Electronic Supplementary Information

N-doped Monolayer Graphene Catalyst on Silicon Photocathode for Hydrogen Production

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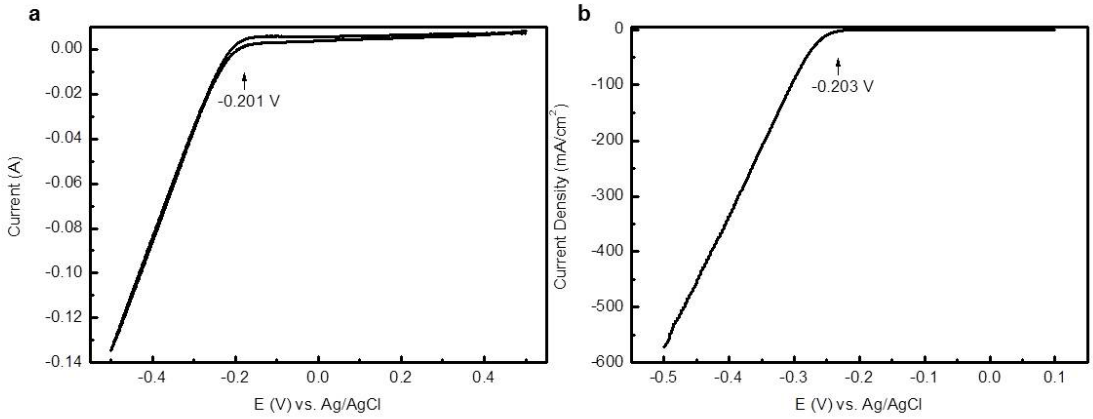

Figure S1. Calibration respect to RHE. Current vs. the applied potential respect to Ag/AgCl reference electrode with using (a) Pt foil for Si PEC cell experiment and **(b)** Pt wire as the counter electrode for RDE experiment.

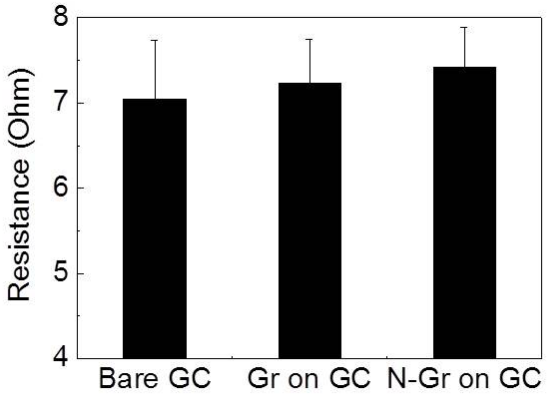

Figure S2. Resistance of bare Glassy Carbon (GC), Gr on GC, and NGr on GC. Impedance spectroscopy analysis revealed that the resistances of the bare GC, Gr-GC, NGr-GC are 7.1 ohm, 7.2 ohm, and 7.4 ohm respectively. Resistances were measured using iR compensation mode in the electrochemical analyzer (CHI 600D, CH Instruments, Inc.).

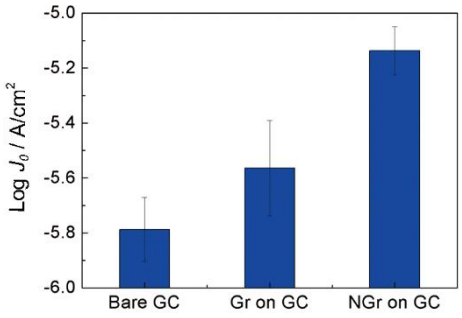

Figure S3. The logarithm of the exchange current densities calculated by extrapolation to the x-axis. Compared to the bare GC, Gr and NGr catalysts show the high activity for the HER.

