Supporting Information

Graphitic carbon nitride - nickel catalyst: from material characterization to efficient ethanol electrooxidation

Agnieszka Lewalska-Graczyk¹, Piotr Pieta¹, Gabriella Garbarino², Guido Busca², Marcin Hołdynski¹, Grzegorz Kalisz³, Anna Sroka-Bartnicka^{3,4}, Robert Nowakowski¹, Mu Naushad⁵, Manoj B. Gawande^{6,7}, Radek Zbořil⁶, Izabela S. Pieta¹*

¹ Institute of Physical Chemistry Polish Academy of Sciences, 01-224 Warsaw, Poland;

² Università degli Studi di Genova, Dipartimento di Ingegneria Civile, Chimica e Ambientale (DICCA), Via Opera Pia 15, 16145 Genova, Italy

³Department of Biopharmacy, Medical University of Lublin, Chodzki 4a, 20-093 Lublin, Poland

⁴ Department of Genetics and Microbiology, Maria Curie-Sklodowska University, Akademicka 19,

20-033 Lublin, Poland

⁵Department of Chemistry, College of Sciences, King Saud University, Riyadh 11451, Kingdom of Saudi Arabia.

⁶ Regional Centre of Advanced Technologies and Materials, Palacký University, Šlechtitelů

27, Olomouc, Czech Republic, 78371.

⁷ Institute of Chemical Technology Mumbai-Marathwada Campus, Jalna, Maharashtra 431213, India.

*Corresponding author: ipieta@ichf.edu.pl

Number of pages: 9 Number of tables: 1 Number of figures: 11 Microscopic images were obtained using a HRTEM TITAN 60-300 instrument with an X-FEGtype emission gun operating at 80 kV. This microscope is equipped with a Cs image corrector and a STEM high-angle annular dark-field detector (HAADF); its point resolution is 0.06 nm in TEM mode. For HRTEM analysis, the powder samples were dispersed in ethanol and sonicated for 5 min. One drop of the resulting solution was then placed on a copper grid with a holey carbon film, after which the sample was dried at room temperature.

The TEM images (Figure S1) show that the gCN(H) matrix adopted a fine sheet-like morphology Taking account both microscopic and spectroscopic data it can be concluded that the gCN(H) material is rater a 'bulk' type than single layer material.





Figure S1. TEM images of (a, b) pristine gCN(H); (c, d) the Ni/gCN(H) nanocomposite, and (e) Ni/gCN(H) elemental mapping.

XPS measurements were performed to determine the chemical state of the elements in the studied samples by a Microlab 350 instrument (Thermo Electron). XPS spectra were acquired using AlK α (h ν = 1486.6 eV) radiation. Survey spectra and high resolution spectra were recorded using pass energies of 100 and 40 eV, and the XPS signal intensity was determined using linear or Shirley background subtraction. Peaks were fitted using an asymmetric Gaussian/Lorentzian mixed function, and the measured binding energies were corrected based on the C1s energy at 285.0 eV.

Figure S2 presents the full survey spectra of gCN(H) and Ni-modified nanocomposites, showing the signals for C, N, O, Cu and Ni. The as-prepared CN was highly pure, consisting mainly of the elements C, N, and O. The atomic ratio of C to N at the surface of the gCN(H) samples was around 0.73, which is close to the ideal value of 0.75 for g- C_3N_4 .⁵⁸⁻⁶⁰



Figure S2. XPS spectra survey of pristine gCN(H) and the Ni/gCN(H)



Figure S3. XPS spectra survey and core levels for C1s, N1s, O1s.

Two different settings for Raman mapping were used. First the 50 pinhole aperture and x 10 air objective was used for experiments. The sharp peaks do not appear in the Raman map when the slit aperture was used. The 50 pinhole aperture allows for penetration of the sample in the ca. 2 micrometer resolution depth. During experiments the optical focus was set up on surface of the sample.

The samples were prepared as a thin powder film. In case of the use the slit aperture the obtained spectrum looks the same (has got the same bands). Depending on the laser energy the intensity, presence and relative peak positions differ as they are the function of incident laser wavelength and resonance Raman effect.



Figure S4. The Raman spectra with different power laser. The spectra are presented in common scale to visualisation of the process of optimization before experiments.



