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# N-doping of graphene: toward a long-term corrosion protection of Cu†

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†Electronic supplementary information (ESI) available: AFM and TEM images of NG3 film; LEIS maps of PG- and NG-coated Cu foils; AFM images of PG- and NG-coated Cu foils, LEIS maps of bare Cu; Optical images of PG- and NG-coated Cu foils; Surface resistivity of PG and NG films; Raman mapping of $Cu_2O$ peak intensity; XPS spectra of Cu 2p and O 1s; Optical images of PG- and NG-coated Cu foils after one month and 6 months of storage in drying oven; Raman spectra of PG- and NG-coated Cu foils after 6 months of storage in drying oven.

The as-grown NG3 film was transferred onto a 300 nm thick $SiO_2$/Si wafer and a TEM grid via the PMMA-assisted method,[49] respectively, as shown in Fig. S1. AFM image shows the distinct contrast between NG3 film and $SiO_2$ substrate as well as some residual PMMA that can also be observed in TEM image. In addition to PMMA particles, many hexagon micrometer-size defects are formed for NG3 film when $NH_3$ pressure exceeds 2 sccm, leading to the discontinuity and nonuniformity of NG3 film.

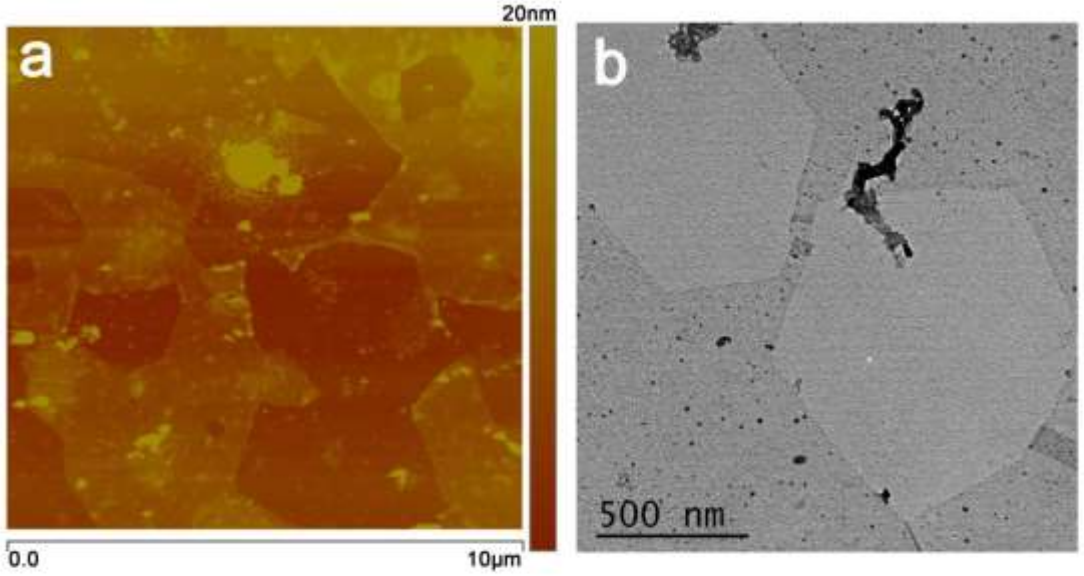

**Fig. S1** (a) AFM image of NG3 film transferred on $SiO_2$/Si and (b) TEM micrograph of NG3 film: the hexagon defects are clearly visible.

Fig. S2 shows the LEIS maps of PG- and NG-coated Cu foils tested at other three random locations for each sample. Different colors of the domains correspond to the different impedance values. The variation in LEIS maps obtained from different locations at the same sample is slightly, suggesting that the uniformity and reliability of PG, NG1 and NG2 films. But the variation in LEIS maps obtained from different locations for NG3-coated Cu foil is larger than other samples due to the discontinuity and nonuniformity of NG3 film. From the LEIS results in Fig. S2, the impedance values of most area for NG1- and NG2-coated Cu foils are higher than those of PG-coated, suggesting the better corrosion resistance of NG1 and NG2 films.

