



HAL
open science

Preparation and characterization of F-, O-, and N-containing carbon nanoparticles for pH sensing

Vladyslav Lisnyak, Alexander Zaderko, Ruslan Mariychuk, Volodymyr Lysenko, Olga Yu. Boldyrieva, Valeriy Skryshevsky, Gauhar Mussabek, Yerzhan Taurbayev, Nazym Zhylkybayeva, Oksana Yu. Tananiko

► To cite this version:

Vladyslav Lisnyak, Alexander Zaderko, Ruslan Mariychuk, Volodymyr Lysenko, Olga Yu. Boldyrieva, et al.. Preparation and characterization of F-, O-, and N-containing carbon nanoparticles for pH sensing. *Applied Nanoscience*, 2021, 10.1007/s13204-021-01725-7 . hal-03419793

HAL Id: hal-03419793

<https://hal.science/hal-03419793>

Submitted on 8 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Preparation and characterization of F-, O-, and N-containing carbon nanoparticles for pH sensing

Vladyslav Lisnyak, Alexander Zaderko, Ruslan Mariychuk, Volodymyr Lysenko, Olga Yu. Boldyrieva, Valeriy Skryshevsky, Gauhar Mussabek, Yerzhan Taurbayev, Nazym Zhylkybayeva, Oksana Yu. Tananiko

► **To cite this version:**

Vladyslav Lisnyak, Alexander Zaderko, Ruslan Mariychuk, Volodymyr Lysenko, Olga Yu. Boldyrieva, et al.. Preparation and characterization of F-, O-, and N-containing carbon nanoparticles for pH sensing. Applied Nanoscience, Open Mind Journals Ltd., 2021, 10.1007/s13204-021-01725-7 . hal-03419793

HAL Id: hal-03419793

<https://hal.archives-ouvertes.fr/hal-03419793>

Submitted on 8 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



2 Preparation and characterization of F-, O-, and N-containing carbon 3 nanoparticles for pH sensing

4 Vladyslav V. Lisnyak^{1,2} · Alexander N. Zaderko³ · Ruslan Mariychuk² · Volodymyr Lysenko⁴ ·
5 Olga Yu. Boldyrieva¹ · Valeriy A. Skryshevsky³ · Gauhar Mussabek^{5,6} · Yerzhan Taurbayev^{5,6} ·
6 Nazym Zhylykybayeva⁶ · Oksana Yu. Tananiko¹

7 Received: 3 January 2021 / Accepted: 31 January 2021
8 © King Abdulaziz City for Science and Technology 2021

9 Abstract

10 A novel sensing system was designed for pH measurements based on the enhanced and quenched photoluminescence (PL) and UV–Vis absorption of the diluted water solutions of F-, O-, and N-containing carbon nanoparticles (FON-CNPs). These FON-CNPs were solvothermally synthesized, dissolved, ultra-filtrated, and separated by thin-layer chromatography. The total fluorine content in them was found to be 1.2–1.5 mmol per gram. Their TGA showed a total weight loss of 52.7% because of the thermal decomposition and detachment of the surface groups and the partial burning of the functionalized shell on the carbon core at temperatures below 1200 °C. TEM and Raman data confirmed the presence of graphitic structures in the carbon core. From the results of ATR FTIR and UV–Vis spectroscopies, we showed that a carbon shell incorporates different functional groups covering the carbon core. The surface groups of the carbon shell include carboxyl, phenolic, and carbonyl groups. Heterocyclic N-containing and amino groups and trifluoromethyl groups supporting the hydrophobicity were also found. We suggested the possible reasons for the pH responses obtained with the sensing system considering them dependent on the de-protonation of functional groups with pH change.

