## Electronic Supplementary Information

### for

# Nano- and ultra-dispersed ZnO and ZnFe<sub>2</sub>O<sub>4</sub> on graphitic carbon nitride as photoelectrocatalysts for the ethanol oxidation reaction

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#### § S1. Experimental

#### § S1-1. Synthesis of g-CN

In the present work, gCN powders were synthesized following previous literature reports,<sup>1, 2</sup> by copolymerization of thiourea with acetylacetone (AcAc).<sup>2</sup> Specifically, 6.00 g of thiourea (Sigma Aldrich,  $\geq$  99.0%) were finely grounded and placed in a beaker with 25 mL of isopropyl alcohol and 0.5 mL of AcAc (Alfa Aesar, 99%). The obtained colloidal solution was sonicated in an ultrasonic bath for 30 min, and subsequently isopropyl alcohol was slowly evaporated. The product was collected in a ceramic crucible and subjected to thermal treatment at 550°C for 2 h in air (heating rate = 3°C/min), yielding dark-yellow powders.

The deposition of gCN on carbon cloth (CC; Quintech, E35, area =  $2 \times 1 \text{ cm}^2$ ) supports was performed by electrophoretic deposition (EPD), basing on a previously reported procedure.<sup>3</sup> The substrates were preliminary cleaned by sonication in water, isopropyl alcohol and acetone. Hence, 40 mg of gCN powders were added in a beaker with 47.5 mL of acetone and 4 mg of previously dissolved iodine (Sigma Aldrich,  $\geq$  99.8%) and the resulting suspension was sonicated for 20 min. Subsequently, EPD experiments were performed using CC as cathode and a graphite anode, applying a potential of 10 V for 10 min, maintaining the suspension under mild stirring. After deposition, each specimen was subjected to thermal treatment in air at 300°C for 1 h (heating rate = 3°C/min).

#### § S1-2. Functionalization with ZnO and $ZnFe_2O_4$ by RF-sputtering

gCN deposits were functionalized with ZnO and ZnFe<sub>2</sub>O<sub>4</sub> by radio frequency (RF)-sputtering from Ar plasmas (purity = 5.0) using a custom-built two-electrode RF plasmochemical reactor (v = 13.56 MHz). Zinc or zinc ferrite targets (Neyco<sup>®</sup>, purity = 99.9%, diameter = 50.8 mm, thickness = 1 or 2 mm, respectively) were fixed on the RF-powered electrode, whereas carbon cloth-supported gCN samples were mounted on the ground electrode. The experimental settings for RF-power (20 W), Ar flow rate [10 standard cubic centimeters per minute (sccm)], total pressure (0.300 mbar), and growth temperature (60°C) were chosen basing on previous results.<sup>4</sup> The deposition times, resulting from preliminary optimization experiments, were 30 and 200 min for ZnO and ZnFe<sub>2</sub>O<sub>4</sub>, respectively. Basing on X-ray photoelectron spectroscopy (XPS) analyses, these operating conditions were set in order to obtain a comparable content of ZnO and ZnFe<sub>2</sub>O<sub>4</sub> in the resulting systems. The use of harsher plasma conditions was intentionally discarded to avoid the obtainment of too compact systems with reduced active area, that might negatively affect the ultimate functional behavior. The functionalized specimens were finally annealed at 350°C for 90 min in air (heating rate = 3°C/min).