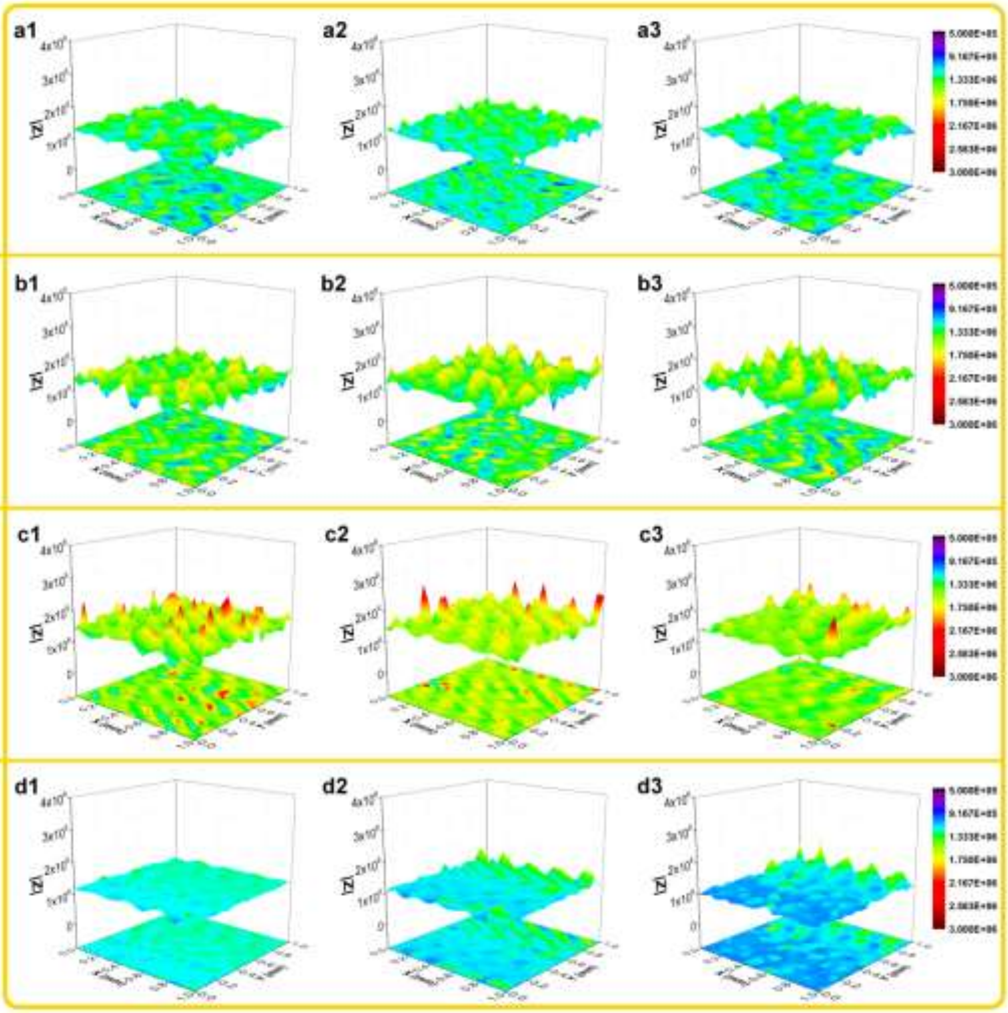

**Fig. S2** LEIS maps of PG and NG-coated Cu foils at different locations for each sample.

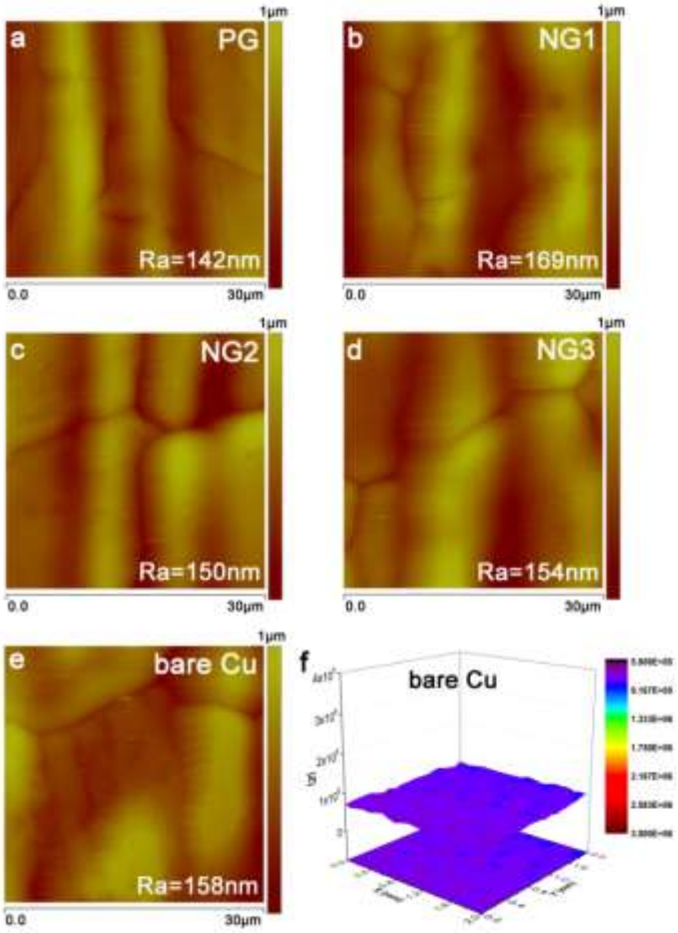

**Fig. S3** (a) AFM images of PG- and NG-coated Cu foil and the corresponding surface roughness. (e) AFM image of bare Cu the corresponding surface roughness. (f) LEIS maps of bare Cu.

