N-doped carbon nanofibers from pyrolysis of free-base phthalocyanine

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ABSTRACT

Heating free-base phthalocyanine (H₂Pc) at around 450 °C under static vacuum results in the formation of a nonvolatile carbonaceous material through oxidative pyrolysis. We used a number of instrumental techniques to characterize its morphology and chemical composition. According to electron microscopy observations, the dominating morphology is fibrous. The estimated length of individual fibers, which appear as rather homogeneous and continuous structures, is several micrometers, with diameters of roughly 200 nm. According to elemental analysis estimates, the per cent contribution of carbon remains approximately the same as in pristine H₂Pc, but about 5.4 at% of nitrogen is substituted by oxygen. Spectroscopic measurements suggest that the oxygen is incorporated into nanofiber structure in the form of different functionalities containing C=O and C–OH bonds. Raman spectroscopy revealed an approximately equal contribution due to *sp*³ and *sp*²-hybridized carbon atoms, which would make one to expect that the thermal stability of nanofibers must be similar to that of defect-containing nanotubes, graphene oxide and nanodiamond. Nevertheless, according to thermogravimetric curves obtained, nanofibers are at least as thermally stable as graphene and defect-free nanotubes. Density functional theory calculations were employed to suggest possible initial steps of H₂Pc oxidative pyrolysis leading to the formation of nanofibers.

1. Introduction

Phthalocyanines (Pcs), including unsubstituted ones, are found among the most stable organic compounds [1–4]. Despite rather high molecular weight of Pcs (for example, 514.6 Da for the free-base H₂Pc), many of them are capable of subliming without decomposition in moderate vacuum under temperatures of up to about 550 °C [1–9], so that even vapor-phase spectral characterization of Pcs is possible [5–7]. Within the group of unsubstituted H₂Pc and its complexes with 3d transition metals, such as FePc, CoPc, NiPc, CuPc and ZnPc, it is important to emphasize the contribution of central atom into their thermal stability and capability to sublime [7]. However, it turns out that the free ligand H₂Pc is not the least thermally stable of this group, being superior to Pc complexes with Mn(II) [7], Cd(II) and Sn(II) [4]. In other words, the principal factor which defines the stability of Pcs is π -hyperconjugation within the extended aromatic polyazamacrocyclic system.

Due to the same structural feature, Pcs exhibit unique chemical and

physical properties, which make them attractive and promising for a variety of applications. In the context of the present study, it is appropriate to mention their hybrids with carbon nanomaterials, in particular, with carbon nanotubes (CNTs), whose potential applications comprise photovoltaic, photoelectronic, field-emission and spintronic devices, nonlinear optical materials, lithium batteries, gas and liquid-phase electrochemical sensors, catalysts for the oxygen and CO₂ reduction reactions, and high-resistance nanocomposites, among others (see [10,11] and general references therein, as well as [12,13] on oxygen electroreduction). In addition to their high thermal stability, most unsubstituted Pcs are also characterized by their extremely low solubility. While, in principle, it is possible to synthesize their substituted analogues which would be soluble in common organic solvents, this option is impractical since it would raise the cost of Pcs by orders of magnitude. The latter circumstance served as a strong motivation to explore the gas-phase functionalization of CNTs with cheap unsubstituted 3d metal(II) phthalocyanines by means of conventional physical vapor deposition [11,14–17], whose implementation requires

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Fig. 1. Comparison of representative SEM images, at different magnifications, for (a-c) pristine H₂Pc crystals, (d-f) P-400-10 sample and (g-l) P-450-10 sample. For P-450-10 sample, two general types of morphology were analyzed: (g-i) the one matching the shape of starting H₂Pc crystals, and (j-l) mostly disordered and denser morphology. Scale bars: (a, d, g, j) 10 µm, (b, e, h, k) 5 µm and (c, f, i, l) 0.5 µm.

rather undemanding conditions of moderate vacuum (roughly of 10^{-2} Torr) and temperatures of 400–500 °C.

