Solvothermal modification of graphitic C₃N₄ with Ni and Co phthalocyanines: structural, optoelectronic and surface properties

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§1. Materials

All the chemicals used for the synthesis are chemically pure. Urea [$(NH_2)_2CO$, 99%, Sigma] for graphitic carbon nitride synthesis, nickel (II) phthalocyanine [$C_{32}H_{16}N_8Ni$, 85%, Sigma] and cobalt (II) phthalocyanine [$C_{32}H_{16}N_8Co$, 97%, Sigma] for carbon nitride modification, ethyl alcohol [99%] as solvothermal media for composite synthesis, methylene blue [$C_{16}H_{18}ClN_3S$, pure 97%], hydrogen peroxide [H_2O_2, 37%], distilled water as a solvent. All chemicals were used as received without further purification.

§2. Synthesis of g-C₃N₄/MPc

Graphitic carbon nitride was produced by thermal decomposition of urea at 550°C in a muffle furnace, by the method described in detail in https://doi.org/10.1134/S106378261912008X. The product was ground in agate mortar until it formed lightweight pale-yellow powder. g-C_3N_4/MPc composites were synthesized by solvothermal route with ethyl alcohol as a solvent. Nickel or cobalt phthalocyanine was taken and mixed with g-C_3N_4 powder in a ratio of 1:10 in 20 ml of ethyl alcohol then the mixture was loaded into steel autoclave with PTFE inlay and heated up to 190 ºC for 3 hours. After solvothermal treatment, the suspension was placed in an evaporating dish and dried at 80 ºC until complete evaporation of ethyl alcohol. The resulting materials are pale greenish-blue powders.