Fig. S4 are representative optical images of the as-prepared PG- and NG-coated Cu foils, showing uniformly colored and highly reflective surfaces. These indicate that all the as-prepared samples are free of oxides at the initial stage of the corrosion test.

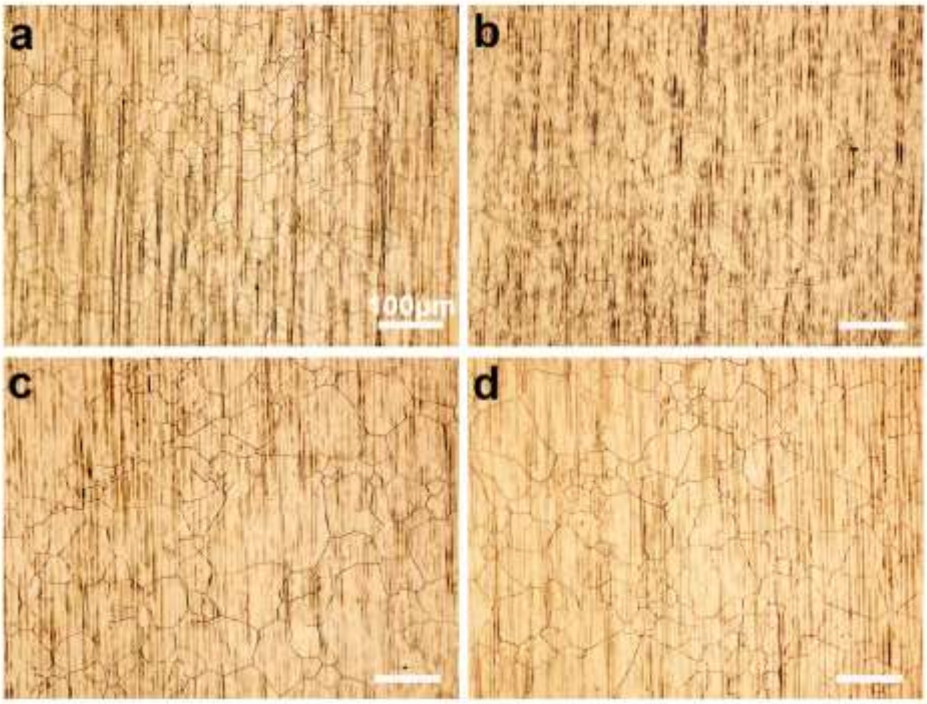

**Fig. S4** (a-d) Optical images of as-prepared PG-, NG1-, NG2- and NG3-coated Cu foils, respectively. Scale bars are 100 μm.

