Supporting Materials

Insights into the Photoelectrocatalytic Behavior of gCN-Based Anode Materials Supported on Ni Foams

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S1. Experimental details

S1.1. Synthesis

gCN^{Ar} powders were synthesized by thermal condensation of melamine (99%, Sigma-Aldrich) in an Ar atmosphere [1]. Briefly, melamine powders were introduced in a closed crucible, placed in a tubular oven and then heated with a constant rate of 3°C/min at 100°C (30 min), 400°C (2.5 h), and finally 550°C (4 h), followed by slow cooling at room temperature. The preparation of gCN^{air} powders was carried out in a similar way, but operating in air in a muffle furnace. In this case, melamine powders (typically 3 g) were transferred into a closed crucible and heated at a rate of 3°C/min at 100°C (30 min), 400°C (2 h), and then 550°C (4 h), followed by cooling at room temperature.

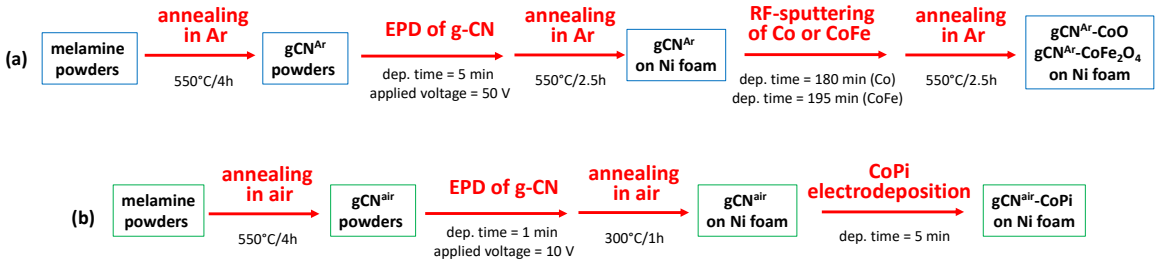

Figure S1. Synthetic protocols used for the preparation of: (a) gCN^{Ar} and (b) gCN^{air} powders, and the corresponding Ni foam-supported samples. The most relevant parameters are also reported.

S1.2. Characterization

High-resolution electron energy loss spectroscopy (EELS) data were acquired on a state-of-the-art double-corrected and monochromated Thermo Fisher Scientific Titan 80-300 microscope operated at 120 kV to limit beam damage while keeping a sub-nm spatial resolution and an energy resolution of 120 meV, a convergence angle of 19 mrad and a collection angle of 90 mrad. EELS spectra were acquired on a Direct detection Gatan K2 camera mounted on a GIF Quantum spectrometer. Dual EELS was used to get absolute energy of the Co *L*, O *K* and Fe *L* edges. EELS data were acquired with 0.2 s/pixel and 0.1 eV/pixel dispersion. High-resolution STEM images were acquired at 300 kV acceleration voltage using a convergence semi-angle α of 21 mrad, 50 pA probe current and a collection angle of 29-160 mrad for high angle annular dark field (HAADF) imaging, and 0-20 mrad for bright field imaging (BF). Image processing was performed using an open source HyperSpy Python software package [2]. Simulated electron diffraction data as well as high-resolution STEM images were calculated using the JEMS software [3].