21 **Keywords** F-,O- and N-containing carbon NPs · Solvothermal synthesis · Photoluminescence · pH nanosensors

A1	✉ Vladyslav V. Lisnyak	Oksana Yu. Tananiko	A19
A2	lisnyak@univ.kiev.ua	otananaiko@gmail.com	A20
A3	Alexander N. Zaderko	1 Faculty of Chemistry, Taras Shevchenko National University	A21
A4	indeo1016@gmail.com	of Kyiv, 64/13 Volodymyrs'ka Str., Kyiv 01601, Ukraine	A22
A5	Ruslan Mariychuk	2 Department of Ecology, Faculty of Humanities and Natural	A23
A6	ruslan.mariychuk@unipo.sk	Sciences, The University of Prešov in Prešov, 17th November	A24
A7	Volodymyr Lysenko	Str. 1, 08001 Prešov, Slovakia	A25
A8	vladimir.lysenko@univ-lyon1.fr	3 Institute of High Technologies, Taras Shevchenko National	A26
A9	Olga Yu. Boldyrieva	University of Kyiv, 64, Volodymyrs'ka Street, Kyiv 01601,	A27
A10	ob@univ.kiev.ua	Ukraine	A28
A11	Valeriy A. Skryshevsky	4 Light Matter Institute, UMR-5306, Claude Bernard	A29
A12	skryshevsky@gmail.com	University of Lyon, 2 rue Victor Grignard,	A30
A13	Gauhar Mussabek	69622 Villeurbanne, France	A31
A14	gauhar.musabek@kaznu.kz	5 Institute of Information and Computational Technologies,	A32
A15	Yerzhan Taurbayev	125, Pushkin Str., Almaty 050000, Kazakhstan	A33
A16	taurbayev@taur.kaznu.kz; taurbayev@mail.ru	6 Faculty of Physics and Technology, Al-Farabi Kazakh	A34
A17	Nazym Zhylykybayeva	National University, 71 Al-Farabi Ave., Almaty 050040,	A35
A18	naz-30@mail.ru	Kazakhstan	A36

22 Introduction

23 Carbon nanoparticles (CNPs), including carbon dots (CDs),
24 are of special attention in a broad range of applications because
25 of their tunable optical properties and excellent biocompatibility
26 (Xia et al. 2019; Sun et al. 2020; Nevar et al. 2020; Tara-
27 senka et al. 2017; Zuo et al. 2018; Pal et al. 2020). These green
28 and nontoxic carbonic nanomaterials were used as the fluo-
29 rophores and absorbers. In case of an increase in the spectral
30 overlap between absorbing species and fluorophore, one can
31 see a decrease in fluorescence/photoluminescence intensity of
32 NPs. This decrease is considered as a response and enables
33 quantitative measurement of the adsorbents. Today, numerous
34 publications are devoted to the application of CNPs as selec-
35 tive photoluminescence on–off–on probes (Novoa De León
36 et al. 2019; Feng et al. 2019; Zan et al. 2020; Wang et al. 2019).

37 On the other hand, many semiconductors showed the pho-
38 toluminescence (PL) intensity and decay lifetime strongly
39 dependent on the value of pH. This pH dependence, in the case
40 of porous Si, is explained by competition between UV-induced
41 hydrogen effusion, hydrogen adsorption from the buffer solu-
42 tion, and surface oxidation. Within the phenomenon, pH sen-
43 sors were already proposed (Benilov et al. 2007). Besides,
44 when different luminescent NPs are storage in the porous Si
45 and nanosilicas, they can be used as specific probe units in
46 multicomponent sensors (Serdiuk et al. 2011; He et al. 2020).

47 Despite a wide variety of CNPs, the fluorine and nitrogen-
48 containing CNPs have rarely been used as effective pH sensors
49 (Long et al. 2018; Su et al. 2019) and for other application
50 until nowadays (Sim Y et al. 2019; Wang et al. 2019; Liu et al.
51 2019; Jiang et al. 2019).

52 In this work, we report on new fluorine-, oxygen-, and nitro-
53 gen-containing carbon nanoparticles (FON-CNP). They were
54 obtained by a one-stage solvothermal method from citric acid,
55 urea, and 3-(trifluoromethyl) aniline. The latter was applied
56 as a source of fluorine and nitrogen. Here, citric acid and urea
57 were pyrolyzed to form the carbon matrix. The resulting FON-
58 CNPs have excellent water solubility and bright PL in aqueous
59 solutions. Remarkably, the PL intensity and UV absorption of
60 FON-CNP showed pH-dependent responses. The PL intensity
61 maintains certain stability over a wide pH range of 1.0–11,
62 showing good reversibility. Based on the pH-dependent behav-
63 ior of FON-CNPs, one can create a sensor system for accurate
64 pH measurements.