The PG and NG films were coated with poly (methyl methacrylate) (PMMA) and then transferred to a quartz plate under the same conditions. The sheet resistance of samples was measured by a Hall effect measurement system (Swin Hall 8800) and the same sample was tested for 3~5 times to ensure reliability. As shown in Fig. S5, the sheet resistance of PG, NG1, NG2, and NG3 is about 1.8, 7.2, 5.8 and 16.2 kΩ sq$^{-1}$, respectively. All NG films present higher sheet resistance than PG film, suggesting that the introduction of N atoms (acting as scattering centers) into the graphene lattice causes the decrease of the conductivity.[32,34]

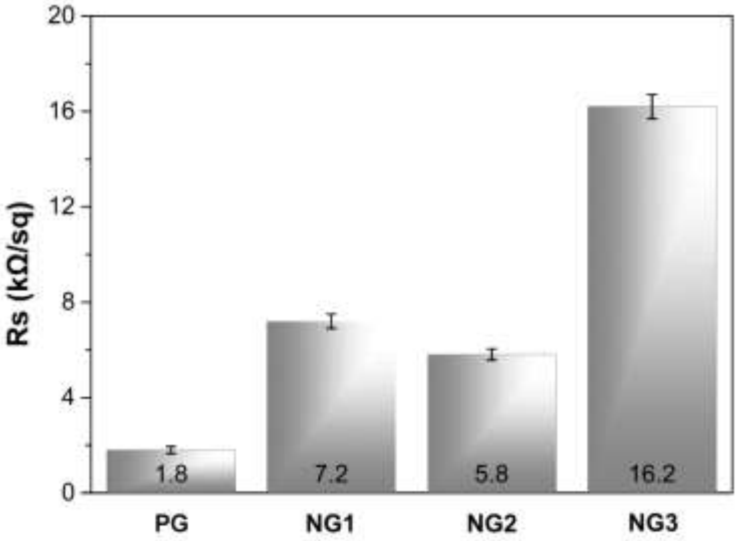

**Fig. S5** Surface resistivity of PG and NG films transferred on quartz plate.

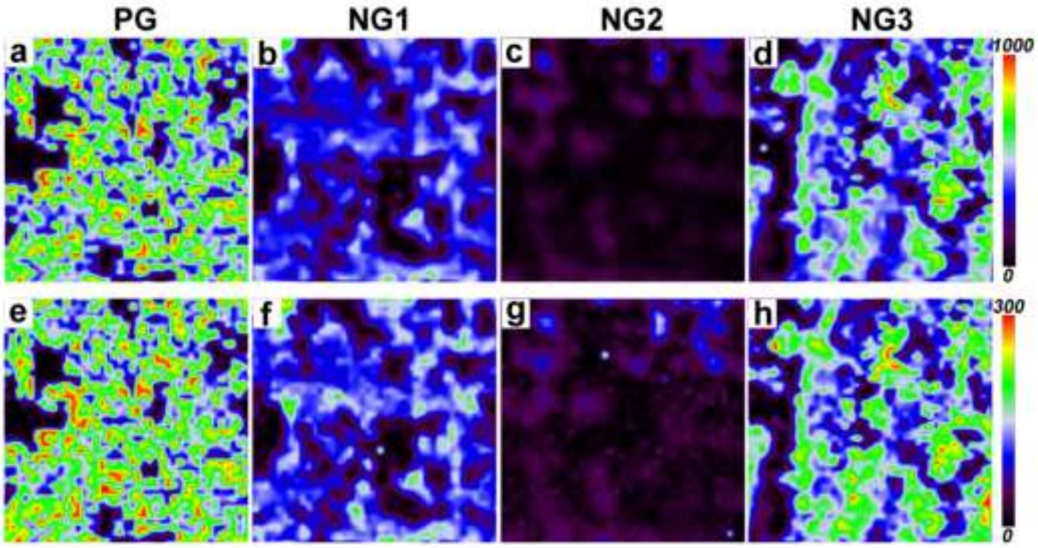

**Fig. S6** Raman mapping (selected area of 40×40 μm$^2$) of the $Cu_2O$ peak intensity at (a-d) 218 cm$^{-1}$ and (e-h) 632 cm$^{-1}$ for PG- and NG-coated Cu foils, respectively.

