Electronic supplementary information (ESI)

Space-confined synthesis of multilayer Cu-N-doped graphene nanosheets for efficient oxygen electroreduction

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Experimental materials

K10 montmorillonite clay, 2,2'-bipyridine (99.0%), copper chloride dehydrate (≥99.0%), sodium chloride (≥99.5%), hydrofluoric acid (≥40 wt%) and anhydrous ethanol (≥99.7%) were purchased from Sinopharm Chemical Reagent Limited Corporation, China. All reagents were of analytical grades and were used as received without further purification. Deionized water was used in the preparation process.

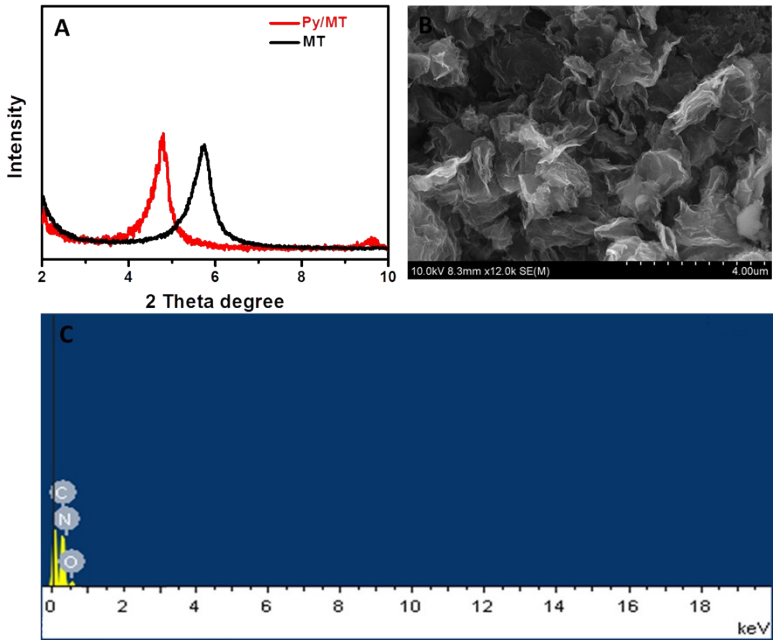

Figure S1 (A) XRD patterns of MT (black) and Py/MT intercalation compounds (red). (B) SEM image of the N-GR-800. (C) The SEM-EDS spectrum for the prepared N-GR-800.

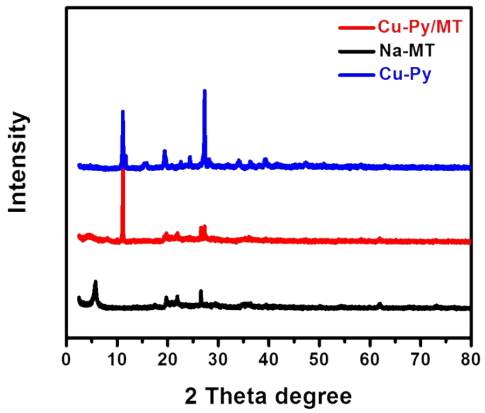

Figure S2 XRD patterns of Na-MT (black), Cu-Py/MT intercalation compounds (red) and Cu-Py (blue).

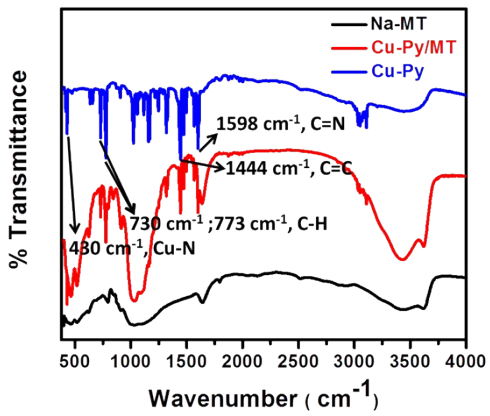

Figure S3 The FT-IR spectrums of Cu-Py (blue), Cu-Py/MT intercalation compounds (red) and Na-MT (black).

