

Self-assembly of guanosine into carbon-based multilayer materials

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Material preparation: 3.0 g guanosine was added to 6 mL ultrapure water and 0.3 M KCl solution, respectively, and the above solution was poured into 50 mL polytetrafluoroethylene lining, and then the lining was put into the hydrothermal reactor and reacted in the oven at 180 °C for 12 h. At the end of the reaction for 12 h, the hydrothermal kettle was cooled to room temperature, the lining was removed, and the reactants were filtered by deionized water through a buchner funnel until the filtrate was clarified. The filtered samples were collected and dried in an oven at 80 °C. After drying for 24 h, the samples were completely dried. After cooling, the samples were ground to obtain samples.

In order to improve the graphitization degree of the materials, the four materials were carbonized at high temperature. 1.0 g of G-180 and K-G-180 were respectively placed in a 30 mL ceramic crucible. The ceramic crucible was placed in the tubular furnace, heated to 1000 °C at the rate of 10 °C min⁻¹ in the nitrogen atmosphere, and maintained at 1000 °C for 2 h. After cooling, the sample was taken out and ground. The ground sample was the required carbon material. The samples treated by G-180 and K-G-180 are denoted as G-1000 and K-G-1000, respectively.

Taking 0.3 g G-1000 and K-G-1000 as carriers, M-G-1000 loaded Rh nanoparticles were prepared by impregnation method. 42 mg of 10 wt% Rh(NO₃)₃ was prepared with 0.1 M dilute nitric acid to form Rh(NO₃)₃ solution. The Rh(NO₃)₃ solution obtained from the configuration was dropped on the above carriers one by one, fully moistened, placed in the ultrasonic cleaning machine for 1 min, and placed in a ventilated place for natural drying. After being completely dried, the dried material is ground and then placed in a porcelain boat. It is heated in a tube furnace at a rate of 5

$^{\circ}\text{C min}^{-1}$ in 10% H_2 atmosphere to 300 $^{\circ}\text{C}$, and reduced at 300 $^{\circ}\text{C}$ for 2 h. After cooling, the sample is taken out and grinded. Samples loaded with G-1000 and K-G-1000 as carriers were G-1000-Rh and K-G-1000-Rh, respectively.

Electrochemical test: The three-electrode system was used for HER testing, with 4.0 mm glassy carbon electrode as the working electrode, The calibration of Ag/AgCl reference electrode was performed in a standard three-electrode system with platinum as both the working and counter electrodes. 1.0 M KOH (13.6) and 0.5 M H_2SO_4 (0.3) electrolytes were saturated with high purity H_2 . The CV curve was recorded at a scan rate 1 mV s^{-1} near the open-circuit voltage. The average value of the two electrode potentials corresponding to the zero current was taken as the thermodynamic potential for the hydrogen electrode reactions. So, the reference electrode calibrations are: in 1.0 M KOH, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.99 \text{ V}$; in 0.5 M H_2SO_4 , $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.26 \text{ V}$, respectively. The sample preparation method was as follows: 3.0 mg sample was weighed and dispersed in 300 μL absolute ethanol and 100 μL deionized water, then 40 μL Nafion solution of 5 wt% was added, and then ultrasonic treatment was carried out for 15 min. Then 5.5 μL of the mixed solution was evenly added to the surface of the working electrode, and then placed in the drying oven for drying. Then the loading capacity of the active material on the working electrode is about $0.3 \text{ mg}\cdot\text{cm}^{-1}$.

Polarization curve test: Polarization curves were tested using 1.0 M KOH (pH=13.6) and 0.5 M H_2SO_4 (pH=0.3) as electrolytes, and linear scanning voltammetry was used at a scanning rate of $5 \text{ mV}\cdot\text{s}^{-1}$. The LSV curves were obtained for 95% iR compensation. The solution resistance required for iR drop compensation is measured by AC impedance method.

Tafel curve test: The Tafel equation, $\eta = a + b \lg j$, describes the semilog relationship between the overpotential (η) of hydrogen evolution reaction and the current density (j) of the reaction. Therefore, through the measurement of the polarization curve, we took the current density as the absciss coordinate and the overpotential as the ordinate coordinate to make the curve to get the Tafel curve, and calculated the slope of the curve to infer the possible reaction process.

Electrochemical Active Area Test (ESCA): The electrochemical active area was measured by cyclic voltammetry in 1 M KOH solution to calculate the double layer

capacitance value. The CV curves of the samples at different scanning rates were measured by gradually increasing the scanning rate from $20 \text{ mV}\cdot\text{s}^{-1}$ to $200 \text{ mV}\cdot\text{s}^{-1}$.