§3. Physico-Chemical Characterization

The element mapping of prepared nanocomposites was made by scanning electron microscopy on TescanVega 3 SBH. The phase composition was researched via Rigaku SmartLab 3 (CuKα, λ = 0.154051 nm). Measurements were carried out in Bragg's angle region from 5 to 80° with a step size of 0.01° integration time or each step is 1s. FTIR spectra were measured on Shimadzu IRTracer-100 in 350–4000 cm^{-1} region, with a diamond ATR module. Surface and porosity of composites were measured by low-temperature nitrogen adsorption/desorption on Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The analysis was carried out at 77 K. DRS spectra and composite stability were measured with a 30mm integrating sphere, in the 350–700 nm region on AvaSpecULS2048CL-EVO spectrometer. Decolorization of methylene blue was
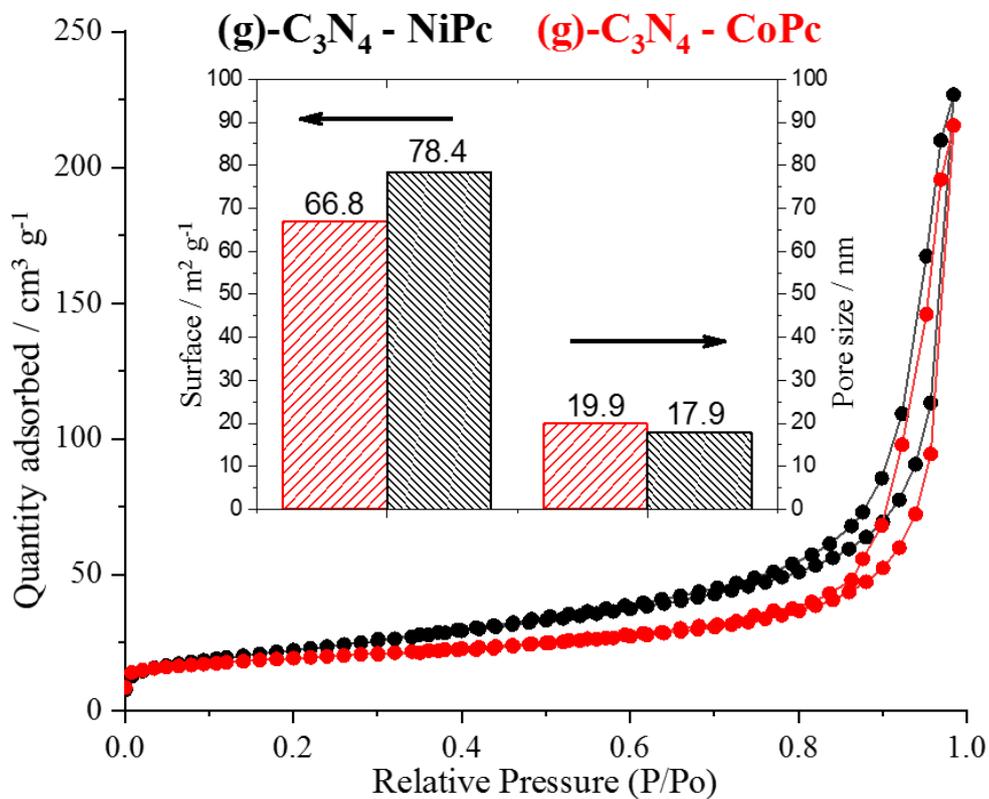
carried out under 70W Xe-lamp irradiation and measured on AvaSpecULS2048CL-EVO spectrometer. Kinetic pH curve and zero potential point analysis made with pH-meter 'pH-150MI'.
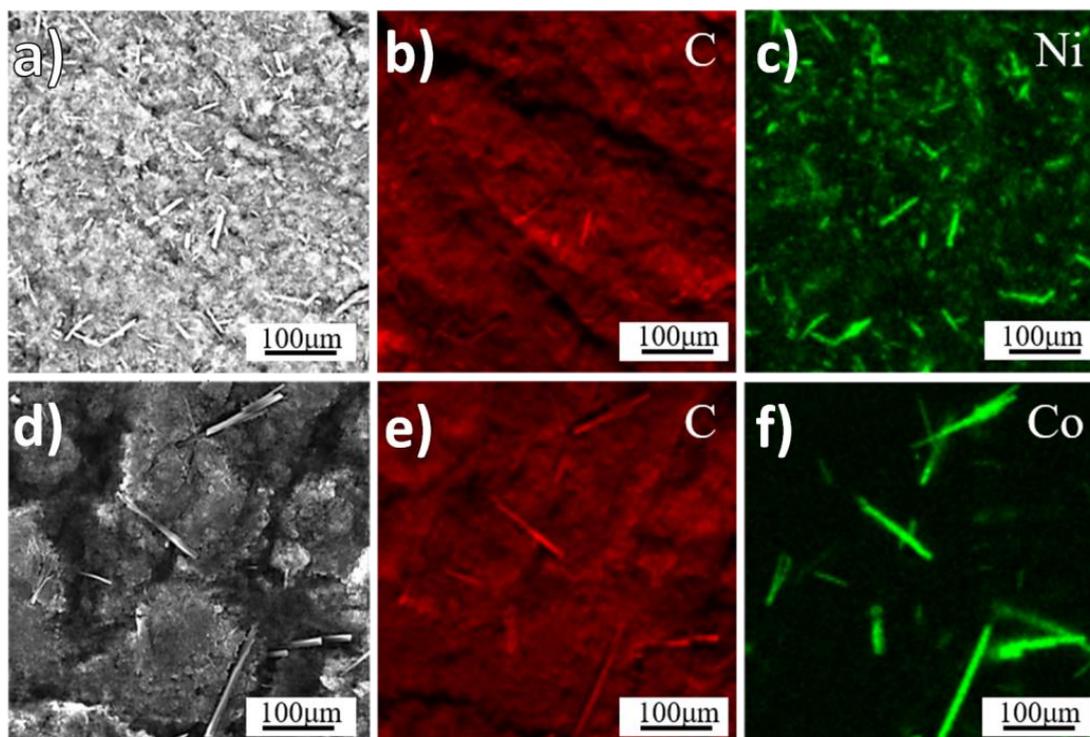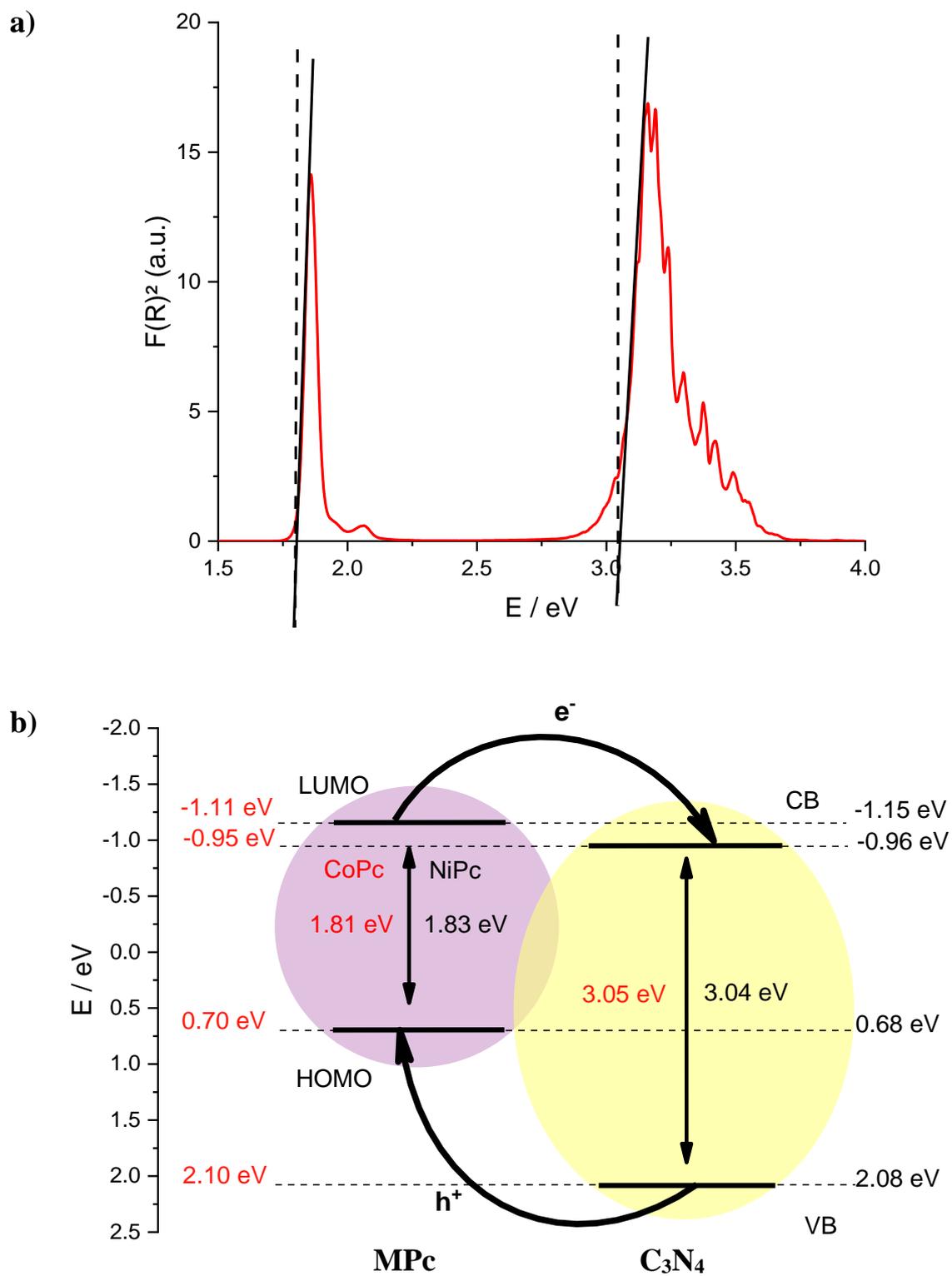