There is one more interesting aspect where two so different types of materials meet, again related to carbon nanostructures. Furthermore, it is also directly related to pyrolysis phenomena. In an endeavor to design a simple and efficient approach to the synthesis of (nitrogen-doped) multi-walled CNTs (MWNTs) and similar carbon nanostructures, since more than two decades ago, several research teams described the nanotube fabrication processes based on pyrolytic decomposition of metal Pcs [18–27]. The starting compounds employed essentially comprise three 3d transition metal(II) complexes: namely, FePc [20–27], CoPc [19,24,26] and NiPc [18,19,24]. The medium and temperature conditions are variable. In particular, MWNTs can be grown under evacuation [18,27] or in vials sealed under vacuum [26],

as well as under acetylene [23] or argon/hydrogen atmosphere [19–22,24,25]. The temperatures of Pc pyrolysis are typically of 800–1000 °C, in extreme cases spanning from 700 °C [18] to 1100 °C [22].

Noteworthy, to the best of our knowledge, free-base H₂Pc does not appear on the list of possible starting materials for carbon nanotube fabrication. The reason is obvious: while the latter is a catalytic process, H₂Pc incorporates no metal, which could serve as a catalyst for efficient CNT growth. Our interest in the free base, within the context of nanotube chemistry, was dictated by quite different considerations. The gas-phase functionalization of CNTs with unsubstituted phthalocyanines via physical vapor deposition proposed by us recently [11,16,17] is particularly straightforward and successful when commercially available and moderate-price complexes such as MnPc, FePc, CoPc,

Fig. 2. Representative HRTEM images, at different magnifications, of characteristic formations found in P-450-10 sample: (a-c) the dominating fibrous structures, with clear separations between individual fibers; (d-e) fused agglomerates of relatively compact nanoparticles; (g) a micrometer-sized rod; (h, i) a micrometer-sized globular formation composed of densely packed nanofibers.

NiPc, CuPc and ZnPc are used, which can sublime without decomposition. At the same time, for certain applications phthalocyanines containing other central metal atoms can be of importance, however, whose thermal stability is insufficient for safe physical vapor deposition, and/or the availability is limited. In this case, the prior gas-phase functionalization of CNTs with H_2Pc followed by its liquid-phase complexation with a metal salt of choice could be a pathway to a broader variety of nanotube-supported unsubstituted Pc complexes.

Recently [28] we attempted to achieve the goal of noncovalent single-walled CNT (SWNT) functionalization with metal-free H_2Pc , under the same conditions as those found to be optimal for the deposition of its metal derivatives (temperature of 450 °C and vacuum of ca. 10^{-2} Torr) [11,16,17]. Nevertheless, the result turned out to be totally unexpected. A minor fraction of phthalocyanine ligand was, as expected, successfully deposited onto SWNTs (synthesized through

chemical vapor deposition process, or CVD), thus yielding the target functionalized material. However, a principal amount of H_2Pc underwent pyrolytic degradation where phthalonitrile, known as the most common starting material for Pc synthesis, was a main decomposition product. In addition to CVD SWNTs, this effect was observed on CVD MWNTs and graphene [28]. The explanation we offered for this anomalous thermal behavior of H_2Pc is based on its covalent attachment to the topological defects (which are ubiquitous in all carbon nanomaterials derived from graphene honeycomb lattice, and exhibit considerable reactivity toward NH and NH_2 groups via nucleophilic addition process), followed by the disintegration of chemisorbed intermediates formed into lower-molecular-weight species, where phthalonitrile dominates.

The experiments described in Ref. 28 gave rise to one more random finding, which was not immediately analyzed and interpreted. Actually,

Fig. 3. Representative EDS results (C, N and O at%) for different selected SEM areas of (a) P-450-10 sample and (b) P-400-10 sample.

it has to do with an experimental error in handling the vacuum system. The main requirement for valid comparison of the results was constant evacuation. This included the blank experiments on H_2Pc sublimation in the absence of carbon nanomaterials, which, under the correct dynamic vacuum of 10^{-1} – 10^{-2} Torr, must result in almost quantitative phthalocyanine recovery. In some blank experiments, however, the

evacuation was interrupted by mistake, and H_2Pc was unable to sublime: the sample remained in the heated zone at 450 °C, losing the characteristic deep violet coloration and acquiring black appearance typical for CNTs, graphene powder and amorphous carbon.