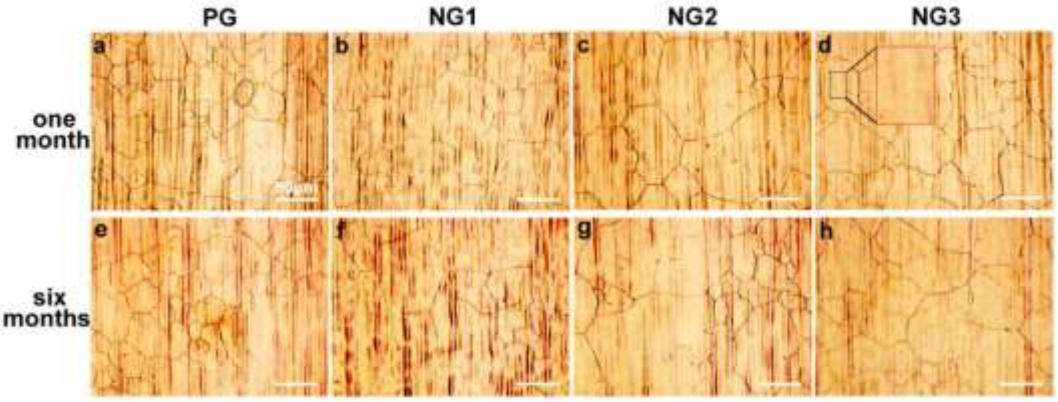

**Fig. S7** Optical micrographs of PG- and NG-coated Cu foils after (a-d) one month and (e-h) 6 months of storage in drying oven (25 °C, 15% R.H.). The scale bars are 50 μm.

As shown in Fig. S8, Raman spectra of PG- and NG3-coated Cu foils after 6 months of storage in drying oven (25 ℃, 15% R.H.) show two major peaks that are assigned to $Cu_2O$ (218 and 632 $cm^{-1}$, also seen main text for related discussion). In contrast, these peaks are barely detected in Raman spectra of NG1- and NG2-coated sample, indicating much less Cu oxide. Moreover, the oxidation degree of all samples after 6 months of storage in drying oven is slighter than that of the same sample exposed in air after three months (Fig. 8d in main text). This observation is consistent with the well-known notion that reduced humidity slows the electrochemical corrosion process.[17,60]

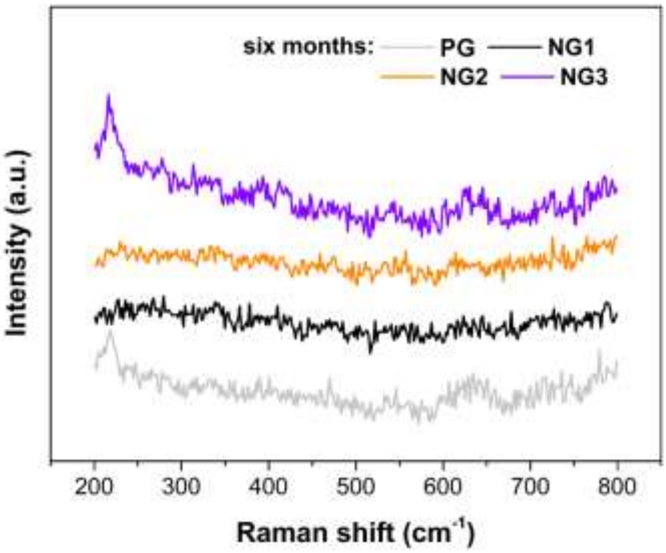

**Fig. S8** Raman spectra of PG- and NG-coated Cu foils after 6 months of storage in drying oven (25 °C, 15% R.H.).