Figure S5. The Raman map of CN sample with the distribution of the 1236 cm⁻¹ band. The two marked points with the black and pink crosses corresponds to each color of the spectra. The white scale bar is 2 micrometers.



Figure S6. The Raman spectra with different power laser.

The characteristic bands at 483 cm⁻¹, 705 cm⁻¹, 750 cm⁻¹, 976 cm⁻¹, 1236 cm⁻¹ are observed in the Raman spectrum corresponding to the vibration modes of CN heterocycles. The ratio I750/I705 is used to show the bulk nature of the studied material.



Figure S7. Raman images of gCN(H) sample with 25μ m slit aperture: a) microscopic image of a sample magnification ×50, with ROI region, distribution of 479 cm⁻¹, 705 cm⁻¹, 750 cm⁻¹, 976 cm⁻¹, 1236 cm⁻¹ band and intensity ratio of 1750:1705, b) visible microscopic image blending with visualization of 750 cm⁻¹ area distribution, surface visualization with magnification ×50, c) Raman spectrum with bands assignments.



Figure S8. Raman images of Ni/gCN(H) sample with 25 μ m slit aperture: a) microscopic image of a sample magnification ×50, with ROI region, distribution of 479 cm⁻¹, 705 cm⁻¹, 750 cm⁻¹, 976 cm⁻¹, 1236 cm⁻¹ band and intensity ratio of 1750:1705, b) visible microscopic image blending with visualization of 750 cm⁻¹ area distribution, surface visualization with magnification ×50, c) Raman spectrum with bands assignments.



Figure S9. Raman images of Ni/gCN(H) sample with 50 μ m pinhole aperture: a) microscopic image of a sample magnification ×50, with ROI region, distribution of 479 cm⁻¹, 705 cm⁻¹, 750 cm⁻¹, 976 cm⁻¹, 1236 cm⁻¹ band and intensity ratio of 1750:1705, b) visible microscopic image blending with visualization of 750 cm⁻¹ area distribution, surface visualization with magnification ×50, c) Raman spectrum with bands assignments.

For both samples, a limited FT-IR transmittance is rather observed indicated by very narrow window with a minimum at ca. 1800 cm⁻¹ (Figure S1). Only very weak signals in the range from 1000–800 cm⁻¹ appeared for Ni/gCN(H) materials, which can be ascribed to the typical stretching vibration of CN heterocycles and breathing vibration of triazine units revealing the

local structure of the obtained gCN(H). Feature at 1800 cm⁻¹ is becoming more narrow with increasing temperature for both gCN(H) and Ni/gCN(H) samples. However, the negative feature 1800 cm⁻¹ is broader in general for Ni/gCN(H) sample, indicating higher accessibility of surface species for electrochemical reactions, what can be further reflected in reactivity increase.¹⁷ Samples treatment at high temperature up to 623 K with a subsequent evacuation caused surface dehydration, dehydroxylation and possibly some carboneous material decomposition. As indicated previously, polymeric gCN(H) becomes unstable at above 873 K and at room temperature (RT) only free hydroxyl species (modes at 3730, 3680 and 3540 cm⁻¹) and CN heterocycles vibration (modes at 1000 cm⁻¹) can be detected (first line in Figure S8), which disappear upon evacuation at 623 K.



Figure S10. FTIR spectra for bare (a, b) gCN(H) and (c) Ni/gCN(H).



Figure S11. (a) CV curves and (b) Nyquist plots for the GC electrode modified with CN at various MeOH concertations in 1 M NaOH. CV experiments were performed at a potential scan rate of 50 mV s⁻¹. EIS spectra were collected at 0.5 V.

EtOH concentration	R _s	CPE _{dl}	α_{dl}	R _{ct}
М	Ω	F s ^{<i>a</i>-1}		Ω
0.5	14.5 ± 0.1	0.35E-3 ± 0.01E-3	0.953 ± 0.006	138.8 ± 1.4
1	14.27 ± 0.1	0.27E-3 ± 0.01E-3	0.981 ± 0.006	93.3 ± 0.7
3	17.53 ± 0.1	0.15E-3 ± 0.01E-3	0.930 + 0.009	60.4 ± 0.5

Table S1. Numerical results of the equivalent electric circuits fittings to the EIS data.