The goal of the present work was to characterize morphology and chemical composition of the above product of H_2Pc pyrolysis by means

Fig. 4. Comparison of FTIR spectra of pristine H₂Pc and P-450-10 sample.

of several instrumental techniques, and to roughly estimate the span of conditions for its formation.

2. Experimental and theoretical methods

2.1. H₂Pc pyrolysis

Free-base phthalocyanine H₂Pc (β -form, 98% purity) was purchased from Sigma-Aldrich; for each experiment, about 200 mg of H₂Pc was used. The tubular quartz reactor employed for most pyrolysis experiments was described previously [28]; its diameter was 25 mm, and length, of 60 cm. The heating device was a Barnstead Thermolyne® 21100 Tube Furnace, which provides stable controllable temperatures of up to 1200 °C. Phthalocyanine was placed onto the bottom of the quartz reactor. This can be done either directly, or with H₂Pc wrapped into aluminum foil to prevent blowing away of the powder upon evacuation: both options provide similar results. After pumping the system out to a vacuum of about 10^{-2} Torr at room temperature, the valve of the reactor was closed, and the furnace was switched on. The tests were performed at four selected temperatures of 350, 400, 450 and 500 °C. The duration of experiments was counted since the moment when the temperature stabilized: it was 2, 5, 10 and 15 h. The sample notation was based on temperature and duration of the experiment: for example, the sample treated at 450 °C for 10 h is denoted as P-450-10.

In addition to the main series of experiments in which quartz reactor was employed, for comparison, we have done several additional tests with H₂Pc heating in a vacuum-sealed vial and in a Pyrex beaker.

2.2. Analytical techniques

Scanning electron microscopy (SEM) characterization of dry samples was done on a JEOL JSM-6510LV microscope operating at 20 kV, which is coupled to an INCA Energy 250 Energy Dispersive X-ray (EDS) Microanalysis System from Oxford Instruments. For high-resolution transmission electron microscopy (HRTEM), a JEOL JEM 2100F was employed at 200 kV voltage; the samples were deposited onto Formvar-covered copper grids from ultrasonicated ethanol suspensions.

Fourier-transform infrared (FTIR) spectra were recorded under room temperature and atmospheric pressure, using a Spectrum 100 FTIR PerkinElmer spectrophotometer, complemented with a universal attenuated total reflection (ATR) sampling accessory. A Thermo-Nicolet Almaça Dispersive Raman and a Thermo Fisher Scientific micro-Raman

Fig. 5. Deconvolution of C 1s, N 1s and O 1s components in XPS spectra of P-400-10 and P-450-10 samples.

Fig. 6. Comparison of Raman spectra of pristine H₂Pc and P-450-10 sample.

Fig. 7. Comparison of TGA and DTA curves for (a) pristine H₂Pc and (b) P-450-10 sample.

spectrometer (laser wavelength for both, $\lambda = 532$ nm) were employed for Raman spectra acquisition. X-ray photoelectron spectroscopy (XPS) studies were performed using a Thermo K-Alpha XPS system using monochromated Al K- α X-rays (energy of 1486.6 eV). The X-ray source was operated at 12 kV accelerating voltage and 6 mA emission. An

electron flood gun was employed for charge compensation. Peak fitting was performed using the Thermo Scientific Advantage XPS software package. The background signal subtraction of each peak region for each sample was removed with the aid of a Shirley background model. Peak deconvolution was achieved by fitting symmetric Gaussian-Lorentzian peaks.

Thermogravimetric and simultaneous differential thermal analysis (TGA and DTA, respectively) curves were recorded on a NETZSCH STA 449C Jupiter apparatus, with an air flow of 30 ml/min and a heating rate of 10 °C/min up to 1000 °C.

2.3. Theoretical calculations

Density functional theory (DFT) calculations were carried out by using the numerical-based module DMol³ [29–32] within the Materials Studio 6.0 software package. The particular computational technique of choice was the general gradient approximation functional PBE (Perdew-Burke-Ernzerhof correlation [33]) in combination with the empirical dispersion correction developed by Grimme [34]; the resulting combination is usually referred to as PBE-D. The double numerical basis set DNP [32], which has a polarization *d*-function added on all non-H atoms and a polarization *p*-function added on all H atoms, was used in conjunction with PBE-D technique. Other computation settings included all-electron core treatment, Fermi orbital occupancy (without thermal smearing) and a global orbital cutoff of 4.7 Å. Full geometry optimization and calculations of electronic characteristics were done with the quality and convergence criteria set to ‘fine’.