65 Experimental

66 Materials

67 3-(Trifluoromethyl)aniline (>99%, CAS#98–16–8) provided
68 by Merck was used for the preparation of the FON-CNPs.

69 Pharmaceutical-grade anhydrous citric acid and pro-analysis
70 quality urea were supplied by LLC Himlaborreaktiv (Bro-
71 vary, Ukraine). LLC Himlaborreaktiv solvents, acids, bases,
72 and reagents in the present study were of analytical purity
73 and were used as received. For dilution, Millipore deionized
74 water was used in the experiments. Phosphate-buffered (PB)
75 solutions of different pH levels were prepared by titrating
76 0.01 mol L⁻¹ phosphoric acid solution with 1 M NaOH solu-
77 tion to the required pH values. The preparation was carried
78 out under control with a pH electrode (InLab Routine Pro,
79 Mettler Toledo).

Synthesis of FON-CNPs

81 The samples of FON-CNPs were synthesized by the sol-
82 vothermal method (Zaderko 2020). In a typical synthesis
83 procedure, we had composed a mixture of 10 g of urea
84 (0.167 mol), 16 g of anhydrous citric acid (0.083 mol), and
85 3.35 g of 3-(trifluoromethyl) aniline (0.021 mol). The mix-
86 ture was placed in a glass reactor and left it open. The reac-
87 tor with the mixture within was placed in an electric oven,
88 which was heated from 25 to 135 °C for 30 min, and held
89 at this temperature for the next 30 min to get a yellow melt
90 from the stored mixture. After that, the reactor temperature
91 was increased from 135 to 165 °C for 10–13 min. After 2 h
92 of heat treatment at this temperature, the melt was trans-
93 formed into a dark brown shining solid. 75 ml of an ethanol/
94 water solution (50/50) was added to the reactor after the
95 synthesis to dissolve the solid. The resulting dark brown
96 solution was then filtered through Whatman filter paper and
97 acidified by adding 20 ml of concentrated HCl. When HCl
98 was added, FON-CNP flocks began to form in the solution.
99 After holding for an hour, the precipitate was separated by
100 vacuum filtration, and the resulting brownish powder was
101 dried in the air.

Instrumentation

102 Fourier-transform infrared attenuation total reflectance
103 (FTIR ATR) spectra were collected on a Shimadzu IRPres-
104 tige 21 instrument. A MIRacle module (Pike Technol-
105 ogy), with a ZnSe crystal plate for the sample contact,
106 was used during FTIR ATR measurements. Transmission
107 electron microscopy (TEM) images were captured
108 on an electronic microscope (Jeol JEM-2100F, 200 kV).
109 Energy-dispersive X-ray (EDX) analysis of TEM imaged
110 samples was carried out on an AZtec X-MAX energy-dis-
111 persion spectrometer from Oxford Instruments. Ultraviolet-
112 visible (UV–vis) absorption spectra were recorded by a
113 UV–vis spectrophotometer (Varian Cary 50) at an UV–Vis
114 scan rate of 600 nm min⁻¹. PL spectra of the solutions of
115 FON-CNPs were measured at 20 °C on the Agilent Cary
116 Eclipse fluorescence spectrophotometer (Xe flash lamp).
117

118 Thermogravimetric analysis (TGA) of dried samples was
 119 carried out in an argon gas flow with a custom instrument
 120 reported elsewhere (Tsapyuk et al. 2020). Measurements
 121 of the total fluoride content (C_F) were done in an aqueous
 122 solution prepared by pyrolytic decomposition of samples
 123 (Zaderko et al. 2019). The Mettler Toledo (SevenExcel-
 124 lence™) pH meter was used to measure pH levels with
 125 maximum measurement accuracy.

