369	3.28
200 nm	16.57	5	4.58	352	4.25
400 nm	18.79	4	5.18	171	7.15