Electronic Supplementary Information

N-doped Graphene Quantum Sheets on Silicon Nanowire Photocathode for Hydrogen Production

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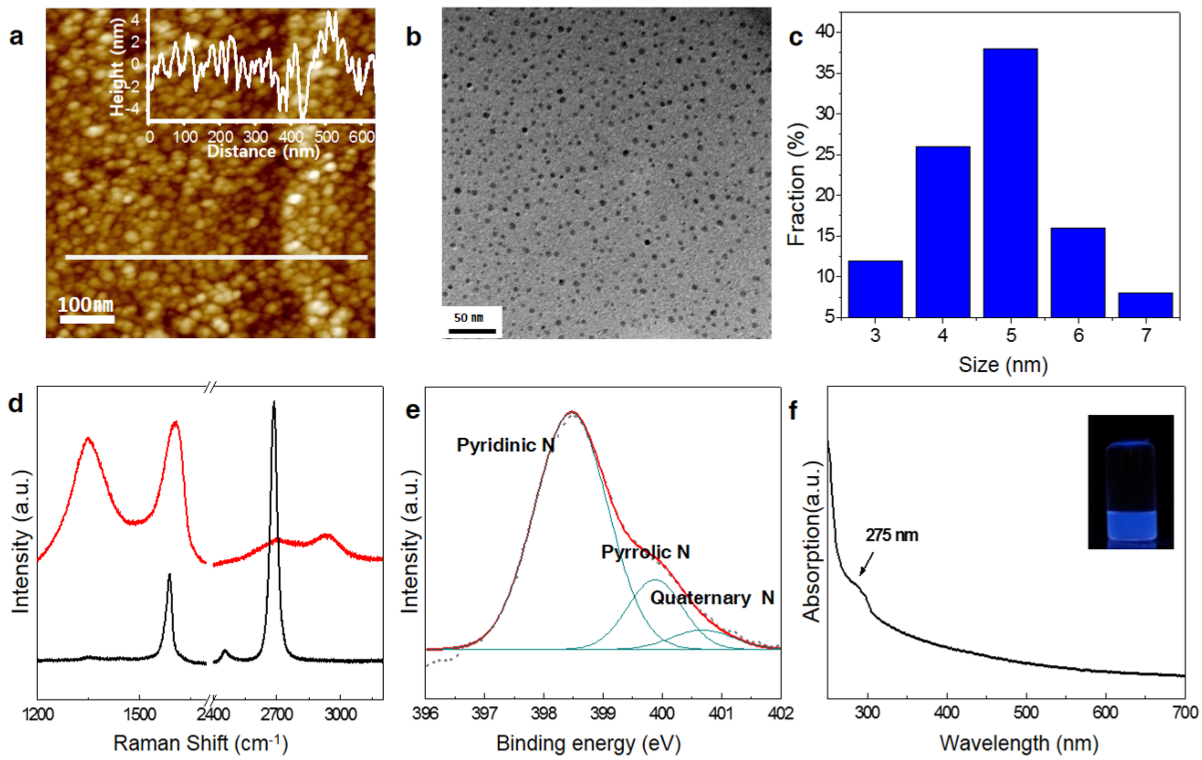

Figure S1. (a) AFM image of nitrogen plasma treated GQSs on Cu foil. Scan size, 600 x 600 nm^2. (b) TEM image of N-GQSs. (c) Histogram showing the size distribution of N-GQSs. (d) Raman spectra of graphene (black) and N-GQSs (red) and (e) detailed N 1s XPS spectra of N-GQSs. (f) UV-vis absorption of the N-GQSs in dichloromethane. The inset shows a photograph of the N-GQSs solution under 365 nm wavelength UV lamp.