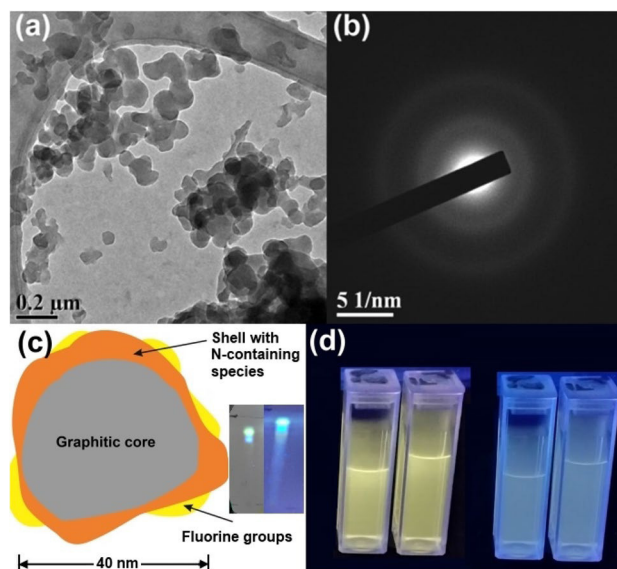
126 Raman spectrum of FON-CNPs was collected in back-
 127 scattered mode with a HORIBA Jobin Yvon-LabRAM ARA-
 128 MIS integrated confocal micro-Raman system equipped with
 129 a microscope (BX41, Olympus, Japan) and a diode-pumped
 130 solid-state laser. A 633 nm laser was focused by an Olympus
 131 100× objective lens (UPLSAPO, NA = 0.95) on the sample
 132 placed in an open-air environment at room temperature. The
 133 excited Raman scattering signal was collected by a Labram
 134 ARAMIS (Jobin–Yvon) spectrometer.

135 Results and discussion

136 EDX analysis confirms the presence of fluorine, oxygen, car-
 137 bon, and nitrogen in the FON-CNPs. According to the chem-
 138 ical analysis, the fluorine content C_F equals 1.2–1.5 mmol
 139 per gram. Figure 1a shows the formation of polydisperse
 140 agglomerates of monodisperse primary particles. Although
 141 the pseudo-spherical NPs are showed a wide range of size
 142 distribution, from 25 to 80 nm, the mean agglomerate
 143 diameter is about 55 ± 5 nm. The SAED pattern confirms
 144 the amorphous structure of the prepared agglomerated NPs
 145 (Fig. 1b).

146 The alcohol–water solutions of FON-CNPs (3 ml, 46 g
 147 of dry FON-CNPs/L in 37 wt/v% alcohol solution diluted
 148 with 2 mL of water) were subjected to ultrafiltration. Giving
 149 a brown solution, the ultra-filtration with 10 kDa membrane
 150 centrifugal filters showed that the FON-CNPs could be com-
 151 pletely filtered for 3 h at 5500 g. To prepare the solution of
 152 FON-CNPs of the smallest molecular weight range, the pre-
 153 pared ultra-filtrate was diluted three times with water and fil-
 154 tered in sequence with centrifugal filters from Vivaspin and
 155 Microsep Omega, equipped with membranes with molecular
 156 weight cut-offs of 5 and 1 kDa, at 5000 g. The filtrates of
 157 0.03 mass% solutions of FON-CNPs after filtering with a
 158 1 kDa membrane showed yellow and white luminescence
 159 under 254 nm and 365 nm excitations, respectively (Fig. 1d).
 160 This confirms a bimodal luminescence nature in the alco-
 161 hol–water solutions of FON-CNPs similar to that observed
 162 by Yang et al. (2020) for green–yellow emitting CDs derived
 163 from xylose and applied in the pH sensing.

164 After ultrafiltration, the resulting yellow solution to be
 165 used in subsequent experiments was subjected to thin-layer
 166 chromatography (TLC) with a silica layer (6 nm silica,
 167 15 μm). On the TLC plate after chromatographing, one



168 Fig. 1 a TEM image and b SEAD pattern of FON-CNPs agglom-
 169 erated with HCl, c Suggested structure of NPs, d Photographs of
 170 FON-CNPs after 10 and 1 kDa filtering under 254 nm and 365 nm
 171 UV light (from left to right), Insert in c Completed chromatograms
 172 of FON-CNPs dissolved in 2:1 isopropanol-water solution on TLC
 173 plates photographed under UV lamp excitation

174 can see two components, which exhibit blue and yellow
 175 luminescence under UV light (see insert in Fig. 1c).