Figure S1 (*a*),(*d*) SEM micrographs and (*b*),(*e*) carbon, (*c*) Ni and (*f*) Co distribution of NiPc- and CoPc-modified *g*-C_3N_4, respectively.
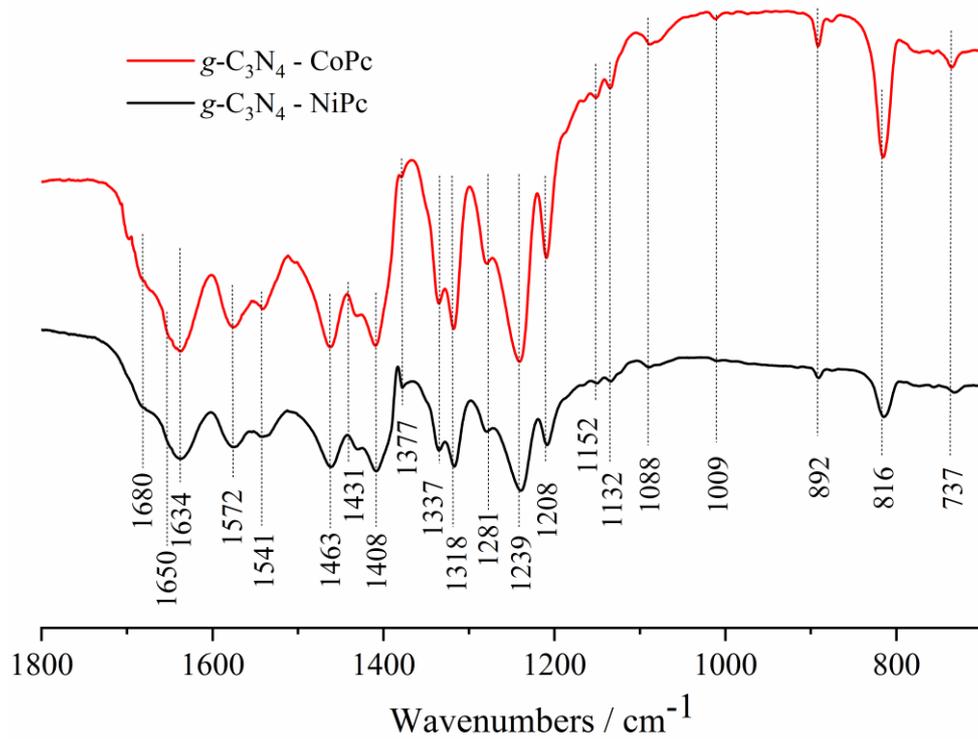
Figure S2 FTIR spectra of *g*-C$_3$N$_4$/NiPc and *g*-C$_3$N$_4$/CoPc nanocomposites