S2. Chemico-physical characterization

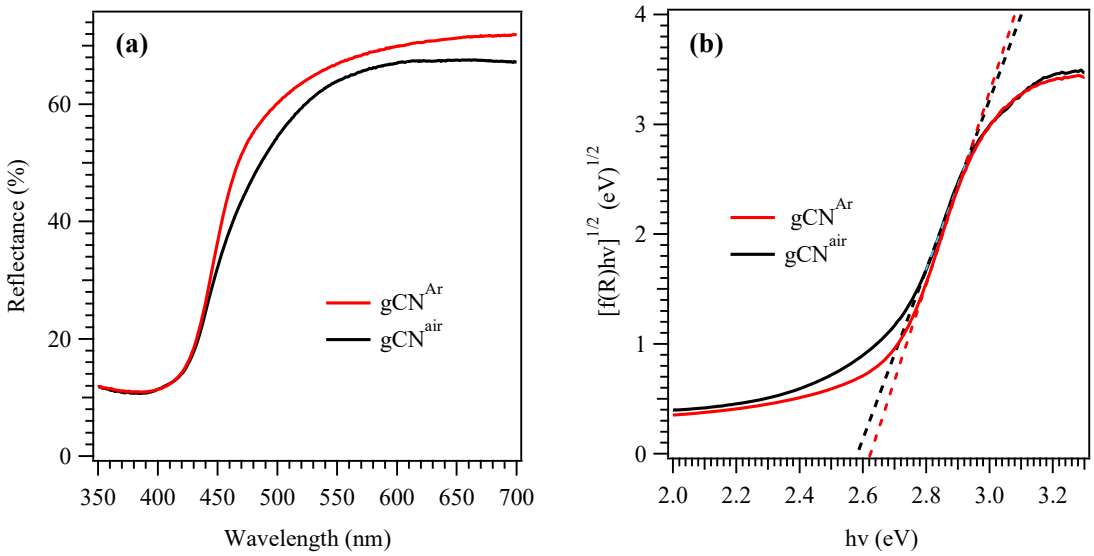

Figure S2. (a) Diffuse reflectance spectrum and (b) corresponding Tauc plot for gCN^{air} powders.

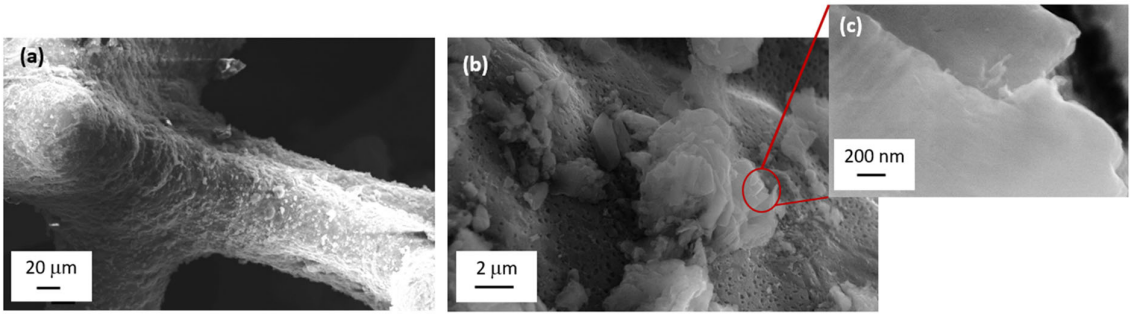

Figure S3. FE-SEM micrographs at different magnification levels for sample gCN^{Ar}.