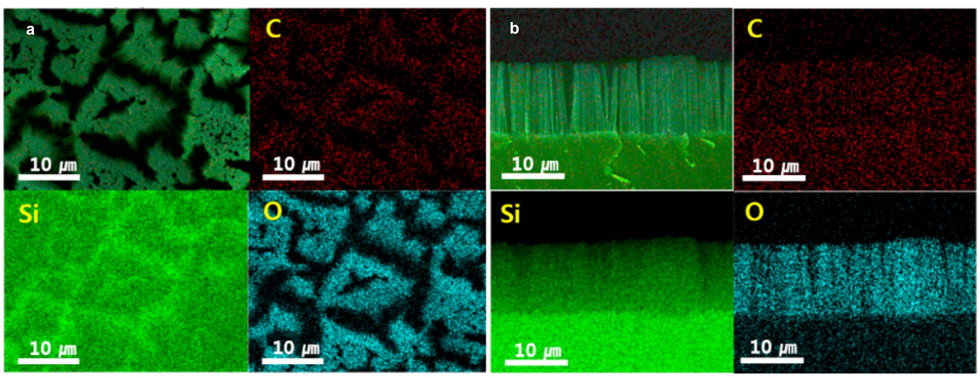

Figure S2. SEM mapping images of N-GQSs decorated on Si nanowires. (a,b) Colour images of all displayed with three elements; C (red), Si (green), and O (blue).

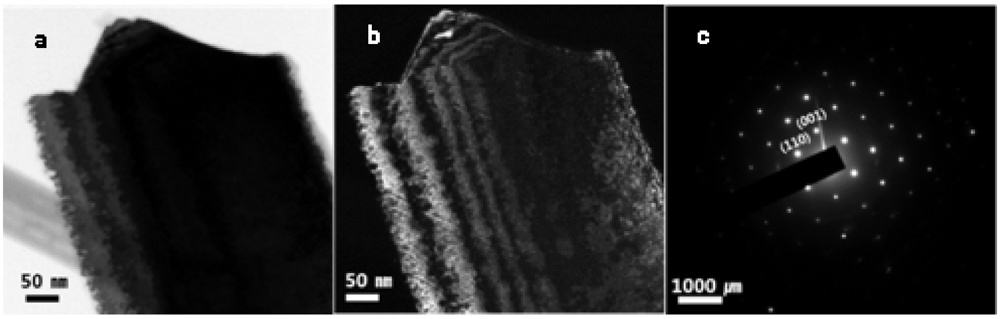

Figure S3. (a) Bright-field and (b) dark-filed TEM images of N-GQSs dispersed on p-SiNWs. (c) Selected area diffraction patterns (SAED) gives p-SiNWs are well etched toward [001] direction. GQS pattern is hardly observed due to the strong silicon lattice.

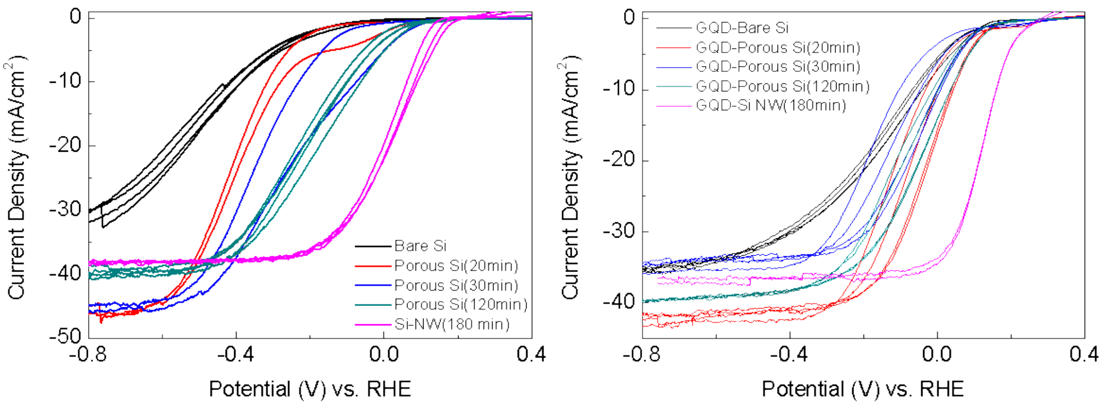

Figure S4. Photoelectrochemical performance of Si photocathode (a) Polarization curves of various Si electrodes without depositing any catalyst. Si nanowire were made by metal-catalyzed electroless method. Each of the etching time is 20 min, 30 min, 120 min, and 180 min. Each cyclic voltammetry was performed during 2 or 4 cycles at a scan rate of 5 mV/s. (b) Polarization curves of various Si electrodes deposited with N-GQSs catalyst.