Figure S3 Adsorption–desorption isotherms, surface area and pore size of the nanocomposite samples.

a)

b)

Figure S4 (*a*) The Kubelka–Munk function of the CoPc-modified sample and (*b*) the optoelectronic structure of *g*-C_3N_4 samples modified with (left) CoPc and (right) NiPc.

Table S1 Optoelectronic properties of g-C$_3$N$_4$/MPc composites and their components.

Sample		E$_g$/eV	E$_{CB}$/eV	E$_{VB}$/eV	Refs
g-C$_3$N$_4$/CoPc	**g-C$_3$N$_4$**	3.05	-0.95	2.10	*This research*
	CoPc	1.81	-1.11	0.70	*This research*
g-C$_3$N$_4$/NiPc	**g-C$_3$N$_4$**	3.04	-0.96	2.08	*This research*
	NiPc	1.83	-1.15	0.68	*This research*
g-C$_3$N$_4$		2.9	-1.2	1.75	[16]
CoPc		1.98	3.11	1.13	[19]
NiPc		1.94	3.09	1.15	[1]

Table S2 Surface properties of initial g-C$_3$N$_4$ and MPc-modified composites

Sample	tgα	pH$_{eq}$	PZC	Center type
g-C$_3$N$_4$	-0.0045	6.91	5.5	acid
g-C$_3$N$_4$/CoPc	0.0045	7.09	6.4	base
g-C$_3$N$_4$/NiPc	0.0030	7.06	5.7	base