3. Results and discussion

As it was mentioned above, an anomalous behavior of H₂Pc in blank sublimation experiments [28] was detected when the constant evacuation to 10^{−1}–10^{−2} Torr was interrupted by mistake. As a result, phthalocyanine was unable to sublime and remained in the heated zone at 450 °C, losing the characteristic deep violet coloration and acquiring black appearance typical for CNTs, graphene powder and amorphous carbon. Further attempts to sublime the material formed at 450 °C or even higher temperature under the correct vacuum were unsuccessful.

Bearing in mind the reports by other research groups on CNT fabrication by means of pyrolytic decomposition of metal Pcs at 700–1100 °C [18–27], we analyzed the possibility of formation of similar carbon nanostructures by using electron microscopy techniques, namely SEM and HRTEM. The general sample morphology was characterized by SEM, in comparison with that for pristine H₂Pc crystals (β -form). As one can see in Fig. 1a–c, the latter are needle-shaped of roughly 10¹–10³ μ m length and 1–10 μ m width. The microstructure of pyrolysates, exemplified here by P-450-10 sample (Fig. 1g–l), reflects to a great degree the dimensions of H₂Pc crystals, which is especially evident in Fig. 1g–i. However, instead of solid appearance, pyrolysis particles are mostly observed as sponge-like agglomerates of irregularly shaped fibers. At some sites of the sample, continuous and denser morphology of agglomerates dominates, with less evident presence of the formations matching the shape and dimensions of H₂Pc crystals (Fig. 1j–l). (It is likely that the more ordered structures were simply crushed during SEM sample preparation, or during pyrolysis extraction from the reactor.) Additionally, one should mention a minor presence of platelet-like formations, like the one seen in top-left part of Fig. 1i.

Even though SEM revealed a fibrous morphology of pyrolysates, reminding in principle that of multi-walled CNTs, this technique is unable to discern whether the fibers have inner cavity. To provide further structural details, we employed transmission electron microscopy. A series of representative HRTEM images of characteristic formations found in P-450-10 sample is shown in Fig. 2. In line with the results of SEM imaging (Fig. 1g–i), the dominating morphology turns to be fibrous one, with clear separations between individual fibers

Fig. 8. Isosurface plots computed for isolated H₂Pc molecule: (a) electrostatic potential (isosurface at 0.016 a. u.), with red and blue lobes corresponding to positive and negative potential, respectively, and atomic charges obtained from Mulliken population analysis; (b) frontier orbitals (isosurfaces at 0.03 a. u.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 2a-c). The estimated length of the latter is several micrometers, with diameters of roughly 200 nm. While these dimensions match, in principle, those of common MWNTs, neither inner cavities nor concentric walls can be discerned here: instead, the nanofibers appear as rather homogeneous and continuous structures. At other sites of P-450-10 sample (Fig. 2h, i), similar nanofibers are densely packed into micrometer-sized globular formations, which apparently match the morphology observed by SEM in Fig. 1j-l. As minor components, we also observed fused agglomerates of relatively compact nanoparticles (Fig. 2d-e), as well as rod-like formations (Fig. 2g), which generally remind MWNTs, but have larger, micrometer-scale dimensions (including the diameter).