176 FTIR ATR spectrum (Fig. 2a) of FON-CNPs was reg-
 177 istered for the sample, which was dried on a Parafilm™ M
 178 substrate. This spectrum confirmed the formation of differ-
 179 ent functional groups forming a shell on the surface. For
 180 all benzene derivatives containing CF_3 groups, an asym-
 181 metric C–F stretching vibration at 1330 cm^{-1} appears with
 182 very strong intensity (Yadav and Singh 1985). A band at
 183 1553 cm^{-1} (C=N) and bands at 1611 and 1666 cm^{-1} (C=C)
 184 can be assigned to stretching vibrations in the aromatic rings
 185 of the carbon (N) skeleton (Rap et al. 2020). According to
 186 Singh and Yadav (2001), three mid-intensity bands peaked at
 187 697 cm^{-1} , 797 cm^{-1} , and 890 cm^{-1} are due to the C–C–C in-
 188 plane bending mode, the symmetric C–F stretching vibration
 189 in the CF_3 group that mixed with the ring-breathing mode
 190 vibrations, and the out-of-plane C–H bending vibrations,
 191 correspondingly.

192 A band at 1128 cm^{-1} could be assigned to the N–H and
 193 C–H stretching vibrations. Unless otherwise stated, here
 194 and below the group frequencies are assigned according to
 195 Socrates (1994) and Coates (2006). Some spectral features
 are consistent with the formation of oxygen-containing
 groups. Two peaks centered at 1708 cm^{-1} and 1666 cm^{-1}
 are from C=O stretching vibrations of carbonyl groups (Bel-
 lamy 1980). A band at 1449 cm^{-1} corresponds to the C–N
 stretching vibrations or the overlapping bands assigned to
 the CH_2 scissoring and C–O–H bending vibrations.