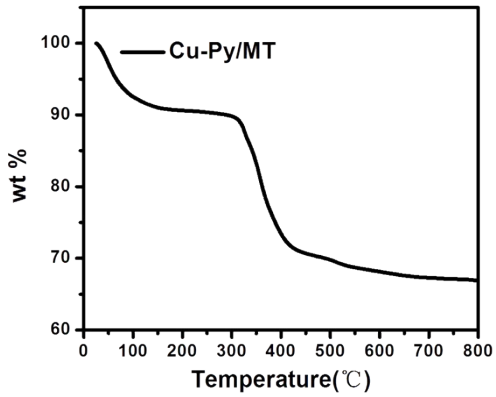

Figure S4 TGA plot of Cu-Py/MT in air atmosphere.

It can be seen from this TGA plot, a small weight loss of ~10 wt% between 25-250 °C corresponding to the loss of the adsorbed H_2O in the interlayer of MT, followed by ~21 wt% weight loss during the temperature range of 250-550 °C corresponding to the pyrolysis of Cu-Py and no further weight loss when temperature reached 800 °C, which stands for the remaining copper oxides and MT templates. The content of Cu-Py in Cu-Py/MT can be estimated by the equation below:

Actual content of Cu-Py in Cu-Py/MT (wt %) = N-C (wt %) + Cu (wt %)

The weight loss (~21 wt%) during the temperature range of 250-550 °C is the weight percentage of N-C in Cu-Py/MT that are easy to form gases when pyrolyzed in air atmosphere.

The weight percentage of Cu can be estimated roughly by the following formula:

$$\mathrm{Cu\ (wt\%)} = \frac{21\ \mathrm{wt\%}}{2 \times \mathrm{M\ (Py)}} \times \mathrm{M\ (Cu)} = 4.3\ \mathrm{wt\%}$$

In the formula above, M (Cu) is the relative atomic mass of copper, while M (Py) refers to the relative molecule mass of 2,2'-bipyridine.

Therefore, the content of Cu-Py in Cu-Py/MT is about 25.3 wt%, which is calculated from the following formula:

Actual content of Cu-Py in Cu-Py/MT (wt %) = N-C (wt %) + Cu (wt %)

=21 wt% + 4.3 wt% = 25.3 wt%

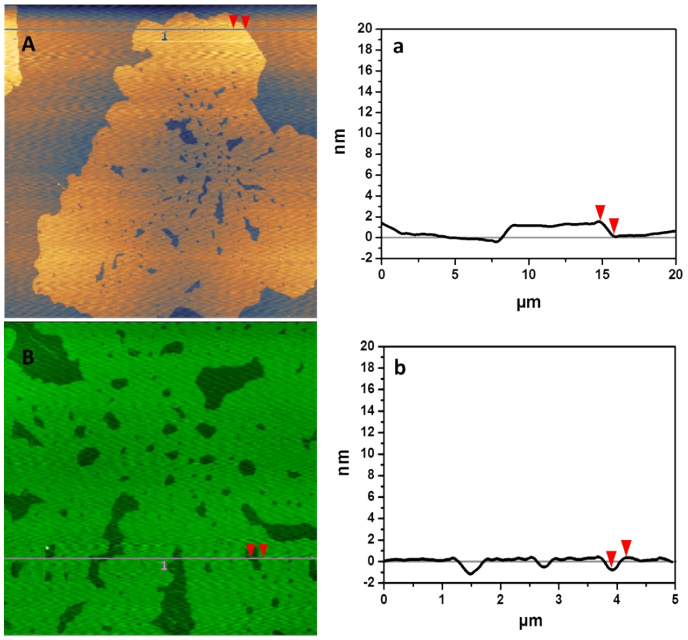

Figure S5 The typical tapping mode AFM images of the prepared Cu-N-GR-800 deposited on a mica substrate in different regions (A and B) and the corresponding height profiles shown in (a) and (b).