An important question to answer is under what conditions (temperature, pyrolysis duration and vacuum) the above structures can efficiently form. As was specified in the experimental section, a series of tests was performed at four selected temperatures of 350, 400, 450 and 500 °C, with the heating duration of 2, 5, 10 and 15 h (counted since the moment when the temperature stabilized). The temperature of 350 °C was too low, where no changes in H₂Pc crystal morphology was detected by SEM even after 15 h, regardless of whether the experiment was carried out in the quartz reactor under vacuum or in a Pyrex beaker under air (Fig. S1a of Supplementary material). Another extreme is the heating at 500 °C, where already after 2 h, more than a half of starting phthalocyanine sublimed, leaving a minor amount (of ca. 10% of the starting reagent) at the reactor bottom (Fig. S1b of Supplementary material). In other words, the residence time of H₂Pc in the hot zone at 500 °C is insufficient. Notable morphological changes were observed starting with 400 °C. At the same time, H₂Pc crystals kept their integrity, and even after 10 h (quartz reactor under vacuum), only signs of their corrosion were observed by SEM, as can be seen from Fig. 1d-f. The temperature at which the rates of H₂Pc pyrolysis and sublimation can roughly equilibrate is 450 °C. Interestingly, the product morphology generally does not depend on heating duration, remaining essentially the same in the experiments performed at 2, 5, 10 and 15 h. The yields were poorly reproducible and fluctuated between about 3 and 90%, which can be explained by impossibility to reproduce air leaks after closing the vacuum line. Nevertheless, the residual pressure turns to be incomparably lower with respect to atmospheric one: in a blank experiment with empty sublimation system (without H₂Pc and heating), it does not increase to > 4 Torr at 10 h after interrupting evacuation. For comparison, heating in a Pyrex beaker under air at 450 °C results in gradual burning of H₂Pc, where the amount of solid residue after 2, 5, 6 and 9-h heating was found to be about 23, 14, 1 and 0%, respectively, of starting phthalocyanine weight. On the other hand,

H₂Pc heated at 450 °C in a small (compared to the size of quartz reactor) vacuum-sealed vial did not undergo evident changes. The above observations point to the crucial role of minor amounts of air oxygen in H₂Pc pyrolysis process, supplied to the sublimation system due to air leaks.

It is logical to expect that, as a result, oxygen covalently bonds to phthalocyanine macrocycles and/or to the products of their thermal transformations. In this case, it must be readily detected by spectroscopic techniques, first of all, by EDS coupled to SEM. In neat H₂Pc (brutto formula C₃₂H₁₈N₈), the C:N atomic ratio is 4:1 (or 80:20 to sum up to 100 at%), with no structural oxygen present. According to EDS analysis of P-450-10 sample probed at 19 different sites (representative results are shown in Fig. 3a), the content of C, N and O turned to be 71.13–93.76, 0–31.54 and 3.64–7.26 at%, respectively, with the corresponding averaged values of 79.27, 14.60 and 5.40 at%. In other words, the per cent contribution of carbon remains approximately the same as in pristine H₂Pc, but about 5.4 at% of nitrogen is substituted by oxygen. In line with the results of SEM imaging of P-400-10 sample (Fig. 1d-f), which is a product of the very early steps of H₂Pc pyrolysis, the average O content is much lower than for P-450-10 sample. Namely, the average content of C, N and O was found to be 77.6, 19.27 and 3.01 at%, though its EDS analysis probed at 11 sites (representative results are exemplified in Fig. 3b) gave generally broader ranges of 71.27–83.56, 7.26–25.13 and 0.94–9.12 at%, respectively. Needless to say that the above values reflect the surface composition of H₂Pc crystals, whose interiors remain intact.

To give an insight into the chemical nature of new structural features resulting from H₂Pc pyrolysis, we employed FTIR and XPS spectroscopies. As one can see from Fig. 4, the main infrared spectral features of pristine H₂Pc in the lower-frequency region are the bands at 712–727 (ν_{CH}), 870 (in-plane vibration), 1000 (N–H in-plane bending), 1092 (C–H in-plane deformation), 1187 (C–N in-plane bending), 1318 (δ_{NH}), 1437 (CC stretching in isoindole moieties), 1500 (C=N stretching) and 1608 cm⁻¹ (C=C deformation of macrocyclic system) [35]. The lower-intensity higher-frequency modes are due to aromatic ν_{CH} vibrations at 3011 and 3048 cm⁻¹, as well as ν_{NH} vibrations at 3288 cm⁻¹. In the spectrum of P-450-10 sample, the latter higher-frequency features do not exhibit substantial changes; nevertheless, the general background in this region is dominated by a low-intensity diffuse absorption band centered at ca. 3500 cm⁻¹, which is indicative of the formation of O–H functionalities. In a similar way, FTIR spectrum of P-450-10 sample in the lower-frequency region shares most features with the spectrum of pristine H₂Pc. At the same, the signals tend to notably broaden due to the appearance of a large number of closely