#### § S1-3. Chemico-physical characterization

FT-IR spectra were recorded in diffuse reflectance mode on a JASCO-4100 instrument (resolution = 1 cm<sup>-1</sup>). Optical spectra were collected in diffuse reflectance on a FLS 1000 spectrophotometer. Band gap (E<sub>G</sub>) evaluation was performed using the Tauc equation:  $[f(R) \times hv]^n vs$ . hv, where f(R) is the Kubelka-Munk function, R is the reflectance, and hv is the photon energy, assuming the occurrence of allowed and indirect electronic transitions (n = 1/2),<sup>4,5</sup> the strongest ones for gCN, the main system component.<sup>6</sup> E<sub>G</sub> values were obtained by extrapolating the straight portion of experimental curves to intersect the energy axis. Photoluminescence (PL) spectra were collected on the same instrument, in the range 350-800 nm, adopting an excitation wavelength of 330 nm. X-ray diffraction (XRD) measurements were carried out in glancing incidence mode ( $\theta_i = 1.0^\circ$ ) using a Bruker AXS D8 Advance Plus diffractometer equipped with a Göbel mirror and a CuK $\alpha$  X-ray source ( $\lambda = 1.54051$ Å), powered at 40 kV and 40 mA. Analyses were performed at the PanLab facility (Department of Chemical Sciences, Padova University) founded by the MIUR Dipartimento di Eccellenza grant "NExuS". XPS analyses were performed through a ThermoFisher ESCALAB QXi apparatus, funded by "Sviluppo delle infrastrutture e programma biennale degli interventi del Consiglio Nazionale delle Ricerche (2019)", using a non-monochromatized Al K $\alpha$  X-ray source (hv = 1486.6 eV). Binding energy (BE) values were corrected for charging phenomena by referencing the adventitious C1s signal (component C<sub>0</sub> in Fig. 1a and S3a-c) at 284.8 eV. Atomic percentages (at.%) were computed by peak area integration, using ThermoFisher sensitivity factors. Peak fitting was carried out by XPSpeak (Version 4.1) software, using Gaussian-Lorentzian sum functions and applying a Shirleytype background subtraction. Zinc Auger  $\alpha$  parameter was calculated as follows:

$$\alpha = BE(Zn2p_{3/2}) + KE(Zn LMM)$$
(S1)

where KE = kinetic energy.<sup>7,8</sup> Field emission-scanning electron microscopy (FE-SEM) analyses were performed using a Zeiss SUPRA 40 VP instrument, at primary beam acceleration voltages of 10-20 kV. Transmission electron microscopy (TEM) analyses, encompassing bright field-high resolution TEM (BF-HRTEM), high angle annular dark field-scanning TEM (HAADF-STEM), electron diffraction (ED), and energy dispersive X-ray spectroscopy (EDXS) elemental mapping experiments, were carried out on an aberration double-corrected cold FEG JEM ARM200F microscope operated at 200 kV, equipped with a large-angle CENTURIO EDX detector, an ORIUS Gatan camera, and Quantum GIF. Due to the fragility of both CC supports and gCN under ion beam irradiation, specimens for TEM observations were prepared by scratching the target material from the substrate, suspending it in ethanol, and final deposition on a TEM grid.<sup>6</sup>

#### § S1-4. Electrochemical tests

Photoelectrochemical tests were carried out using an Autolab PGSTAT204 potentiostat/galvanostat workstation, using carbon cloth-supported samples, a Pt coil and a Hg/HgO (MMO) electrode as working (WE), counter (CE), and reference-electrode (RE), respectively. All the recorded potential values *vs.* MMO ( $E_{MMO}$ ) were converted into the RHE scale using the equation:<sup>9</sup>

$$E_{RHE}(V) = E_{WE}(V) + E_{MMO}(V) + 0.0592 \times pH$$
(S2)

 $(\mathbf{a}\mathbf{a})$ 

where  $E_{WE}$  indicates the bias applied to the working electrode. Electrochemical measurements were carried out both in the dark and under illumination, using in the latter case a white light LED lamp (Philips LUMILEDS LXML-PWN1 0120). Linear sweep voltammetry (LSV) curves were initially recorded in 0.5 M KOH solution and then in 0.5 M KOH + 0.5 M ethanol solution (scan rate = 5 mV/s). The reported LSVs have been plotted as obtained after the sole current normalization to the geometric electrode area, without performing any additional data treatment/eleboration. Chronoamperometric (CA) analyses (see Fig. 3a in the main paper) were carried out under visible light irradiation, at a fixed potential value of 1.55 V vs. RHE. During the first 30 min, the current was recorded in KOH 0.5 M solution, and ethanol was subsequently injected so as to obtain a KOH 0.5 M + EtOH 0.5 M solution. Tafel slopes were determined from the plots of potential *vs.* log(current density).<sup>9</sup>

Applied bias photon-to-current efficiency [ABPE (%)] curves were obtained by the following equation:<sup>4, 10</sup>

ABPE (%) = 
$$[j_{photo} \times (1.23 - E_{RHE})] / P \times 100$$
 (S3)

where  $j_{photo}$  (mA/cm<sup>2</sup>) and P are, respectively, the photocurrent density at the potential  $E_{RHE}$  and the incident light power density (150 mW/cm<sup>2</sup>). Given that ABPE results do not correspond to a true solar-to-hydrogen measurement,<sup>11</sup> in the present work they were used only as a qualitative diagnostic indicator for a relative comparison of material performances. Accordingly, Table S1 reports the relative maximum efficiency (ABPE<sub>max</sub>) for the composite specimens, normalized with respect to the bare gCN sample.



