Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (ESI)

Pyrazine-incorporated graphdiyne nanofilm as a metal-free electrocatalyst for hydrogen evolution reaction

Ryota Sakamoto,*[a,b] Ryo Shiotsuki,[a] Keisuke Wada,[a] Naoya Fukui,[a] Hiroaki Maeda,[a] Joe Komeda,[a] Ryosuke Sekine,[a] Koji Harano,[a] and Hiroshi Nishihara[a]

a. Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

b. JST-PRESTO, 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

sakamoto@chem.s.u-tokyo.ac.jp

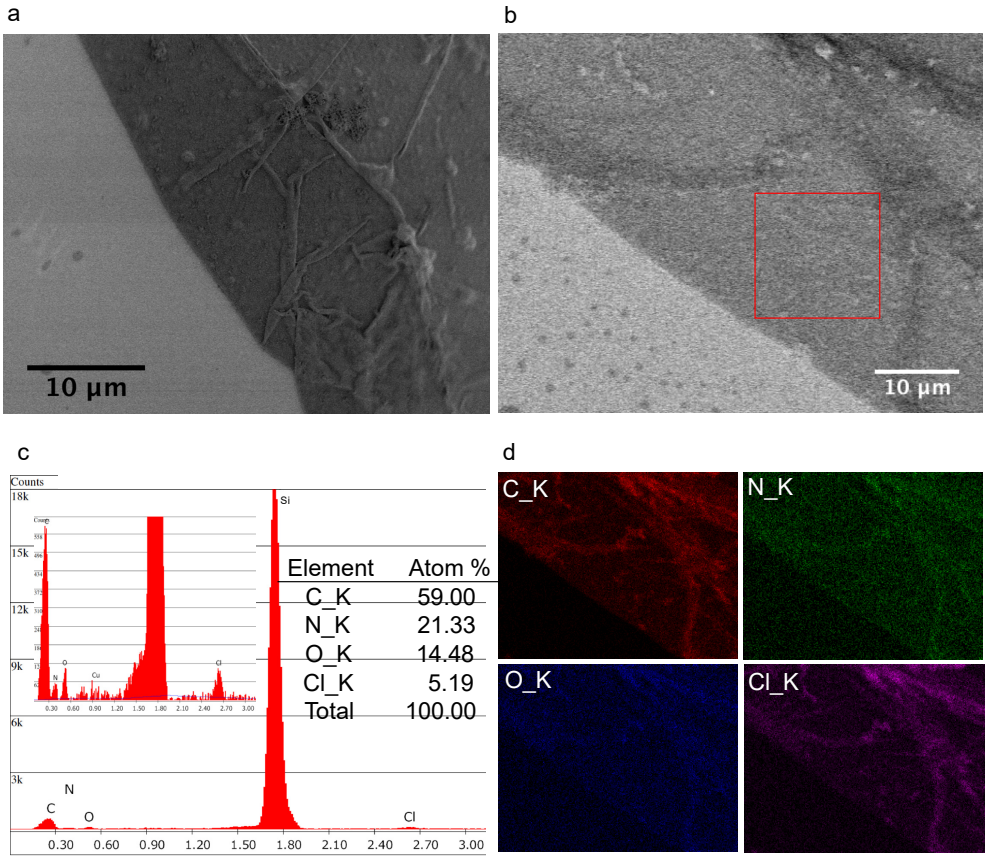


Fig. S1 (a,b) SEM image of a **PR-GDY** nanofilm on a Si/SiO_2 substrate. (c,d) EDX spectrum [red square region in (b)] and mapping.

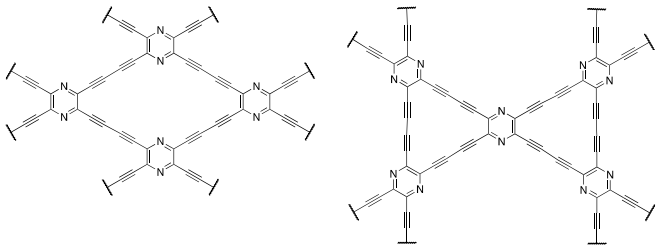


Fig. S2 Two possible 2D lattices for **PR-GDY**.