The ICP measurements for the content of Cu in Cu-N-GR-800

The content of Cu in Cu-N-GR-800 was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II). By heating treatment of Cu-N-GR-800 at 600 °C for 3h with a heating rate of 3 °C min^{-1} in air atmosphere, residual species CuO were obtained and then dissolved in hydrochloric acid solution. Through ICP test, the weight percentage of Cu in Cu-N-GR-800 is 3.6 wt%.

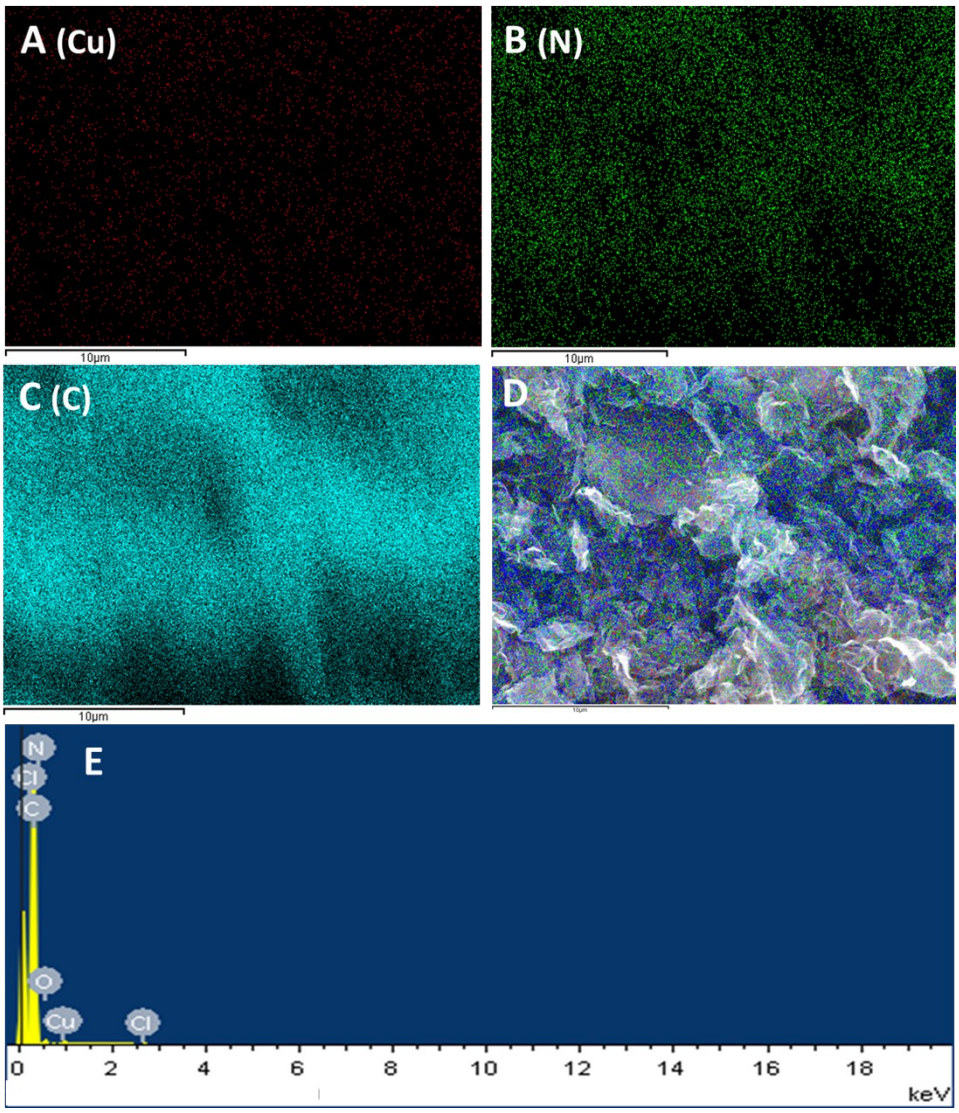

Figure S6 The SEM-EDS mapping images for Cu (A), N (B), C (C) and total element mapping image for Cu, N, C, O and Cl (D), and the SEM EDS spectrum (E) for the prepared Cu-N-GR-800.