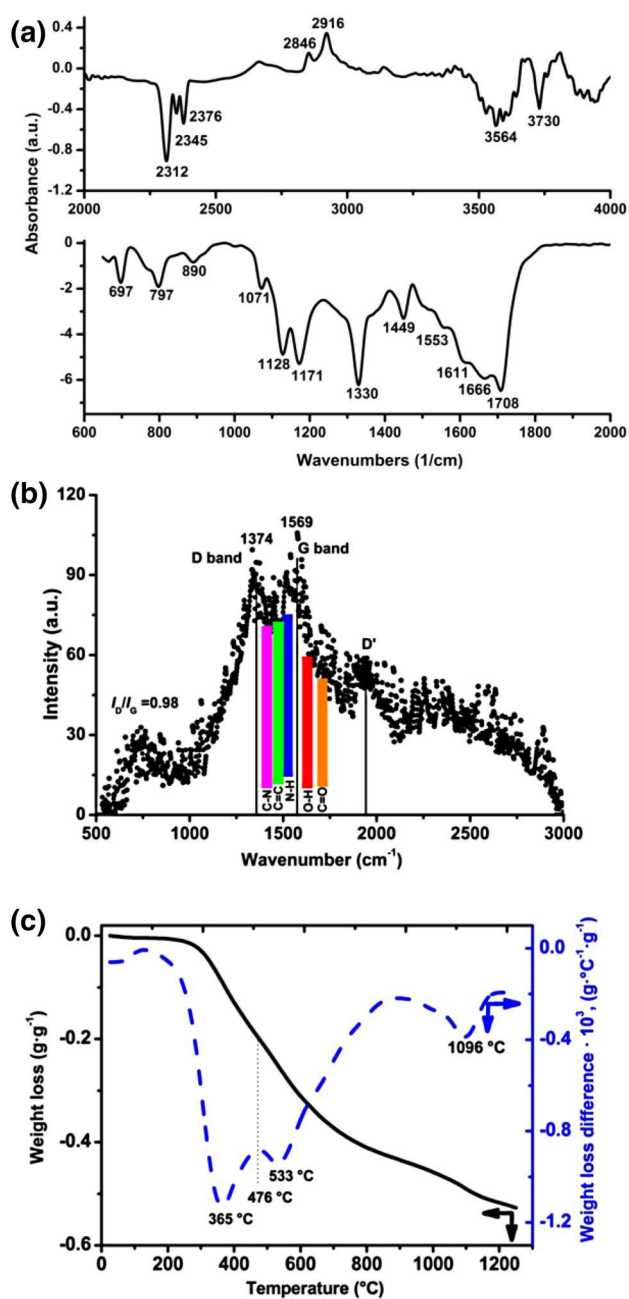


Fig. 2 Spectra **a** FTIR ATR and **b** Raman, and **c** TG analysis of FON-CNPs

196 The complex of spectral bands observed between 1500
197 and 1800 cm^{-1} includes the contribution of the NH_2 and
198 CHN bending vibrations and that of CNH stretching vibra-
199 tions. According to Larkin (2011), the quadrant ring and
200 semi-circle stretching vibrations in heterocycles absorb in
201 this spectral region. Broadband absorption in the region of
202 1000–1320 cm^{-1} covers the whole range of frequencies in
203 which the C–OH, C–C, C–N, and C–O stretching vibra-
204 tions are registered. A peak at 1071 cm^{-1} is from C–O
205 stretching vibrations, and it can contain the isopropanol

206 contribution (Coblentz Soc., Inc. 2018). While the broad-
207 band at 3200–3600 cm^{-1} could be assigned to the O–H
208 stretching vibrations overlapped with N–H vibrational fre-
209 quencies in aromatic and heterocyclic groups, and those of
210 imino groups (Lin 2018). The reversed Christiansen peaks
211 at 2916 cm^{-1} and 2846 cm^{-1} are attributed to asymmetri-
212 cal and symmetrical stretching vibrations of $-\text{CH}_2$. These
213 peaks are from isopropanol solvent (Shahravan et al. 2012)
214 and Parafilm™ M substrate. According to Kauffman et al.
215 (2011), three bands at 2312 cm^{-1} , 2345 cm^{-1} , and 2376 cm^{-1}
216 are from adsorbed CO_2 surface species. Broadband with a
217 peak at 3564 cm^{-1} could also include the contribution from
218 defects forming hydroxyl and from isopropanol conformers
219 (Coblentz Soc., Inc. 2018). In the highest wavenumber
220 region, presumably, a peak at 3730 cm^{-1} could be assigned
221 to free hydroxyl ions or the hydroxyl coverage of FON-
222 CNPs. Besides, according to Larkin (2011), the combination
223 band deriving from the bands involving the CO_2 in-phase
224 stretching and out-of-phase stretch could be observed as two
225 doublets in the 3730–3500 cm^{-1} range. Presumably, the rea-
226 son for increasing the PL efficiency is the constitutional and
227 shell nitrogen-containing groups.

228 Figure 2b shows the Raman spectrum of the sample,
229 where the *D*, *G*, and *D'* bands are seen. In the present study,
230 the width of the *D* band is very wide, reflecting the wide
231 distribution of crystallite sizes. One should note that the
232 ratio I_D/I_G equals 0.98, so by Cancado's general formula
233 (Cancado et al. 2006), which allows the determination of
234 the crystallite size L_a by Raman spectroscopy, the L_a value of
235 39.3 nm was calculated. A Raman peak at 1569 cm^{-1} , which
236 is assigned to the *G* band of graphitic structures, can overlap
237 with the abundant Raman bands, those vibrations most likely
238 assigned to the bending $-\text{OH}$ vibrations, deformation N–H
239 vibrations, ring C=C vibrations, and C=O and C–N stretch-
240 ing vibrations (Lin-Vien et al. 1991; Mochalin et al. 2009;
241 Mermoux et al. 2014; Tarasenko et al. 2017). The result-
242 ing broad asymmetric peak showed a low signal-to-noise
243 ratio. In fact, the reason for this observation is rather strong
244 fluorescence, which agrees with the results of PL studies
245 on nanocolloids. An analysis of the Raman spectrum shows
246 a typical feature of nanostructured materials, which is the
247 redshift of the *D* band, by 50 cm^{-1} , as compared with the
248 literature data (Smith and Godard 2009).