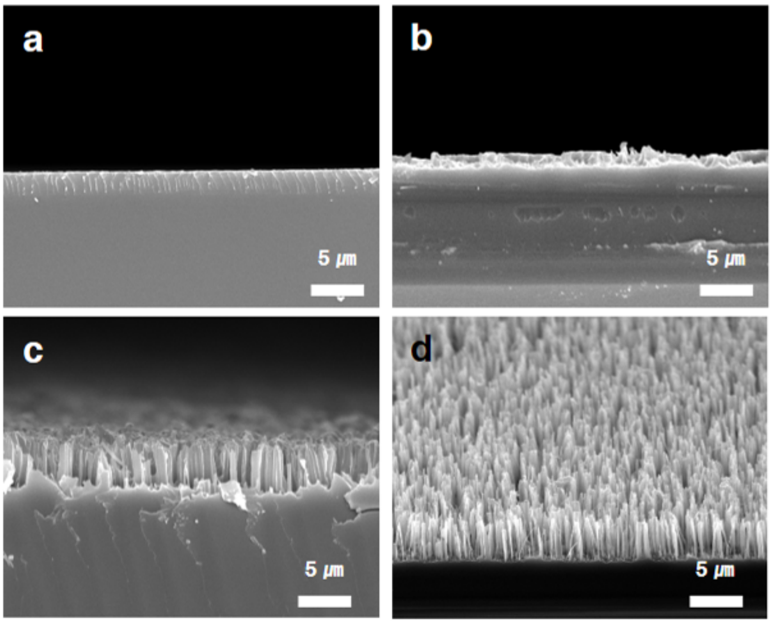

Figure S5. SEM images of cross-sectional views of p-type (100) Si wafers etched in 5 M HF and 0.015 M $AgNO_3$ solution at different etching times. The etching times are (a) 20 min, (b) 30 min, (c) 120 min, and (d) 180 min.

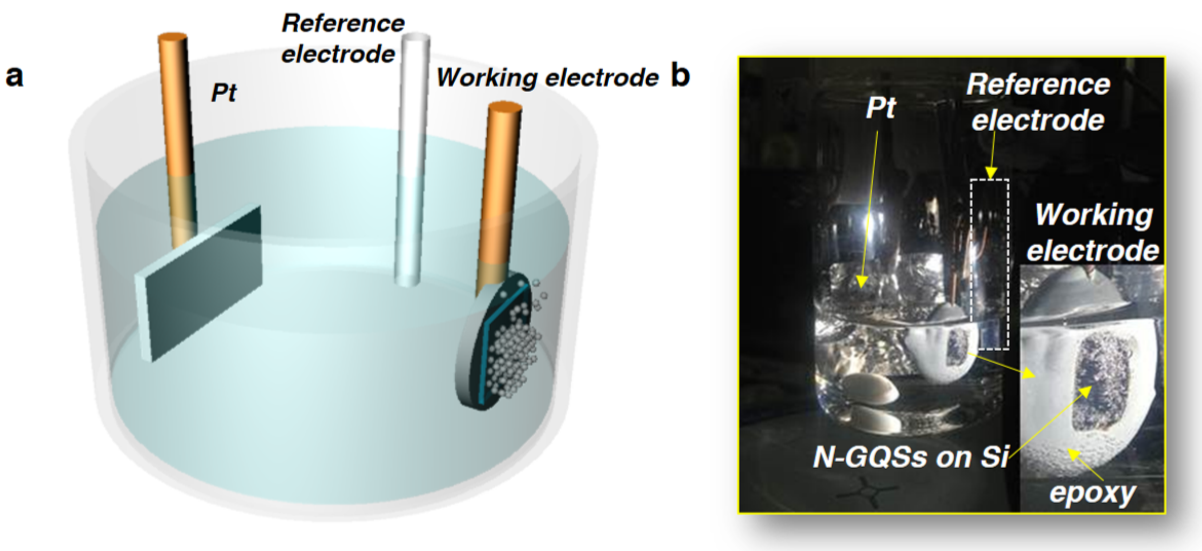

Figure S6. (a) Schematic illustration and photograph images of hydrogen evolution reaction on N-GQSs/Si photocathode.