**Fig. S1** (a) FT-IR, (b) optical absorption spectra, (c) Tauc plots, and (d) PL spectra for gCN-based electrocatalysts.

FT-IR spectral features (Fig. S1a) well-matched literature data for carbon nitride-based materials obtained by similar thermal condensation routes. In particular, the broad band centered at 3200 cm<sup>-1</sup> was ascribed to stretching vibrations of uncondensed -NH<sub>x</sub> groups (x = 1, 2) and to an additional contribution from -OH moieties derived from air exposure,<sup>12, 13</sup> as also confirmed by XPS data. The signal at 890 cm<sup>-1</sup> was attributed to N-H deformation modes.<sup>14</sup> The multi-component band in the 1200-1700 cm<sup>-1</sup> range was assigned to the characteristic stretching modes of gCN heptazine heterocycles,<sup>9</sup> whose presence was also confirmed by the corresponding ring breathing mode at 810 cm<sup>-1</sup>.<sup>12</sup>

To evaluate the light-harvesting properties of the fabricated specimens, optical analyses were carried out. All the recorded UV-Vis spectra (Fig. S1b) showed a net absorption increase for  $\lambda < 450$  nm, consistent with the interband transitions of graphitic carbon nitride,<sup>4, 9</sup> the main system component. The extrapolated band gap values (Fig. S1c) were all very close [E<sub>G</sub> = 2.30 eV (gCN), 2.40 eV (gCN-ZnO) and 2.33 eV (gCN-ZnFe<sub>2</sub>O<sub>4</sub>)].

PL spectra (Fig. S1d) were dominated by the presence of a relatively broad emission band for all specimens, similarly to previously reported gCN-based systems.<sup>6, 9</sup> As can be observed, the signal intensity was quenched upon graphitic carbon nitride functionalization with either ZnO or ZnFe<sub>2</sub>O<sub>4</sub>, indicating a parallel suppression of charge carriers recombination, and anticipating an improvement of photoelectrochemical properties.<sup>15</sup> The band redshift for gCN-ZnO can be related to an additional contribution to the emission process, due to a transition occurring in the case of ZnO NPs, correlated to the material defectivity.<sup>16</sup>



**Fig. S2** XPS wide-scan spectra for gCN, gCN-ZnO, gCN-ZnFe<sub>2</sub>O<sub>4</sub> samples. Quantitative analyses yielded the following atomic percentage (at.%) ratios: N/C = 1.02, 0.94 and 0.88, for gCN, gCN-ZnO and gCN-ZnFe<sub>2</sub>O<sub>4</sub>; Zn/N = 0.28, for gCN-ZnO, and 0.18, for gCN-ZnFe<sub>2</sub>O<sub>4</sub>; Fe/N = 0.32, for gCN-ZnFe<sub>2</sub>O<sub>4</sub>; Zn/Fe = 0.50, for gCN-ZnFe<sub>2</sub>O<sub>4</sub>. Zn at.% values were estimated to be  $\approx$ 9.0 and 6.0 % for gCN-ZnO and gCN-ZnFe<sub>2</sub>O<sub>4</sub>, respectively. Calculations were performed excluding the adventitious carbon contribution (related to component C<sub>0</sub> in Fig. 1a and S3).



Fig. S3 C1s and N1s photoelectron peaks for gCN (a-b) and gCN-ZnO (c-d) electrocatalysts.



Fig. S4 (a) Sketch of graphitic carbon nitride structure: non-equivalent C and N sites are marked with color codes used in Fig. 1a-b and S3. (b) Contribution of the  $N_2$  component (arising from uncondensed amino groups) to the overall N1s signal for the analyzed specimens.



Fig S5 O1s photoelectron peaks for: (a) gCN, (b) gCN-ZnO, (c) gCN-ZnFe<sub>2</sub>O<sub>4</sub>.