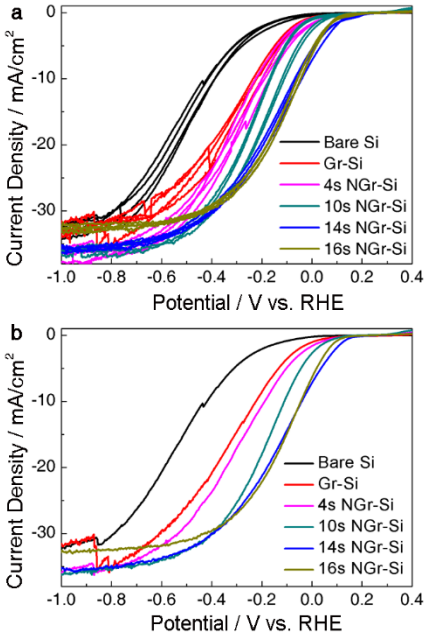

Figure S4. Photoelectrochemical performance of NGr-Si photocathode with variation of the amount of Pt solution. (a) Polarization curves of NGr on Si electrode. Each cyclic voltammetry was performed during 4 cycles at a scan rate of 0.05 V/s. The durations of the plasma treatment on Gr were introduced with high purity N_2 gas for 4 sec, 10 sec, 14 sec, and 16 sec. For comparison, cyclic voltammogram of Gr without plasma treatment on Si electrode is presented. (b) Representative data from polarization curves of NGr on Si electrode of Figure S4 a.