Electrochemical AC Impedance spectroscopy (EIS): The surface electron transfer resistance of the characterized material was measured by AC impedance method in 1 M KOH solution. The overpotential in the test was set to 100 mV, with a frequency range from 100,000 Hz in the high frequency region to 0.01 Hz in the low frequency region and an amplitude of 10 mV.

Raman characterization: Raman is an efficient method to identify and quantify defective and graphitic structure. In Raman spectroscopy, the peaks can be deconvoluted into D1 ($\sim 1350 \text{ cm}^{-1}$), D2 ($\sim 1620 \text{ cm}^{-1}$), D3 ($\sim 1500 \text{ cm}^{-1}$), D4 ($\sim 1200 \text{ cm}^{-1}$) and G ($\sim 1580 \text{ cm}^{-1}$) regions, representing the disordered graphite microcrystalline edge, the disordered graphitic microcrystalline, amorphous carbon, ionic impurity and ideal graphitic structure, and the integrated intensity ratio of D1 band and G band is used to evaluate the degree of defects (W, Qi et al, Carbon, 2019, 143, 915-936).

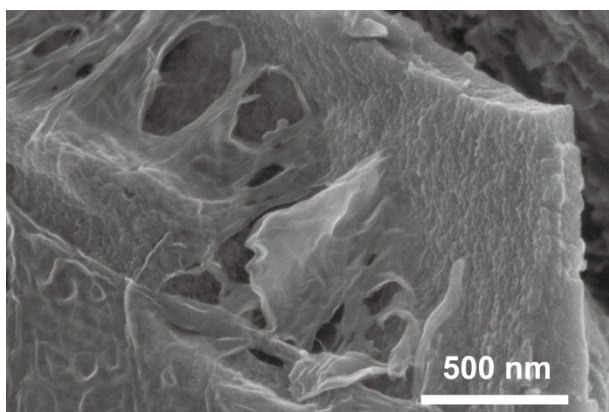


Figure S1. SEM images of G-1000

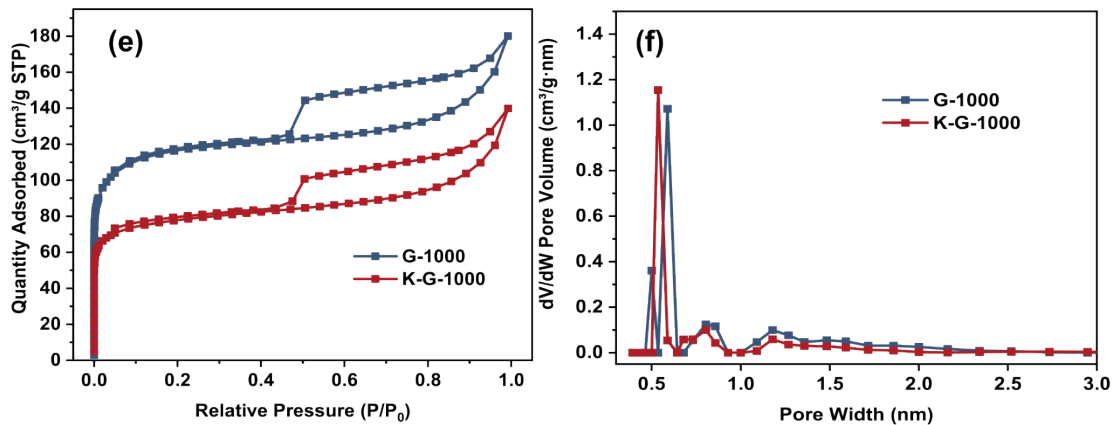


Figure S2. (a) N_2 adsorption- desorption isotherms of K-G-1000 and G-1000; (b) Pore size distribution of K-G-1000 and G-1000.