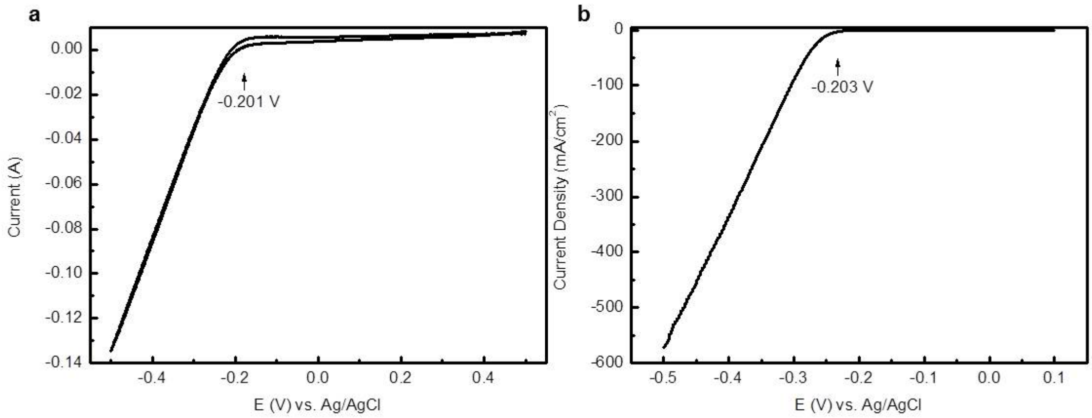

Figure S7. Calibration respect to RHE. Current vs. the applied potential respect to Ag/AgCl reference electrode with using (a) Pt foil for Si PEC cell experiment and **(b)** Pt wire as the counter electrode for rotating disk electrode (RDE) experiment.

Table S1. Summary of the experimental data of 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	Current density at reversible potential vs. RHE [mA/cm^{2}at 0 V vs. RHE]	ABPE[#] (%)
Under illumination (p type Si)	Planar Si	-0.17	-0.29	-0.42	0.34	0.02
	Si NW	0.17	0.12	0.09	21.61	0.91
	N-GQSs/ planar Si	0.13	0.03	-0.04	6.78	0.16
	N-GQSs/ Si NW	0.26	0.19	0.16	34.49	2.29
Under dark condition (n^+ type Si)	Planar Si	-0.63	-0.78	-0.85		
	Si NW	-0.42	-0.51	-0.56		
	N-GQSs/ planar Si	-0.44	-0.55	-0.62		
	N-GQSs/ Si NW	-0.37	-0.42	-0.45		
Photovoltage *	Planar Si	0.46				
	Si NW	0.59				
	N-GQSs/ planar Si	0.57				
	N-GQSs/ Si NW	0.63				
RDE analysis	Graphene/ GC	-0.20	-0.32	-0.37		
	N-GQSs/ GC	-0.11	-0.22	-0.25		
	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.

ABPE is the applied bias photon-to-current efficiency.

Table S2. Summary of the photoelectrochemical data of various catalysts on p-type Si electrodes.

Catalyst	Synthesis and Loading method	Electrolyte	Activity			Ref. (Year)
			Onset Potential vs. RHE (V)	ABPE (%)	E (V) at -5 mA/cm^2	
Planar Si (our study)						
without catalyst (bare)		1M $HClO_4$	-0.17	0.02	-0.42	
Graphene (Gr)	CVD grown graphene & transfer	1M $HClO_4$	0.01	0.04	-0.21	
N-doped graphene quantum sheets (N-GQSs)	CVD grown graphene, plasma treatment, GQSs solution & drop casting	1M $HClO_4$	0.12	0.16	-0.04	
Pt	Nanoparticle by metal catalyzed electroless method	1M $HClO_4$	0.24	1.19	0.11	
Reduced graphene oxide (rGO)	Hummers` method & drop casting	1M $HClO_4$	-0.01	0.03	-0.20	
Si nanowire(our study)						
bare		1M $HClO_4$	0.15	0.91	0.13	
rGO	Hummers` method & drop casting	1M $HClO_4$	0.18	0.77	0.13	
N-GQSs	CVD grown graphene, plasma treatment, GQSs solution & drop casting	1M $HClO_4$	0.26	2.29	0.19	
Pt	Nanoparticle by metal catalyzed electroless method	1M $HClO_4$	0.26	1.19	0.19	
Planar Si(Ref.)						
bare[1]		0.2 M potassium hydrogen phthalate (KHP) with 0.5 M K_2SO_4, buffered to pH 4.5 using KOH.	-0.29*	0.03	-0.423*	[1](2011)
Pt[1]	Nanoparticle by metal catalyzed electroless method		0.21*	1.1	0.15*	
rGO	Hummers` method & drop casting	H_2SO_4 solution containing 0.5 M K_2SO_4 (pH = 1.8)	-0.28*	~0*	-0.49*	[2](2013)
bare[2]		H_2SO_4 and 0.5 M K_2SO_4 (pH 1)	-0.42*	~0*	-0.55*	[3](2012)
Pt[2]	Nanoparticle by metal catalyzed		0.27*	~2.22*	0.2*	