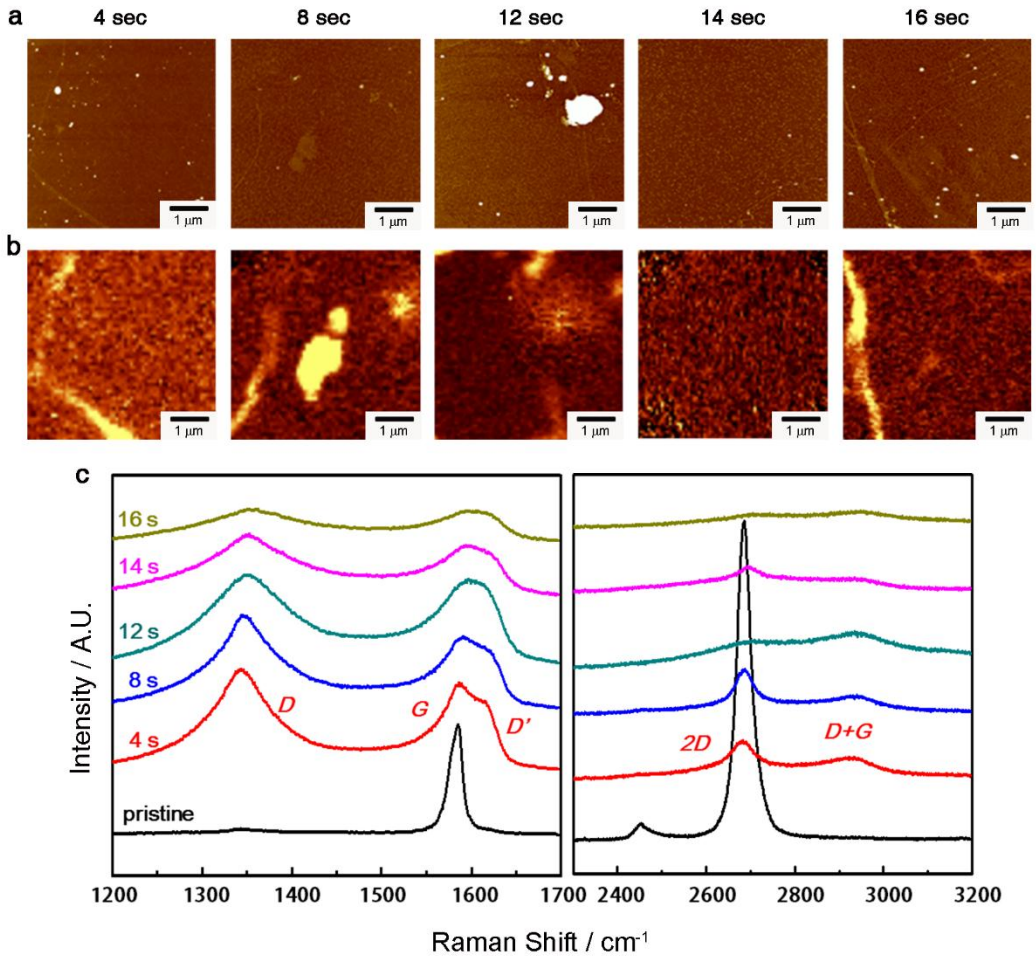

Figure S5. Surface morphology of monolayer Gr and NGrs. (a) AFM images and (b) Raman characterization of a pristine Gr sample as a function of the exposure time to N_2 plasma and the each image was taken the same area measured by AFM. Numbers on each figure indicate the exposure time. All figures have a size of $6.5 \times 6.5\mu m^2$ (c) Raman spectra of the samples. Numbers on the left side of the left figure indicate the exposure time. Raman peaks are indexed accordingly.

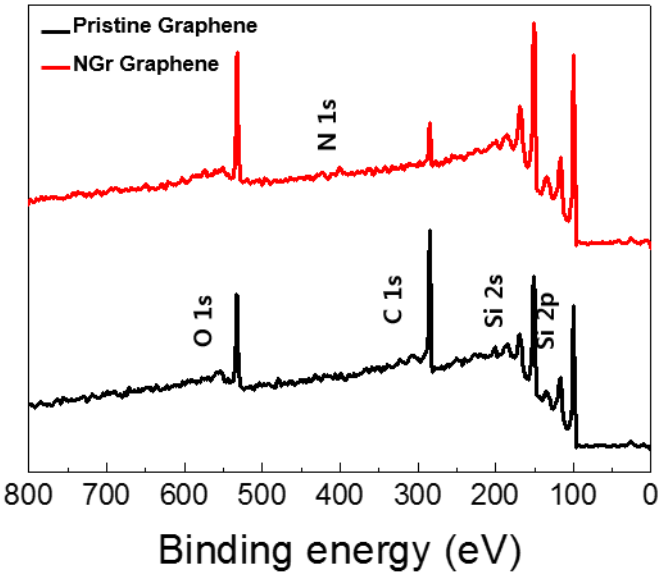

Figure S6. XPS spectra of Gr and NGr. The C 1s is 76.78 atomic weight % (at. %) for Gr and 57.17 at. % for NGr, N 1s is 0.00 at. % for Gr and 2.20 at. % for NGr, and O 1s is 23.22 at. % for Gr and 40.63 at. % for NGr, respectively.

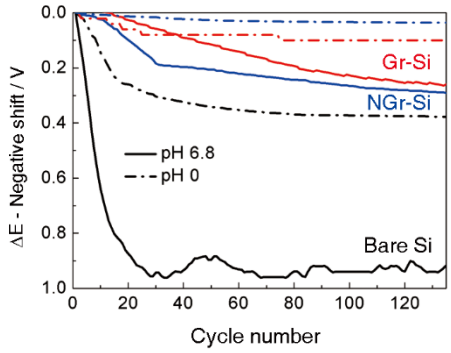

Figure S7. The change of onset potential of bare Si (black line), Gr-Si (red line), and NGr-Si (blue line) electrodes. The onset potential measured from the first CV sweep was a standard, and the difference between the measured onset potential during the CV cycles and the value of the first sweep was investigated; this difference is defined as ΔE – negative shift. The onset potential was measured with increasing the number of cyclic voltammetry in 1M $HClO_4$ (pH 0, dash dot line) and 0.4 M NaH_2PO_4 and 0.6 M Na_2HPO_4 (pH 6.8, solid line) electrolytes, respectively.