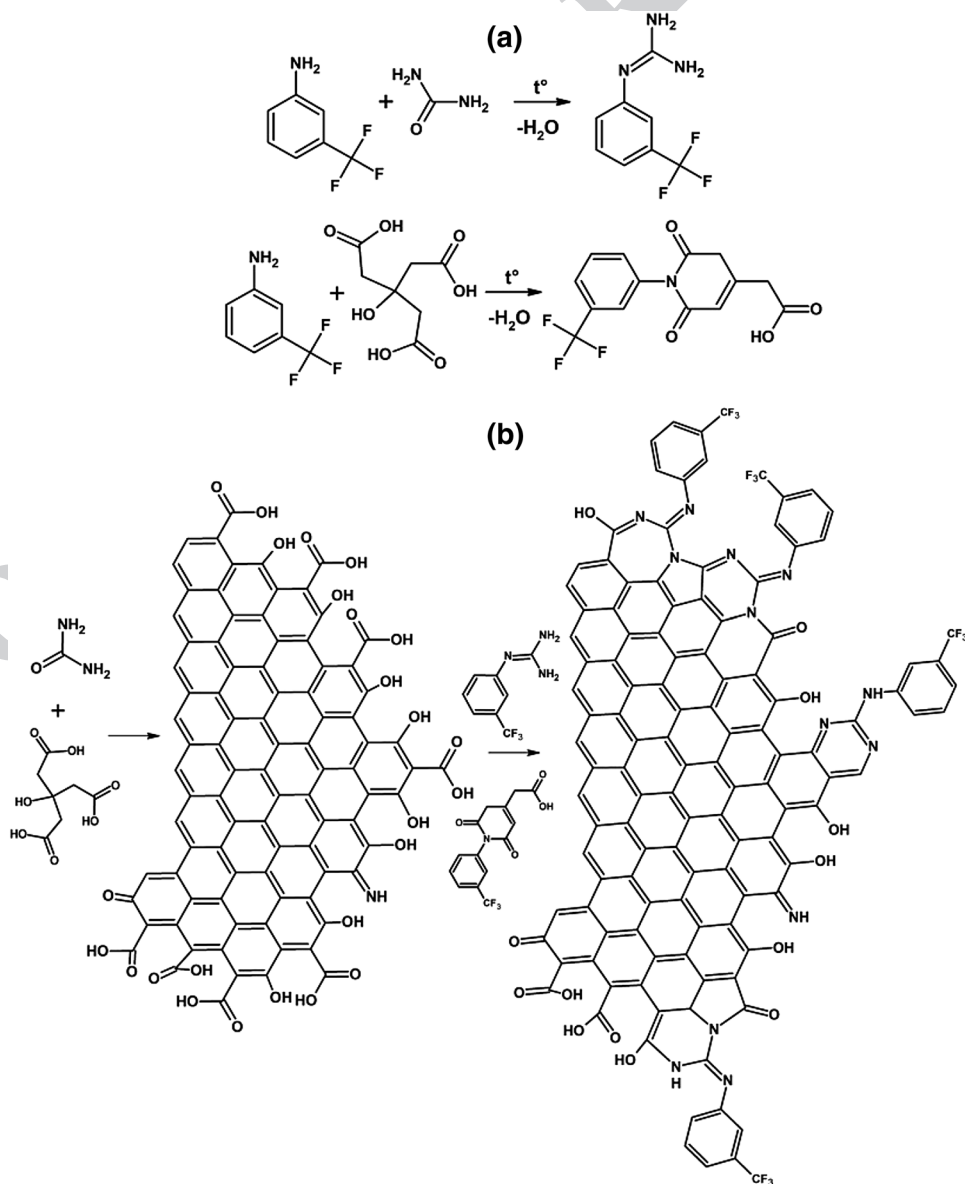
249 According to TGA data (Fig. 2c), the FON-CNPs are
250 stable below 200 $^{\circ}\text{C}$, and the total weight loss of 52.7% is
251 because of the thermal decomposition and detachment of the
252 surface groups and the partial burning of the carbon shell.
253 The content of physisorbed molecules, which are desorbed
254 below 140 $^{\circ}\text{C}$, is negligible, only 0.4%. The differential ther-
255 mal gravimetric (DTG) curve revealed three main weight
256 loss peaks at 365 $^{\circ}\text{C}$, 533 $^{\circ}\text{C}$, and 1096 $^{\circ}\text{C}$. Here, the effect
257 at 533 $^{\circ}\text{C}$ has a complex nature, and one can see the shoulder
258 on the DTG curve between 650 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$. Actually, the

259 first and second weight loss effects are difficult to separate
 260 precisely. If they are separated by the temperature corre-
 261 sponding to the smallest weight change (of about 476 °C),
 262 the effect peaked at 365 °C will give 19.6% weight loss,
 263 while the effect at 533 °C–23.3% weight loss. The third
 264 effect at 1096 °C corresponds to 9.4% weight loss. From the
 265 above consideration, the schematic of the synthesis and the
 266 suggested products are depicted in Fig. 3.