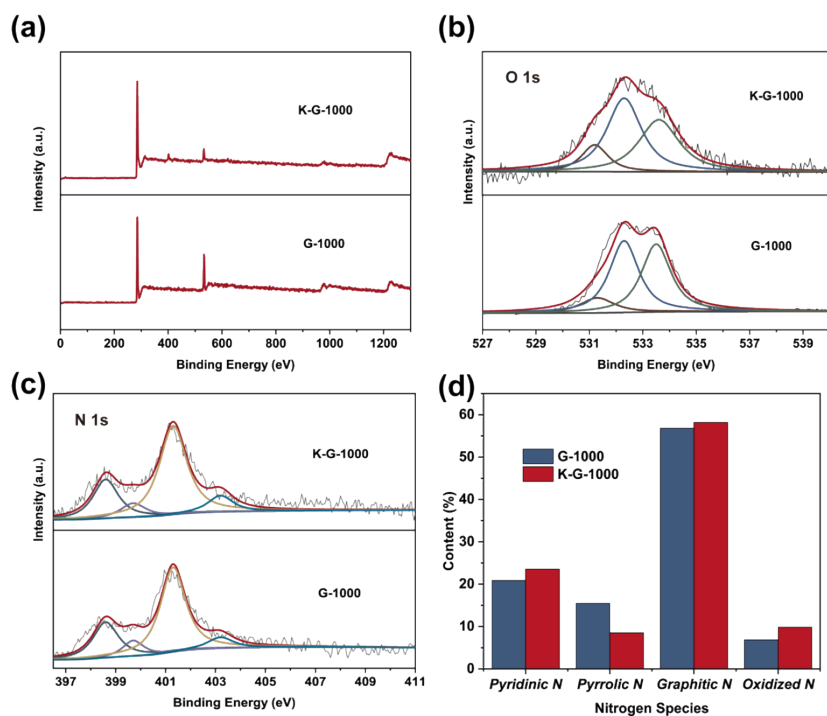


Figure S3. XPS spectra analysis of K-G-1000 and G-1000 (a) survey; (b)-(c): high resolution spectra of O 1s and N 1s; (d) distribution of nitrogen species.

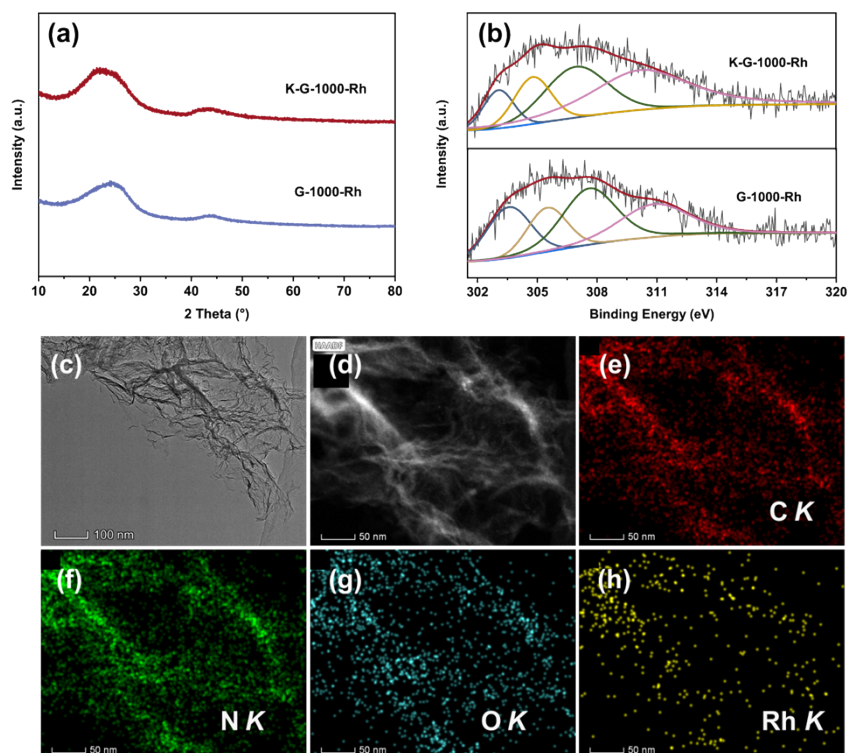


Figure S4. (a) XRD patterns of K-G-1000-Rh and G-1000-Rh; (b) high resolution spectra of Rh 3d; (c) TEM images of K-G-1000-Rh; (d-h) HAADF-STEM image and mapping of C, N, O and Rh.