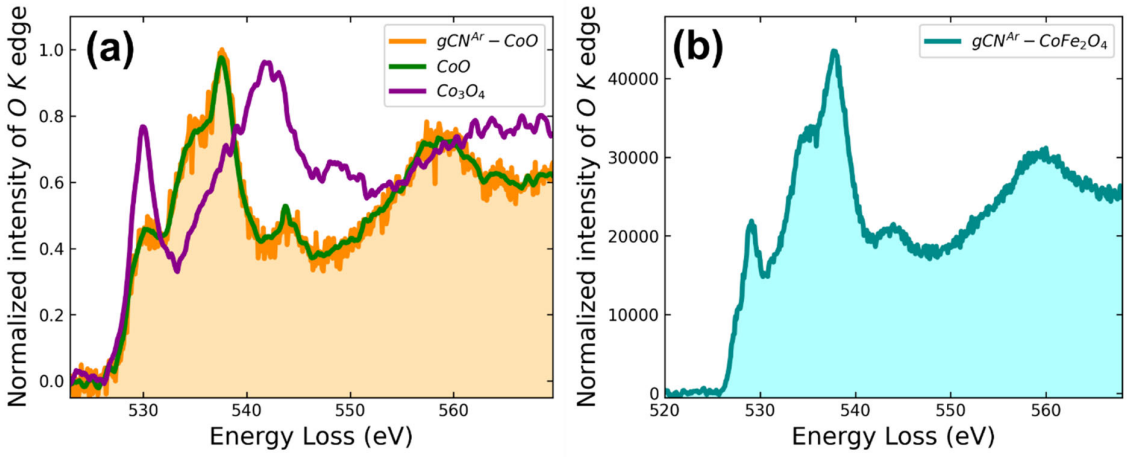

Figure S4. (a) O K edge EELS spectrum acquired on a Co-containing nanoparticle (orange) for gCN^{Ar}-CoO, compared to reference spectra taken on powders of CoO (green) and Co_3O_4 (purple). (b) EELS spectrum of the O K edge collected on specimen gCN-$CoFe_2O_4$.

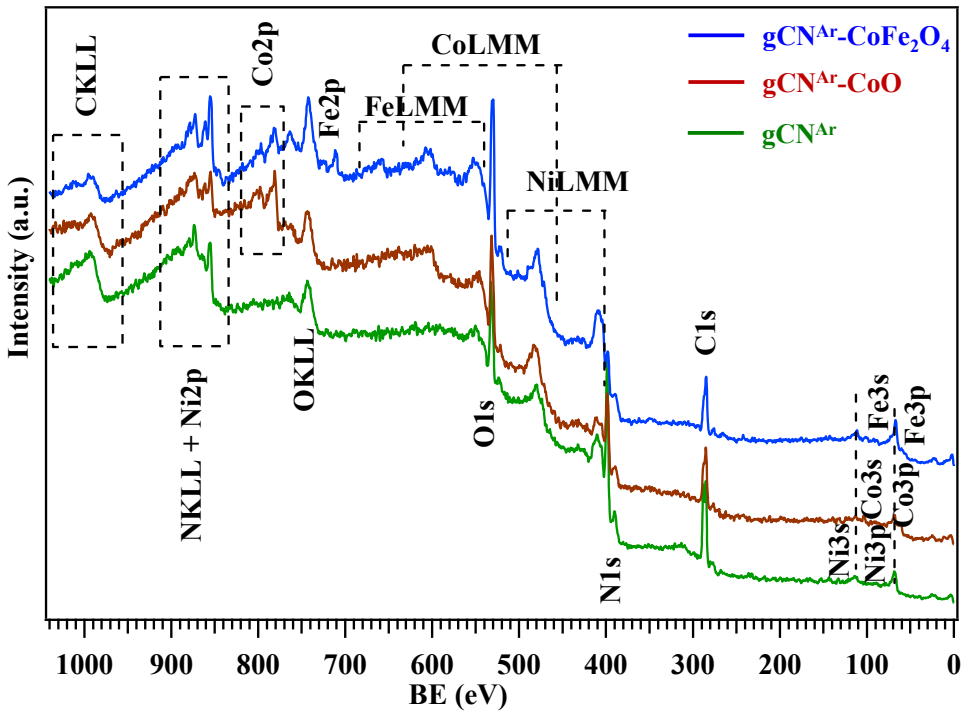

Figure S5. Wide-scan XPS spectra of gCN^{Ar} deposits before and after functionalization with CoO and $CoFe_2O_4$. Quantitative analyses yielded the following atomic percentage ratios: N/C = 1.0, 0.8 and 0.7, for gCN^{Ar}, gCN^{Ar}-CoO and gCN^{Ar}-$CoFe_2O_4$; Co/N = 0.20, for both gCN^{Ar}-CoO and gCN^{Ar}-$CoFe_2O_4$; Fe/N = 0.41, for gCN^{Ar}-$CoFe_2O_4$; Co/Fe = 0.50, for gCN^{Ar}-$CoFe_2O_4$. Co atomic percentage (at.%) values were estimated to be 7.0 and 4.0 % for gCN^{Ar}-CoO and gCN^{Ar}-$CoFe_2O_4$, respectively. Calculation was performed excluding the adventitious carbon component.