O1s peak was fitted with three components (Fig. S5), of which the O<sub>0</sub> band resulted from different contributions depending on the analyzed sample. For bare gCN (Fig. S5a), O<sub>0</sub> (BE  $\approx$  530.3 eV) corresponded to carbonylic groups from the CC substrate,<sup>17, 18</sup> whereas for gCN-ZnO and gCN-ZnFe<sub>2</sub>O<sub>4</sub> (Fig. S5b-c) O<sub>0</sub> also contained the contribution from lattice oxygen in ZnO and ZnFe<sub>2</sub>O<sub>4</sub>.<sup>19-22</sup> Band O<sub>1</sub> (BE = 531.5 eV) was attributed to -OH groups chemisorbed on gCN,<sup>23, 24</sup> and signal O<sub>2</sub> (BE = 533.0 eV) derived from adsorbed water.<sup>23, 24</sup>



Fig S6 Zn LMM Auger peaks for (a) gCN-ZnO and (b) gCN-ZnFe<sub>2</sub>O<sub>4</sub>.



Fig. S7 Representative FE-SEM images for (a) gCN, (b) gCN-ZnO, and (c) gCN-ZnFe<sub>2</sub>O<sub>4</sub> specimens.



**Fig. S8** XRD patterns for gCN-based specimens and for the bare carbon cloth (CC). In all cases, only signals attributed to the CC support could be observed.



**Fig. S9** Low magnification BF-TEM images for gCN-ZnO (a-b) and gCN-ZnFe<sub>2</sub>O<sub>4</sub> (c-d). In (a), a graphite fiber from the CC support is also imaged.



**Fig. S10** LSV curves for the target electrocatalysts, recorded: (a) in KOH 0.5 M under illumination; (b) in KOH 0.5 M + EtOH 0.5 M in the dark.



**Fig. S11** Tafel plots recorded in in KOH 0.5 M + EtOH 0.5 M under illumination, corresponding to the LSV curves in Fig. 3a. Dashed and continuous lines indicate experimental and fitting curves, respectively.

Material	Electrolyte	j <sub>1.65</sub> (mA/cm <sup>2</sup> )	E <sub>onset</sub> (V)	Tafel slope (mV/dec)	E <sub>Wmax</sub> (V)	<b>ABPE</b> <sub>max</sub>
gCN	KOH 0.5 M + EtOH 0.5 M	0.12	1.68	316	0.80	1.0
gCN-ZnO		0.23	1.59	295	0.77	3.0
gCN-ZnFe <sub>2</sub> O <sub>4</sub>		0.42	1.55	170	0.73	8.0

**Table S1** Summary of representative photoelectrochemical results for the target specimens: photocurrent densities at 1.65 V ( $j_{1.65}$ ) vs. RHE, onset potential (evaluated at 0.15 mA/cm<sup>2</sup>), Tafel slope values under illumination, potential of maximum efficiency ( $E_{Wmax}$ ) corresponding to the maximum in the ABPE curves plotted in Fig. 3b in the main paper text), and relative maximum efficiency (ABPE<sub>max</sub>), normalized with respect to the bare gCN specimen.

Material	Electrolyte j (mA/cm <sup>2</sup> )		Tafel slope (mV/dec)	Ref.
gCN	KOH 1 M + EtOH 1 M	0.56 <sup>a</sup>	290	25
gCN	KOH 0.5 M + CH <sub>3</sub> OH 0.5 M	≈0.10 <sup><i>a</i></sup>	n.a.	26
gCN NSs	NaOH 0.5 M + CH <sub>3</sub> OH 0.1 M	0.10 <sup>a</sup>	n.a.	27
gCN NSs	KOH 1 M + CH <sub>3</sub> OH 1 M	≈3.0×10 <sup>-3 b</sup>	n.a.	28
gCN NRs	NaOH 0.5 M + CH <sub>3</sub> OH 0.1 M	0.09 <sup>a</sup>	n.a.	27
C NTs	H <sub>2</sub> SO <sub>4</sub> 0.5 M + CH <sub>3</sub> OH 1 M	≈0.015 <sup>a</sup>	n.a.	29
Pt/g-CN	KOH 1 M + CH <sub>3</sub> OH 1 M	≈0.21 <sup>b</sup>	n.a.	30
Pt/g-CN	KOH 1 M + EtOH 1 M	0.02 <sup>b</sup>	n.a.	31
Pt/gCN	H <sub>2</sub> SO <sub>4</sub> 1 M + CH <sub>3</sub> OH 2 M	≈0 <sup>a</sup>	n.a.	32
Pt/gCN	H <sub>2</sub> SO <sub>4</sub> 1 M + CH <sub>3</sub> OH 1 M	≈0.45 <sup>a</sup>	n.a.	33
Pt-gCN	KOH 1 M + CH <sub>3</sub> OH 1 M	≈60×10 <sup>-3 b</sup>	n.a.	28
Au/gCN	KOH 1 M + CH <sub>3</sub> OH 1 M	≈0.18 <sup>b</sup>	n.a.	30
Ni/gCN	NaOH 1 M + EtOH 3 M	< 6×10 <sup>-3</sup> a	n.a.	34
ZnO-gCN	KOH 0.5 M + CH <sub>3</sub> OH 0.5 M	≈0.20 <sup><i>a</i></sup>	n.a.	26
gCN-Pt	H <sub>2</sub> SO <sub>4</sub> 0.1 M + CH <sub>3</sub> OH 1 M	≈0.1 <sup><i>a</i></sup>	n.a.	35
gCN-TiO <sub>2</sub> <sup>1</sup>	H <sub>2</sub> SO <sub>4</sub> 0.1 M + CH <sub>3</sub> OH 1 M	≈0.4 <sup><i>a</i></sup>	n.a.	35