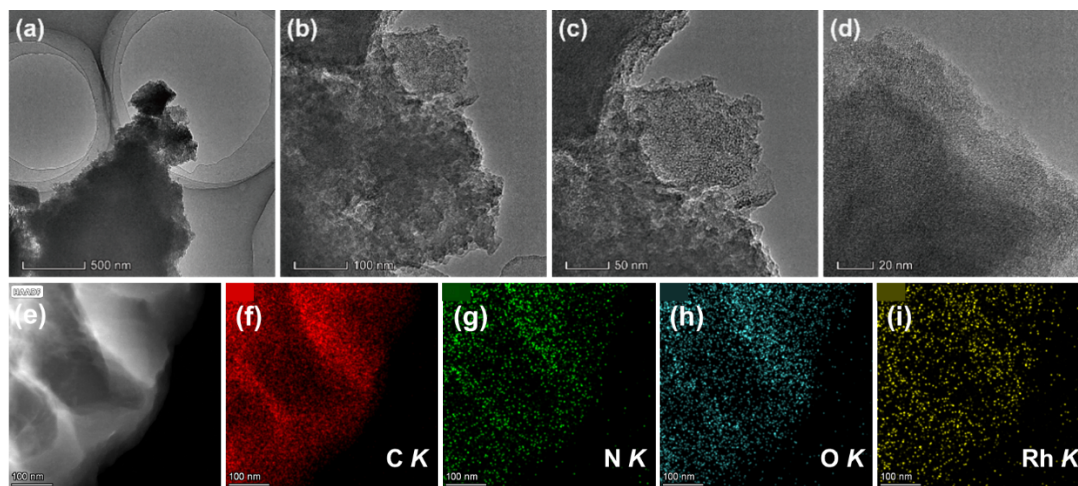


Figure S5. Characterization by transmission electron microscopy of G-1000-Rh (a-b) TEM images of G-1000-Rh; (c-d) HRTEM images of G-1000-Rh; (e-i) HAADF-STEM images of G-1000-Rh and EDS elemental of C, N, O, Rh mapping correspondingly.

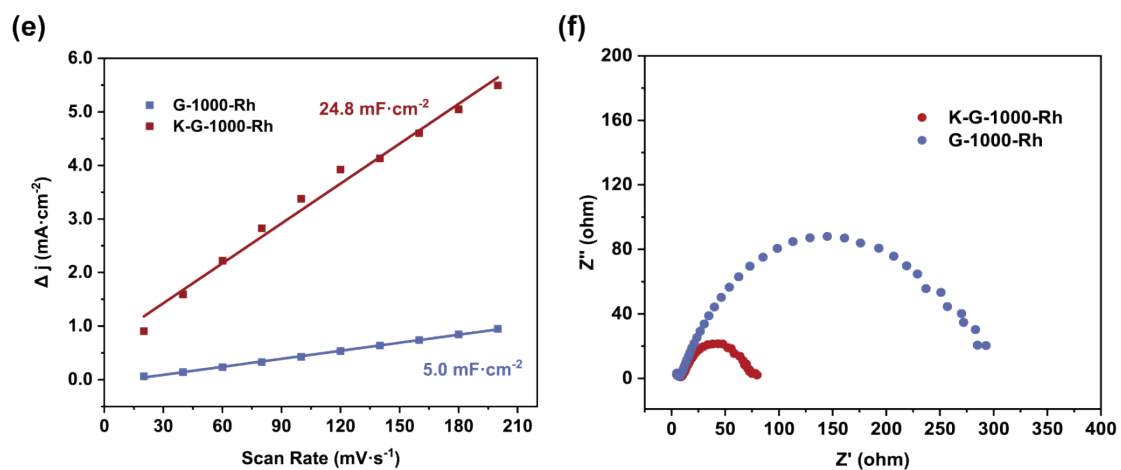


Figure S6. (a) Scan Rate-Current density plotted curve; (b) Impedance diagram.

Table S1. Textural properties of G-1000 and K-G-1000.

Samples	BET Surface Area (m ² ·g ⁻¹)	V _{total} (m ³ ·g ⁻¹)	V _{meso} (m ³ ·g ⁻¹)	V _{micro} (m ³ ·g ⁻¹)
G-1000	353.24	0.21	0.14	0.06
K-G-1000	237.60	0.15	0.09	0.03