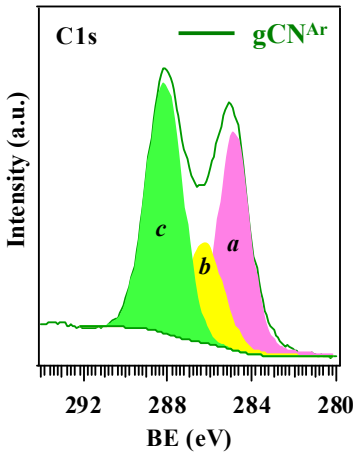

Figure S6. C1s peaks for bare gCN^{Ar} supported on Ni foam.

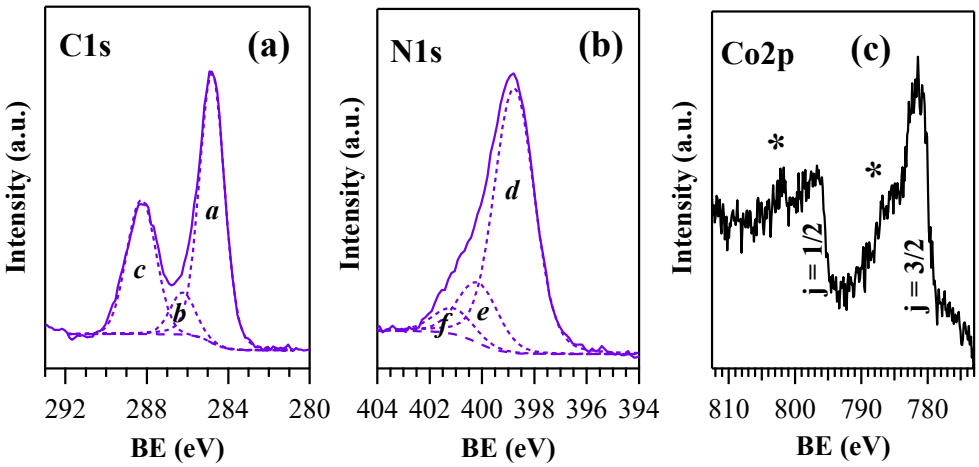

Figure S7. C1s (a) and N1s (b) photopeaks for gCN^{air} along with Co2p (c) signal for gCN^{air}-CoPi. In (c), stars (*) indicate shake-up peaks. Co atomic percentage (at.%) was estimated to be 2.0 %. Calculation was performed excluding the adventitious carbon component.