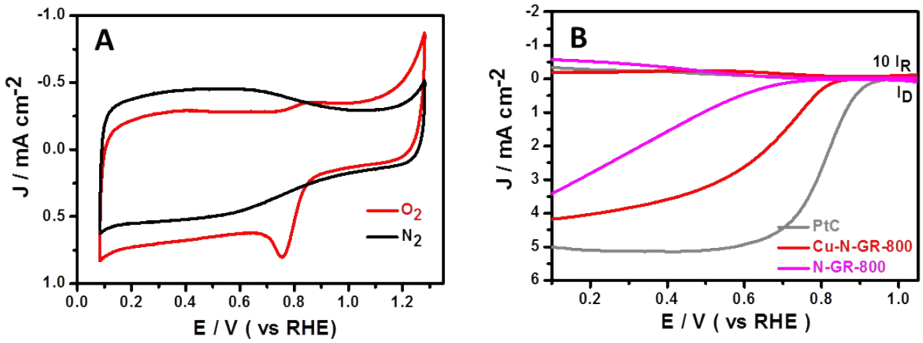

Figure S7 CV curve of Cu-N-GR-800 in N_2-saturated or O_2-saturated 0.1 M $HClO_4$; (B) RRDE polarization curves for Cu-N-GR-800, N-GR-800 and commercial Pt/C (20 wt%) in O_2-saturated 0.1 M $HClO_4$ at a rotation rate of 1600 rpm. The loading amount of catalysts on the electrode is 0.48 mg/cm^2 for Cu–N–GR-800 and N-GR-800, and 0.1 mg/cm^2 for Pt/C electrode. For all the measurements, the scan rate is 5 mV/s.

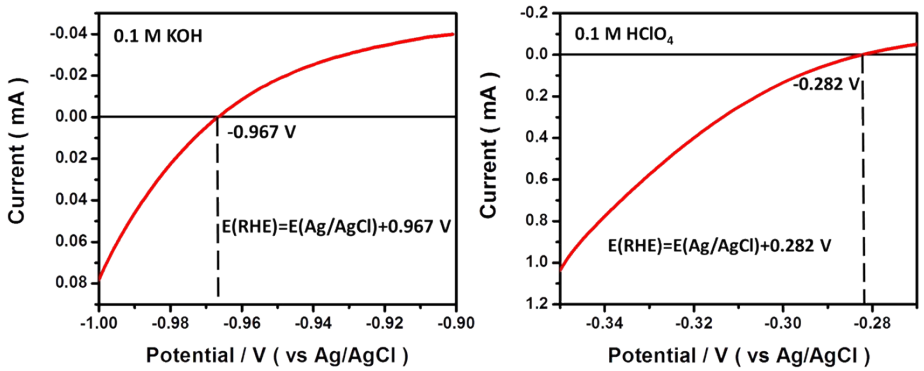

Figure S8 Calibration to reversible hydrogen electrode (RHE).

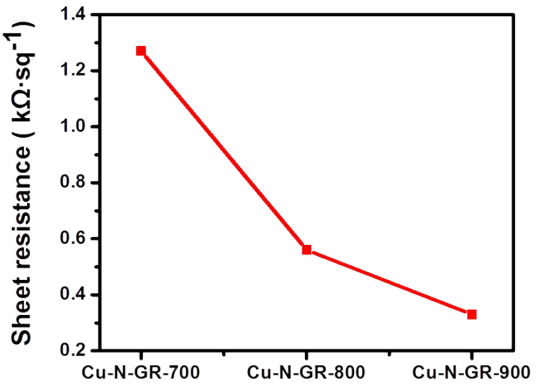

Figure S9 Sheet resistance of the prepared Cu-N-GR nanosheets at different temperatures.

Table S1 Fitting results from EIS experiments.

	R_s (Ω)	R_{ct} (Ω·cm^2)	W_s (Ω·cm^2)
Cu-N-GR-700	10.2	30.93	116.7
Cu-N-GR-800	9.38	20.30	30.54
Cu-N-GR-900	8.88	12.79	296.3