Fig. 9. Proposed initial steps of H₂Pc oxidative pyrolysis. (a) The model system is two phthalocyanine molecules (2H₂Pc) with a mutual orientation as in the β -crystalline form. The distance of 3.061 Å (dotted line) is the only approach between the two molecules which is closer than typical separations of > 3.1 Å. The LUMO isosurface (at 0.03 a.u.) plot shown on the right indicates a possible site of nucleophilic attack with O₂ molecule (red arrows). (b) The product of nucleophilic addition of O₂ onto the surface phthalocyanine molecule of 2H₂Pc model. The pyrrole ring where O₂ attached undergoes strong distortion from macrocyclic plane, so that its N(H) atom approaches (dotted line) one of H(C) atoms of the subsurface molecule. In order to form a new N–H bond between the latter two atoms, a few existing covalent bonds have to be broken (marked with the solid red lines). In the resulting structure (c) the surface macrocycle turns to be strongly distorted, and both molecules become reactive due to the presence of several sites with high unpaired electron density (spin density isosurface at 0.03 a. u. on the right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

related structural elements. In addition to that, here one can see at least two new features. The first one is a broad and intense band at 1590 cm⁻¹, which apparently combines aromatic ν_{CC} , $\nu_{C=N}$, $\nu_{C=O}$ in quinones and/or conjugated ketones, and δ_{NH} vibrations in secondary amines [36,37]. The second feature at 1723 cm⁻¹ corresponds to $\nu_{C=O}$ vibrations in COOH groups. What was totally unexpected is the appearance of clearly distinguishable nitrile ($\nu_{C=N}$) band at 2227 cm⁻¹, along with a small peak at 2165 cm⁻¹ attributable to $\nu_{C=C}$ vibrations.

The deconvolution of C 1s and N 1s peaks in XPS spectra of P-400-10 and P-450-10 samples (Fig. 5) reveals a series of characteristic components found in the XPS spectrum of pristine H₂Pc [38]. The particular common C 1s features are the lowest energy peak at 284.7 eV due to *sp*² carbon atoms in phenylene rings, the one at 286.3 eV corresponding to C atoms connected to two nitrogen atoms (N–C–N) and its satellite at 287.5–288.0 eV. One should note that C=O group may also show a C 1s peak in the latter region, which would agree with the above interpretation of FTIR spectra, and that some contribution in the C1s spectrum of P-400-10 at ~286 eV can be due to C–O bonds. In addition, the intermediate-energy peak at 285.5–285.8 eV detected for

both pyrolysates can be attributed to C atoms in broken macrocyclic system. A special similarity between pristine and pyrolyzed H₂Pc can be observed in the case of N 1s deconvolution, where all three materials exhibit two peaks at 398.6–398.7 and 400.1–400.2 eV due to *meso*-bridging and central nitrogen atoms, respectively [38]. As it could be expected, the most interesting picture is observed in O 1s spectra of the two pyrolyzed samples. They turn to be very different to each other. In the case of P-400-10 sample, one can clearly separate two peaks at 531.6 and 533.8 eV. The former can be assigned to carbonyl groups C=O: such a peak can be found in XPS spectra of oxidized carbon nanomaterials including MWNTs [39] and graphene oxide (GO) [40]. The presence of the higher-energy peak at 533.8 eV was interpreted elsewhere in different ways: for example, it was attributed to carboxylic functionalities in GO [41–43], as well as to C–O(H) and ether groups [39,40]. Interestingly, in the O 1s deconvolution for P-450-10 sample, corresponding to a more developed degree of pyrolysis, only one peak at 532.5 eV can be found. Again, different assignments can be suggested: in particular, to C=O/O–C=O groups [41–43], or to a combination of COOH, anhydride, ester and lactone functionalities [39].