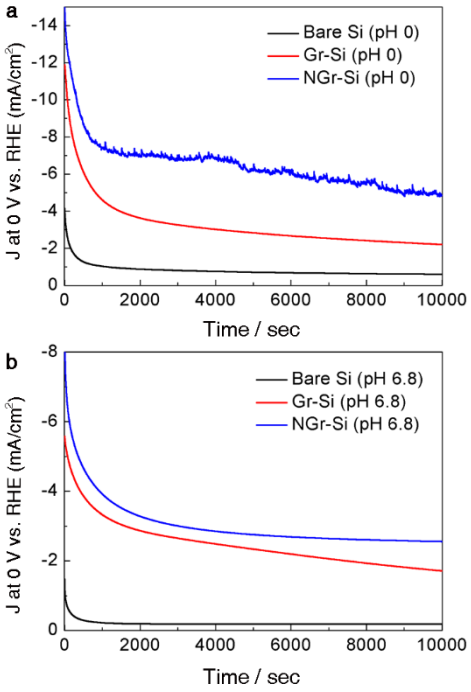

Figure S8. The change of photocurrent density at 0 V vs. RHE of bare Si (black line), Gr-Si (red line), and NGr-Si (blue line) electrodes with the increase of time at (a) pH 0 (1M $HClO_4$) and (b) pH 6.8 (0.6 M NaH_2PO_4 and 0.4 M Na_2HPO_4), respectively. At pH 0, NGr-Si electrode shows a spiky plot during a chronoamperometry test because hydrogen bubbles stick to hydrophobic surfaces until sudden bursts occur.

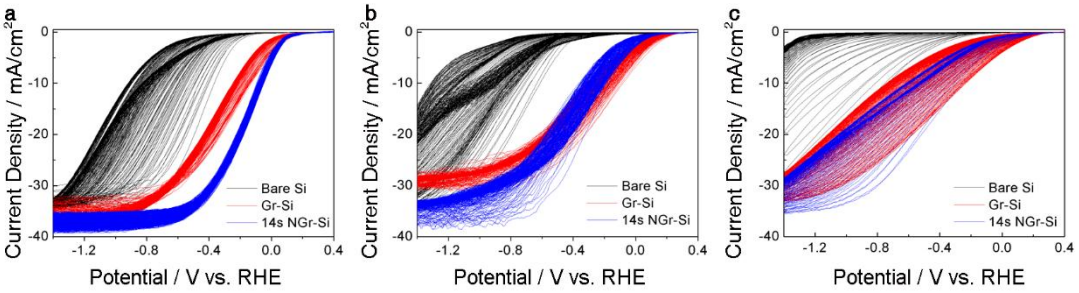

Figure S9. The stability test of bare Si, Gr-Si, and NGr-Si photocathodes. CV results of Si photocathodes during 300 cycles with a scan rate of 0.05 V/sec at (a) pH 0, (b) pH 3.8, and (c) pH 6.8. Polarization curves of each photoelectrodes were shifted negatively vs. RHE as the number of cycles increased.