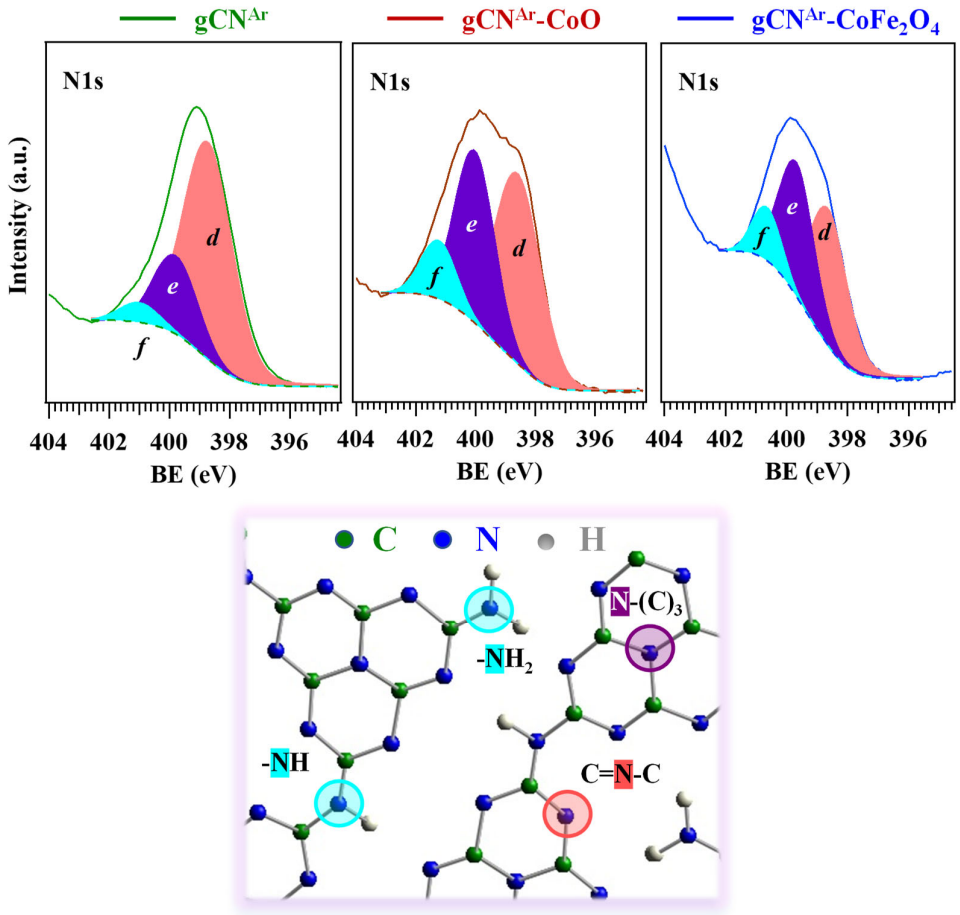

Figure S8. Top panel: N1s photopeaks for gCN^{Ar} deposits on Ni foams before and after functionalization with CoO and $CoFe_2O_4$. Bottom panel: Schematic representation of gCN structure [4], in which non-equivalent N sites are marked. Color codes as in top panel.

The N1s signals resulted from three contributing bands (Figures S7b and S8, top panel): ***d***, the predominant one, due to attributable to N centers in C=N-C moieties (BE = 398.6 eV), [4-12]; ***e***, ascribed to tri-coordinated N atoms in $N-(C)_3$ moieties (BE = 399.8 eV) [8,13-20]; ***f***, due to carbon atoms in uncondensed $C-NH_x$ (x = 1, 2) groups on gCN ring edges (BE = 401.0 eV) [9,10,13-15,17,19] (see Figure S8, bottom panel). The percentage contribution of component ***f*** to the overall N1s signal was evaluated to be 4.9, 11.0, and 12.4 % for gCN^{Ar}, gCN^{Ar}-CoO, and gCN^{Ar}-$CoFe_2O_4$ specimens, respectively.

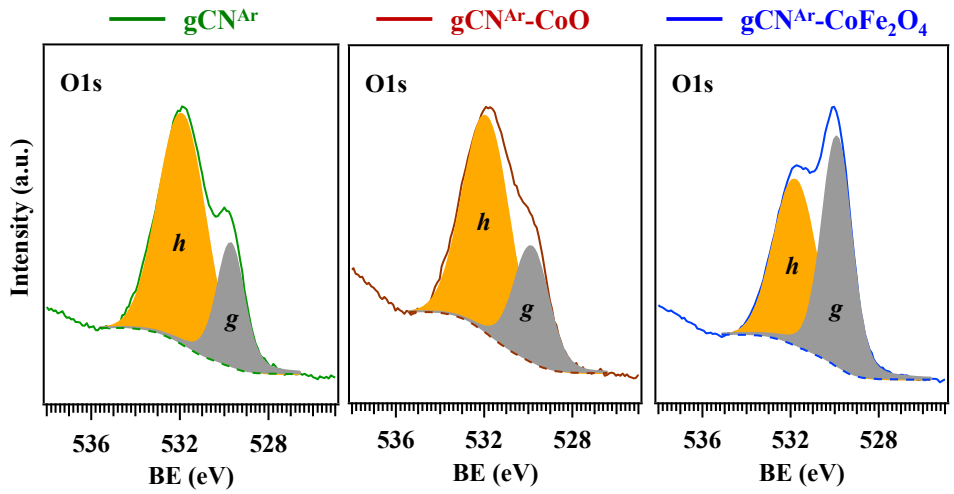

Figure S9. O1s photopeaks for gCN deposits supported on Ni foams before and after functionalization with CoO and $CoFe_2O_4$.