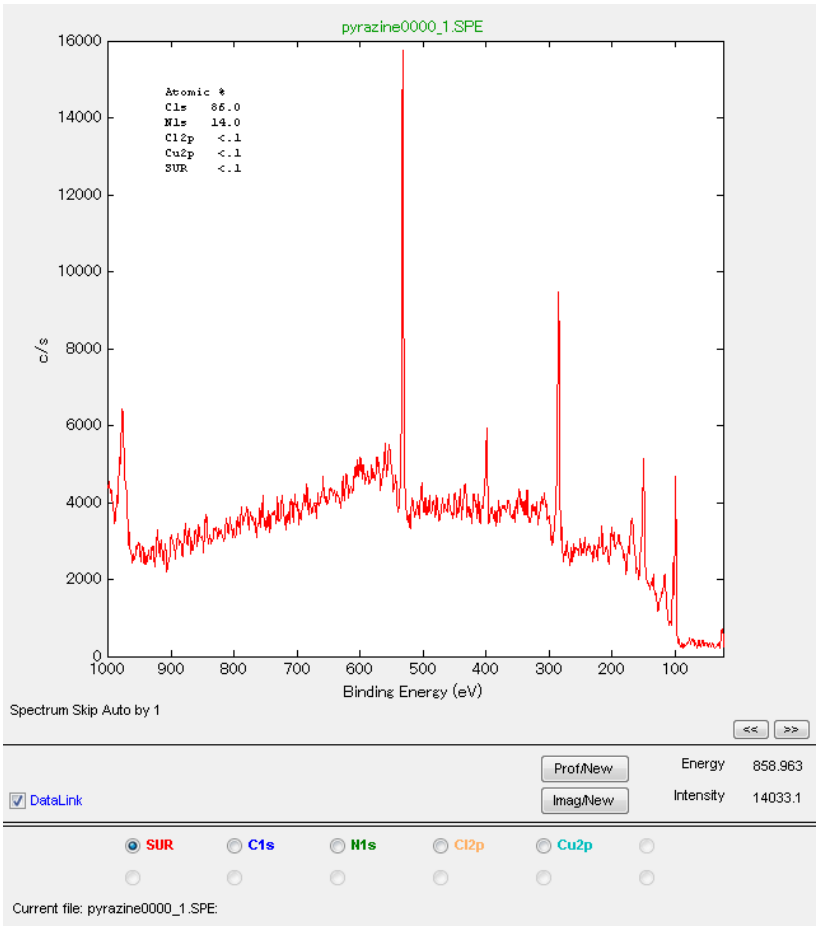


Fig. S3 Quantification of the C/N ratio of **PR-GDY** in XPS.

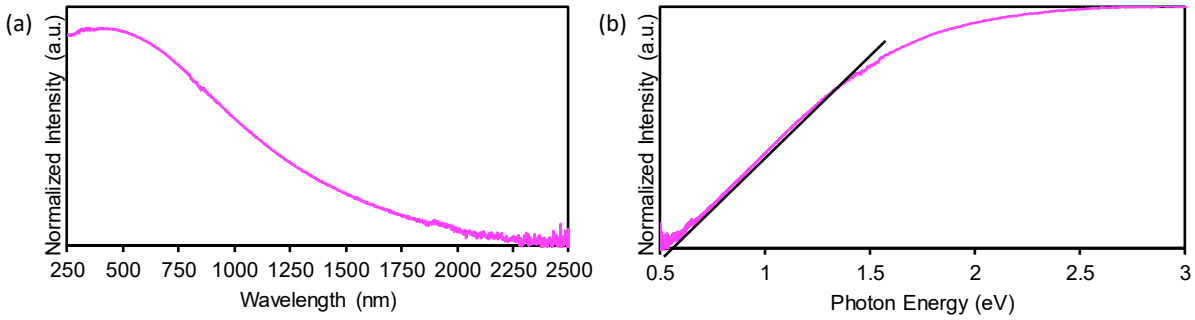


Fig. S4 (a,b) Absorption spectra of **PR-GDY** (as a pellet; magenta solid lines) with horizontal axes in nm and eV, respectively.