	electroless method					
Pt[3]	Nanoparticle by metal catalyzed electroless method	0.5 M aq. K_2SO_4 adjusted to pH ~ 2 using H_2SO_4	0.25*	2.1	0.2*	[4](2011)
bare[4]		1M $HClO_4$	-0.5*	~0*	-0.07*	[5](2011)
Mo_3S_4	Molecular cluster synthesis & drop casting		0.1*	~0.2*	0.04*	
bare[5]		0.5M H_2SO_4	-0.36*	~0*	-0.54*	[6](2011)
Si nanowire(Ref.)						
bare[1]		0.2 M KHP with 0.5 M K_2SO_4, buffered to pH 4.5 using KOH.	0.03	0	N/A	[1](2011)
Pt[1]	Nanoparticle by metal catalyzed electroless method		0.23*	1	0.16*	
bare[2]	Nanoparticle by metal catalyzed electroless method	H_2SO_4 and 0.5 M K_2SO_4 (pH 1)	~-0.16*	~0*	~-0.3*	[3](2012)
Pt[2]			~0.39*	~2.1*	~0.33*	
Pt[3]	Nanoparticle by metal catalyzed electroless method	0.5 M aq. K_2SO_4 adjusted to pH ~ 2 using H_2SO_4	0.13*	0.21	0.04*	[4](2011)
bare[4]		1M $HClO_4$	-0.08*	~0*	-0.22*	[5](2011)
Mo_3S_4	Molecular cluster synthesis & drop casting		0.12*	~0.38*	0.08*	
rGO	Hummers` method & drop casting	H_2SO_4 solution containing 0.5 M K_2SO_4 (pH = 1.8)	0.12*	0.15*	-0.04*	[2](2013)

*: Values were measured and extrapolated by our group referring to the figures and data from the references.

The onset potential is defined as the potential at a photocurrent density of -1 mA/cm^2.

Table S3. Summary of the electrochemical data of RDE system for various catalysts on GC electrodes.

Catalyst/Substrate (adhesive)	Loading method	Electrolyte	Activity			Ref. (Year)
			Tafel Slope (mV/dec)	Exchange current J_0 (A/cm^2)	Exchange current $\log(J_0)$ (A/cm^2)	
Our Study						
Monolayer Graphene	CVD grown graphene	1M $HClO_4$	74	2.7E-6	-5.57	
N-GQSs	CVD grown graphene and plasma treatment	1M $HClO_4$	45	7.1E-5	-4.15	
Pt	Annealing from mixed precursors	1M $HClO_4$	42	3.86E-4	-3.41	
Carbon based catalyst (Ref.)						
N doped Graphene	Annealing from mixed precursors	0.5M H_2SO_4	116	7.04E-8	-7.15	[7](2014)
P doped Graphene	Annealing from mixed precursors	0.5M H_2SO_4	133	8.97E-9	-8.05	[7](2014)
N, P doped Graphene	Annealing from mixed precursors	0.5M H_2SO_4	91	2.4E-7	-6.62	[7](2014)
graphitic-C_3N_4@N-graphene/glassy carbon (Nafion)	Exfoliation & Polycondensation	0.5M H_2SO_4	51.5	3.5E-7	-6.46	[8](2014)

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