<sup>&</sup>lt;sup>1</sup> Heat treatment at 400°C for 4 h in a muffle furnace.

Material	Electrolyte j (mA/cm <sup>2</sup>		Tafel slope (mV/dec)	Ref.
gCN NSs/ TiO <sub>2</sub> NTs	KOH 1 M + CH <sub>3</sub> OH 1 M	≈0.12 ÷ 0.35 <sup>b</sup>	n.a.	36
Ni(OH) <sub>2</sub> / OMC	NaOH 0.1 M + EtOH 0.1 M	< 0.048 <sup>a</sup>	n.a.	37
Co-Pd/ Sn/rGO	H <sub>2</sub> SO <sub>4</sub> 0.5 M + EtOH 0.5 M	0.02 <i>a</i>	n.a.	38
Pd-Ru/CNFs	KOH 1 M + EtOH 1 M	KOH 1 M +         0.02 a           EtOH 1 M         0.02 a		39
Pt/C	NaOH 0.5 M + EtOH 0.1 M	0.08 <sup>a</sup>	n.a.	40
Pt/C	NaOH 0.1 M + EtOH 0.01 M	≈0.22 <sup>a</sup>	310	41
Pt/C	H <sub>2</sub> SO <sub>4</sub> 0.5 M + EtOH 0.5 M	0.26 <i>a</i>	n.a.	42
Pt/C	H <sub>2</sub> SO <sub>4</sub> 1 M + CH <sub>3</sub> OH 1 M	≈0.30 <sup><i>a</i></sup>	n.a.	33
Pt/C	H <sub>2</sub> SO <sub>4</sub> 0.1 M + CH <sub>3</sub> OH 1 M	≈0.4 <sup><i>a</i></sup>	n.a.	35

**Table S2** EOR and methanol oxidation reaction (MOR) performances of selected representative electrocatalysts based on graphitic carbon nitride or other carbonaceous materials, containing various metals or oxides. Representative data pertaining to Pt/C systems are also reported for comparison. n.a. = data not available. <sup>*a*</sup> dark conditions; <sup>*b*</sup> light conditions. NSs = nanosheets; NRs = nanorods; NTs = nanotubes; OMC = ordered mesoporous carbon; rGO = reduced graphene oxide; CNFs = carbon nanofibers.



Fig. S12 LSV curves collected under illumination in KOH 0.5 M + EtOH 0.5 on fresh samples (solid lines), and repeated after three (dotted line) and six months (dashed lines), upon storage of the specimens under ordinary laboratory conditions.



**Fig. S13** XPS photopeaks for gCN-ZnO before (black line) and after (red line) the completion of photoelectrochemical tests indicated in the caption to Fig. S12.



**Fig. S14** XPS photopeaks for gCN-ZnFe<sub>2</sub>O<sub>4</sub> before (black line) and after (red line) the completion of photoelectrochemical tests indicated in the caption to Fig. S12.



Fig. S15 (a) Square of photocurrent density  $(j^2)$  curves for gCN-based electrodes. (b) Corresponding XPS valence band spectra.



**Fig. S16** Interfacial band structure for the gCN/ZnO heterojunction. The marked Fermi level energy  $(E_F)$  has been extrapolated by the intercept of the square photocurrent density curves with the potential axis (Fig. S15a). Valence and conduction band edge positions (VB and CB, respectively) were obtained by photoelectron spectroscopy measurements (Fig. S15b) and optical band gap values. The band gap for gCN is 2.30 eV (see Fig. S1b-c and related observations), whereas that of ZnO is 3.37 eV.<sup>43</sup>

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