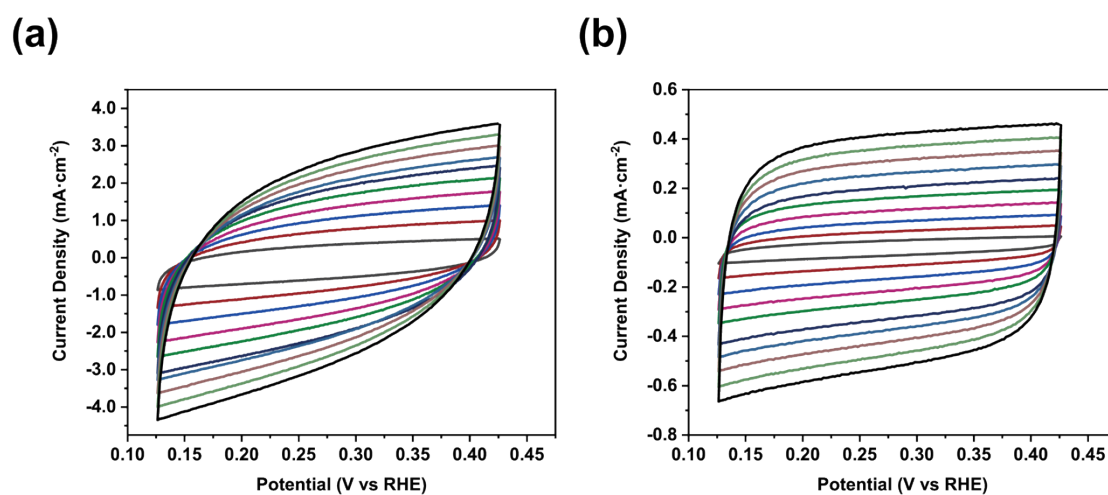


Figure S7. The cyclic voltammety curve of M-G-1000-Rh in the sweep speed range of 20-200 mV·s⁻¹ (a) K-G-1000-Rh; (b) G-1000-Rh.

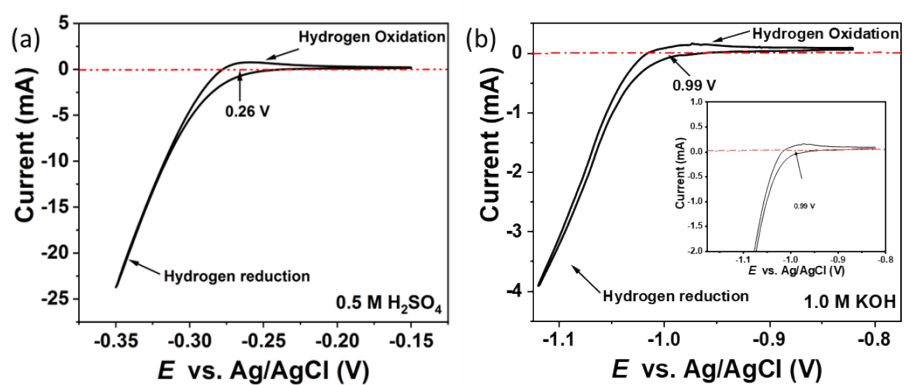


Fig. S8 Calibration of the Ag/AgCl reference electrode in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH.

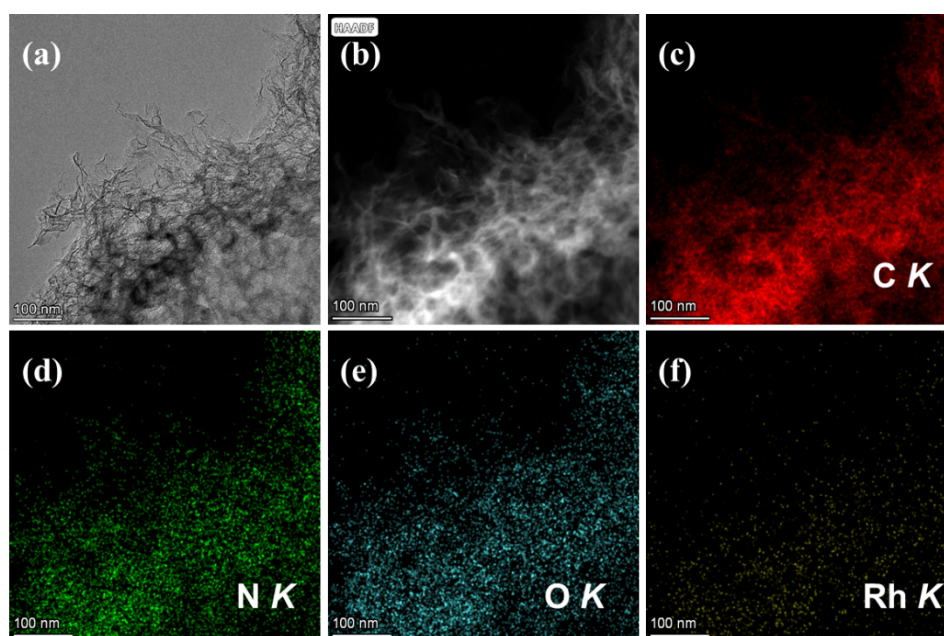


Fig.S9 (a) TEM image and (d-h) HAADF-STEM image and mapping of C, N, O and Rh of K-G-1000-Rh after the electrochemical test.