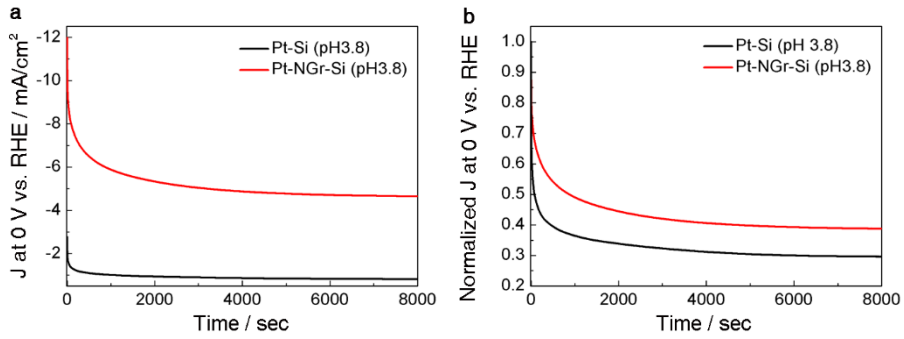

Figure S10. Chronoamperometry test of Pt-Si and Pt-NGr-Si photocathodes at pH 3.8. (a) The change of photocurrent density at 0 V vs. RHE of Pt-Si (black line) and Pt-NGr-Si (red line) electrodes with the increase of time at pH 3.8. (b) The change of normalized photocurrent density (J/ J_{init}) at 0 V vs. RHE with the increase of time at pH 3.8. J_{init} is the initial current density in the chronoamperometry test.

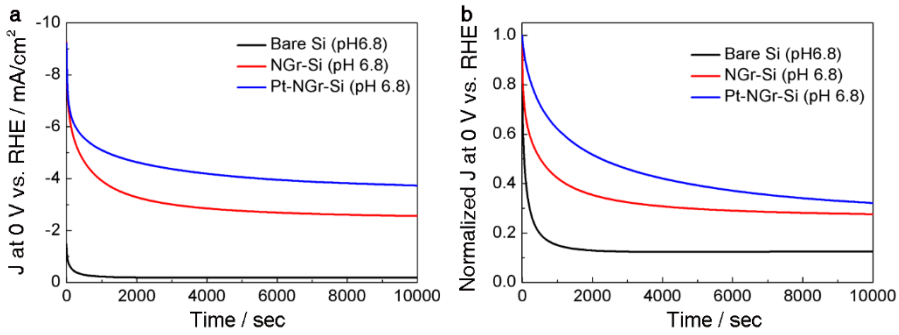

Figure S11. Chronoamperometry test of bare Si, NGr-Si, and Pt-NGr-Si photocathodes at pH 6.8. (a) The change of photocurrent density at 0 V vs. RHE of bare Si (black line), NGr-Si (red line), and Pt-NGr-Si (blue line) electrodes with the increase of time at pH 6.8. (b) The change of normalized photocurrent density (J/ J_{init}) at 0 V vs. RHE of each photoelectrodes with the increase of time at pH 6.8.

Table S1. Summary of the experimental data for Si and Glassy Carbon (GC) electrodes.

Condition	Electrode	Onset potential [E (V) at -1 mA/cm^{-2}]	E (V) at -5 mA/cm^{-2}	E (V) at -10 mA/cm^{-2}	Solar-to-Hydrogen Conversion Efficiency (%)
Under illumination (p type Si)	Bare Si	-0.17	-0.29	-0.42	0.02
	Gr--Si	0.01	-0.13	-0.21	0.04
	14s NGr-Si	0.12	0.02	-0.04	0.16
	Pt-Si	0.24	0.16	0.11	1.19
	Pt-NGr-Si	0.35	0.29	0.25	3.05
Under dark condition (n^+ type Si)	Bare Si	-0.63	-0.78	-0.85	
	Gr-Si	-0.49	-0.61	-0.69	
	14s NGr-Si	-0.44	-0.55	-0.62	
Photovoltage*	Bare Si	0.46			
	Gr-Si	0.50			
	14s NGr-Si	0.56			
RDE (GC) under dark condition	Bare GC	-0.24	-0.33	-0.37	
	Gr-GC	-0.18	-0.28	-0.31	
	14s NGr-GC	-0.16	-0.26	-0.29	
	Pt-GC	-0.02	-0.04	-0.05	

* The photovoltage is defined as the difference between the onset potential under the dark and illumination condition. This value was calculated from the consideration of the following reference; Y. W. Chen, J. D. Prange, S. Dühnen, Y. Park, M. Gunji, C. E. Chidsey and P. C. McIntyre, *Nature Mater.*, 2011, **10**, 539-544. (Ref. 5 in the main article)