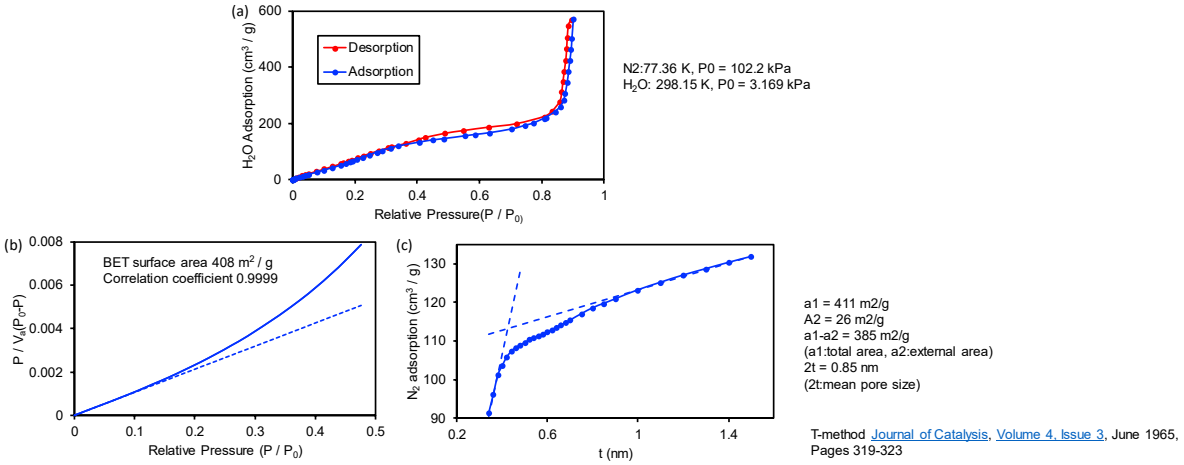
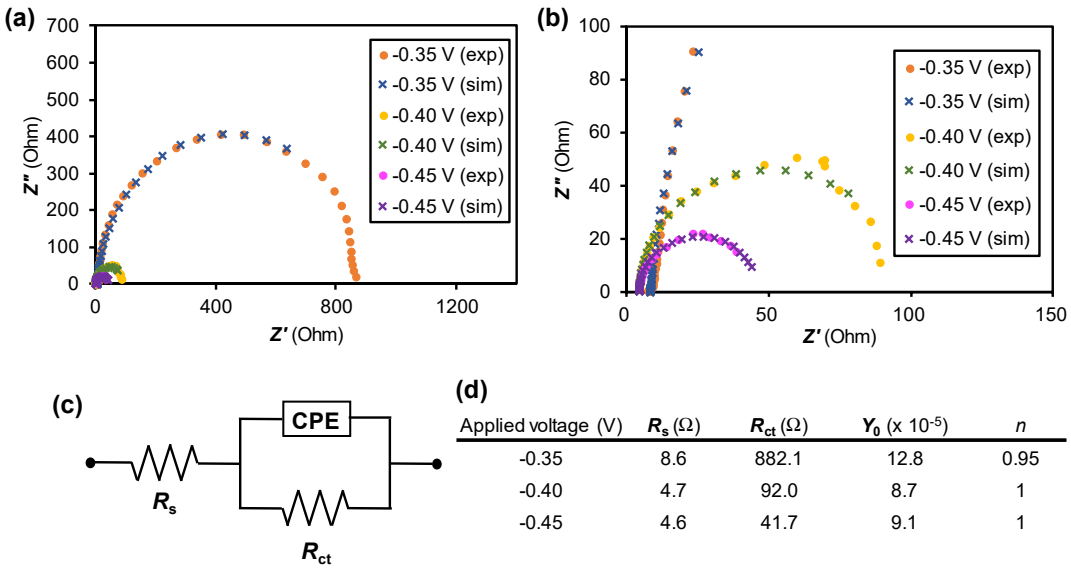


Fig. S5 (a) H_2O adsorption (blue symbols) and desorption (red symbols) isotherms at 298 K for **TP-GDY**. (b) BET analysis for the N_2 isotherm. (c) t-plot for the N_2 isotherm.



(d)

Applied voltage (V)	R_s (Ω)	R_{ct} (Ω)	Y_0 (x 10^{-5})	n
-0.35	8.6	882.1	12.8	0.95
-0.40	4.7	92.0	8.7	1
-0.45	4.6	41.7	9.1	1

Fig. S6 (a) Nyquist plots for **TP-GDY** on GC in 0.5M H_2SO_4 at various electrode potentials. (b) Close-up of the Nyquist plots at around the origin. (c) Equivalent circuit for the simulation of the Nyquist plots. $\boldsymbol{R_{ct}}$ and $\boldsymbol{R_s}$ denote charge transfer and internal resistances, respectively, while CPE indicates a constant phase element, the impedance ($\boldsymbol{Z_{CPE}}$) of which is represented using equation $\boldsymbol{Z_{CPE}} = 1 / (j\omega)^n \boldsymbol{Y_0}$, where j, ω, n, $\boldsymbol{Y_0}$ are the imaginary unit, frequency of the alternating current, CPE exponent and constant, respectively. (d) Parameters extracted from the Nyquist plot simulation.

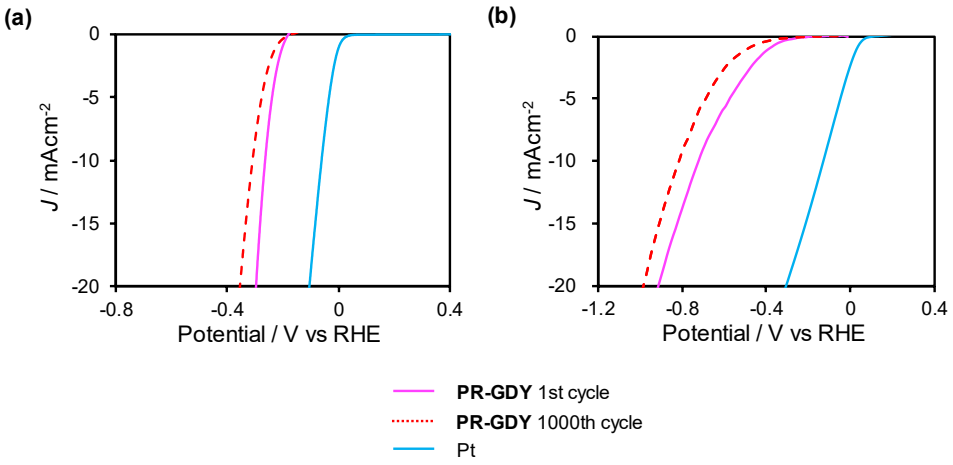


Fig. S7 (a,b) Linear sweep voltammograms (1st and 1000th sweeps) for GC modified with **PR-GDY** in (a) 0.5 M H_2SO_4 and (b) 0.1M $NaHCO_3$ + 0.1M Na_2CO_3.