The most striking changes due to pyrolysis were observed by Raman spectroscopy. As it is evident from Fig. 6, almost no Raman features of pristine H₂Pc can be found in the spectrum of P-450-10 sample. Instead, two broad bands appear, which are centered at 1337 and 1585 cm⁻¹. This resulting general appearance of Raman spectrum is very typical and well familiar within the area of carbon nanomaterials: the two modes observed are called disorder (D) and graphite (G) bands, which correspond to *sp*³ and *sp*²-hybridized carbon atoms. They can be found in the spectra of essentially all nanocarbons, at variable *I*_D/*I*_G intensity ratios, and at Raman shifts fluctuating within a few tens of cm⁻¹. Particular values of the latter are as follows (D and G band, respectively): for CVD SWNTs with defects, 1332–1351 and 1583–1590 cm⁻¹ [11,17,44]; for MWNTs, 1334–1355 and 1562–1604 cm⁻¹ [44–47]; for graphene, 1339 and 1572 cm⁻¹ [48]; for GO, 1338–1355 and 1565–1590 cm⁻¹ [42,43,49]; for nanodiamond, 1320 and 1590 cm⁻¹ [43,50]. Furthermore, related nitrogen-doped materials exhibit a very similar spectral pattern, with the following examples of Raman shifts for D and G band, respectively: CNTs, 1360 and 1580 cm⁻¹ [51]; carbon nanoparticles, 1350 and 1585 cm⁻¹ [52]; graphene, 1330 and 1580 cm⁻¹ [53]. In the present case (Fig. 6), an *I*_D/*I*_G intensity ratio close to 1 is indicative of an approximately equal contribution due to *sp*³ and *sp*²-hybridized atoms.

In order to more closely relate the products of H₂Pc pyrolysis to a particular nanocarbon form, we compared TGA and DTA curves measured for P-450-10 sample with those obtained for pristine H₂Pc (Fig. 7). As a general rule, when the presence of *sp*³-hybridized C atoms is insignificant, nanomaterial decomposes completely at 750–800 °C (for TGA measurements in air atmosphere), as it is observed for graphene [48] and purified SWNTs [44,54]. In contrast, a high content of *sp*³-hybridized C atoms, which manifest itself in Raman spectra as a high-intensity D band, strongly reduces the final decomposition temperature in air to roughly 600 °C: this is the case of MWNTs [43–47], GO [42,43,49] and nanodiamond [43,50]. As follows from the TGA curve presented in Fig. 7b, the material constituting P-450-10 sample is at least as thermally stable as graphene and defect-free SWNTs, exhibiting a final decomposition temperature of 827 °C. Here, the first minor weight loss of 4.5% is due to impurities adsorbed from air (including water), which is followed by two almost indistinguishable steps starting at 435 and 683 °C, with the corresponding DTA maxima at 574 and 778 °C. From comparison with the results of SEM and TEM imaging, one can suggest that these two steps match the existence of nanofiber phases of lower (Figs. 1g-i and 2a-c) and higher (Figs. 1j-l and 2h, i) packing density, respectively. In the case of neat H₂Pc, the first slight weight loss of 4.5% (apparently due to impurities) is followed by three main steps at 481–549 (25.2%), 549–620 (30.8%) and 620–860 °C (39.7%), with the corresponding DTA peaks at 543, 596 and 759 °C. The first two weight losses are very steep, whereas the third one is very similar to the main weight loss observed for P-450-10 sample, both in terms of the slope and the final decomposition temperature. One can suggest that the residue formed after reaching ca. 600 °C is most likely very similar in structure and composition to the nanostructured products of H₂Pc pyrolysis (to P-450-10 sample in particular). As a whole, TGA/DTA results turned to be totally unexpected given the high content of *sp*³-hybridized carbon atoms in pyrolyzed H₂Pc found by Raman spectroscopy.

Due to a high complexity of phthalocyanine molecule and to the need to consider intermolecular interactions in the solid phase, it is virtually impossible to suggest a straightforward mechanism of H₂Pc oxidative pyrolysis. What we attempted to do, by employing DFT calculations (at the PBE-D/DNP level of theory), is to envision its very first steps: namely, how the interaction of macrocyclic molecules found on the surface of β -form of crystalline H₂Pc with molecular oxygen can generate reactive chemical species, capable of further high-temperature transformations. First of all, one has to identify possible sites within an isolated H₂Pc molecule, which can serve as a target for nucleophilic attack with O₂ molecule. Fig. 8a shows electrostatic potential

distribution in H₂Pc along with atomic charges obtained from Mulliken population analysis. One can see that the most positively charged atoms (and thus, the most plausible sites for nucleophilic O₂ addition) are the C atoms of 16-membered macrocyclic system. All of them are connected to two adjacent N atoms of the macrocycle and have an atomic charge from 0.263 (two pyrrole rings without H atom) to 0.291 (two pyrrole rings with H atom), providing an important contribution into both LUMO and HOMO orbitals of phthalocyanine system (Fig. 8b). In turn, logically, the latter type of C atoms can attract O₂ nucleophile more efficiently.