The O1s peak could be fitted by two bands (Figure S9): ***g***, centered at BE = 529.8 eV, related to NiO from the Ni foam substrate [21], as well as to oxygen in CoO and $CoFe_2O_4$ networks, for functionalized specimens [22-26]; ***h***, centered at BE= 531.9 eV, assigned to -OH groups chemisorbed onto N vacancies [5,7,14,16,26,27]. The percentage contribution of bands ***g*** (***h***) to the overall O1s signal were 26.9% (73.1%), for gCN^{Ar}; 30.5% (69.5%), for gCN^{Ar}-CoO; 52.1% (47.9%), for gCN^{Ar}-$CoFe_2O_4$.

S3. Functional tests

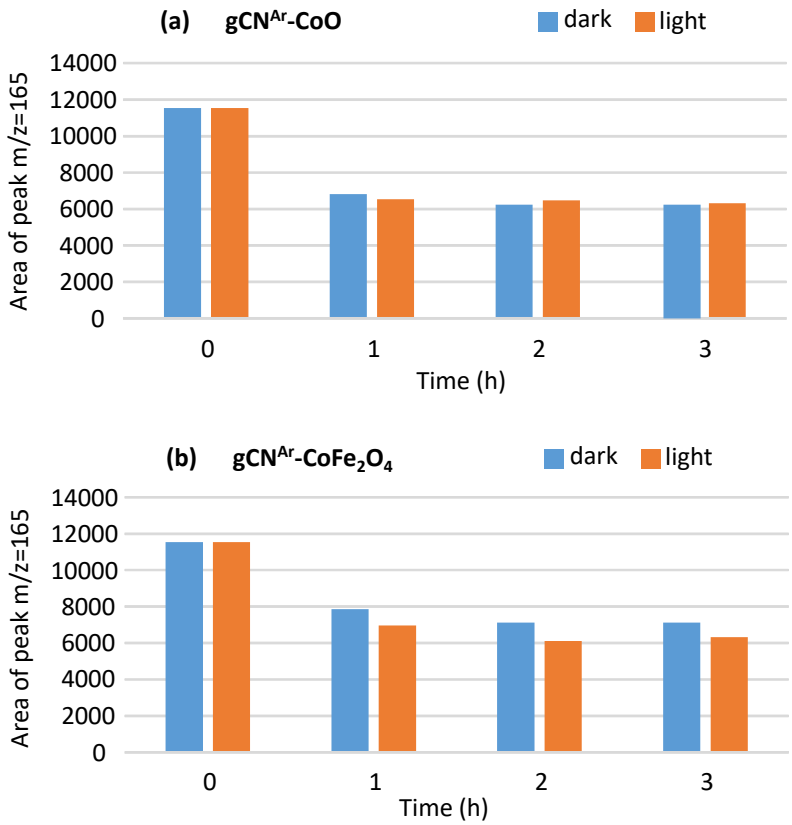

Figure S10. Determination of potassium hydrogen phthalate (KHP) concentration *vs.* time for (a) gCN^{Ar}-CoO and (b) gCN^{Ar}-$CoFe_2O_4$. Quantification of KHP was carried out by measuring the m/z = 165 peak area by flow injection analysis - electrospray mass spectrometry (FIA-ESI/MS). Both samples showed a comparable degradation efficiency in the dark and under illumination, in line with their modest photoactivity (see the main paper text).

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