At the second step, we analyzed a possible behavior of the product of O₂ addition onto the site identified above. Due to computational limitations, the model system considered included only two phthalocyanine molecules (referred to as 2H₂Pc; Fig. 9a) laying at the crystal surface, with the same mutual orientation as the one observed in the β -crystalline form. In the optimized geometry of 2H₂Pc, all intermolecular separations are > 3.1 Å, except for one distance of 3.061 Å (dotted line). The LUMO isosurface plot shown on the right of Fig. 9a indicates the possible site of nucleophilic attack with O₂ molecule (red arrows). After the addition of O₂ onto the superior (that is, found on crystal surface) phthalocyanine molecule, the pyrrole ring where O₂ was attached undergoes strong distortion from macrocyclic plane, so that its N (H) atom approaches (dotted line) one of H(C) atoms of the subsurface molecule (Fig. 9b). The formation energy for this species (denoted as 2H₂Pc + O₂) is 37.27 kcal/mol, i.e., the process is endothermic. In order to form a new N–H bond between the latter two atoms, a few existing covalent bonds have to be broken (marked with solid red lines) to avoid hypervalency. In the resulting structure (2H₂Pc + O₂b; Fig. 9c), whose formation is highly endothermic (73.36 kcal/mol), the surface macrocycle turns to be strongly distorted, and both surface and subsurface molecules become reactive due to the appearance of several sites with high unpaired electron density (spin density plot on the right of Fig. 9c). The most important factor for inducing further pyrolytic transformations is a radical character of the subsurface phthalocyanine species, acquired as a result of H atom abstraction by the surface H₂Pc molecule.

4. Conclusions

Heating free-base phthalocyanine H₂Pc at temperatures around 450 °C under static vacuum prevents its sublimation recovery, but instead results in the formation of a carbonaceous material through oxidative pyrolysis. According to electron microscopy observations, the dominating morphology of pyrolysate is fibrous, usually with clear separations between individual fibers. The estimated length of the latter is several micrometers, with diameters of roughly 200 nm. While these dimensions match, in principle, those of common MWNTs, neither inner cavities nor concentric walls can be discerned by TEM: instead, the nanofibers appear as rather homogeneous and continuous structures. According to the elemental analysis by SEM-coupled EDS, the per cent contribution of carbon remains approximately the same as in pristine H₂Pc, but about 5.4 at% of nitrogen is substituted by oxygen. The results of FTIR and XPS spectroscopy suggest that the oxygen is incorporated into nanofiber structure in the form of different functionalities containing C=O and C–OH bonds, which might include COOH, anhydride, ester and lactone groups. Raman spectroscopic measurements revealed an approximately equal contribution due to *sp*³ and *sp*²-hybridized carbon atoms, which would make one to expect that the thermal stability of nanofibers must be similar to that of defect-containing CNTs, graphene oxide and nanodiamond, whose final decomposition temperature in air is roughly 600 °C. Nevertheless, as follows from the TGA and DTA curves obtained, N-doped nanofibers are at least as thermally stable as graphene and defect-free SWNTs, exhibiting a final decomposition temperature of 827 °C. Based on the results of DFT calculations, one can suggest that oxidative pyrolysis of β -crystalline form of H₂Pc can be initiated through the nucleophilic

addition of O₂ molecule onto one of pyrrole rings of phthalocyanine molecule laying at the crystal surface.

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CRediT authorship contribution statement

Vladimir A. Basiuk: Conceptualization, Methodology, Supervision, Resources, Writing - original draft, Writing - review & editing, Visualization. **Lina M. Bolivar-Pineda**: Investigation, Validation, Visualization. **Victor Meza-Laguna**: Investigation, Validation, Visualization. **Alexey M. Glushenkov**: Investigation, Visualization, Resources. **Billy J. Murdoch**: Investigation, Visualization, Resources. **Elena V. Basiuk**: Resources, Writing - original draft, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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