267 At the first stage of the synthesis, aniline reacts with
 268 urea and citric acid, as a result, thermolysis products are
 269 formed and water is split off (Fig. 3a). It is likely that het-
 270 erocyclic nitrogen-containing compounds are formed due
 271 to thermolytic condensation when citric acid reacts with
 272 urea (Fig. 3b). At a further stage, thermolysis products can
 273 participate in the construction of a growing carbon particle,
 274 enriching it with nitrogen atoms and trifluoromethyl groups.

275 **The aqueous solution of the FON-CNPs is yellow-
 276 ish and transparent under sunlight illumination. Figure. 4a
 277 shows two specific absorption peaks at 246 and 350 nm
 278 (Fig. 4a), attributed to the π - π^* (aromatic C=C) and n - π^*
 279 (the C=O bond) transitions according to Wang et al. (2017).
 280 Furthermore, according to Shen et al. (2013), Xiang et al.
 281 (2018), and Ding et al. (2016), the observed short- and long-
 282 wavelength absorption bands, at ca. 277 nm and at 435 nm
 283 and ca. 511 nm, can be attributed to the $\pi \rightarrow \pi^*$ (aromatic
 284 C=C) and $n \rightarrow \pi^*$ (C-N) transitions of nitrogen-containing
 285 groups in the FON-CNPs, respectively. To consider the effect
 286 of constitutional (structural heterocyclic) nitrogen
 287 and the active surface functional groups, we examined the
 288 response of FON-CNPs to various pH conditions in the
 289 PB buffer with variable pH values (Fig. 4b). At a wave-
 290 length of 212 nm, the FON-CNPs have a good response

Fig. 3 Schematic illustration of FON-CNPs synthesis **a** thermolysis and **b** thermolytic condensation



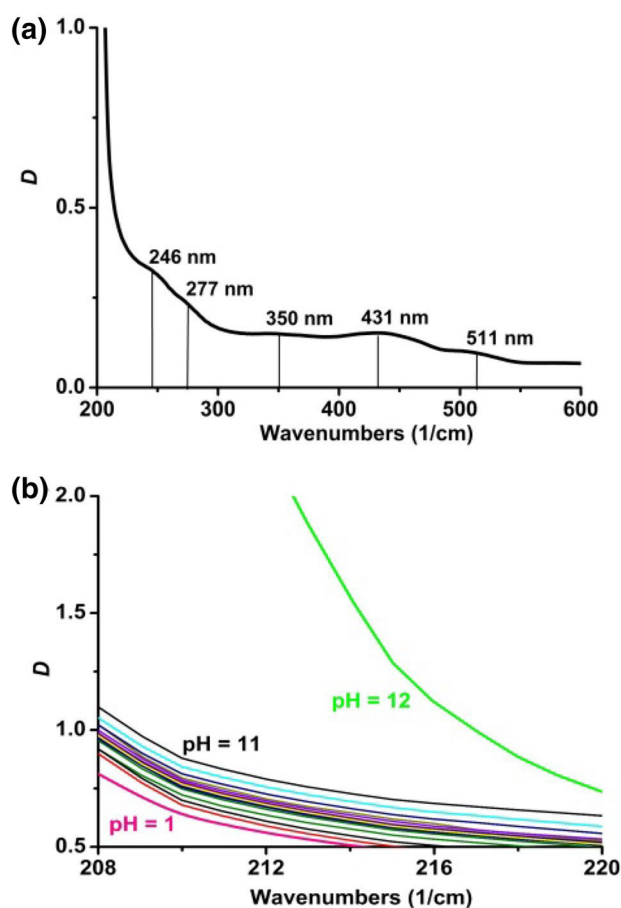


Fig. 4 **a** UV–Vis spectrum of FON-CNPs in water solution (0.03 mass%) and **b** pH-dependent response of FON-CNPs in different pHs (from top to bottom)

291 to the pH range from 1 to 6. In the absorbance (D) range
 292 from 0.55 to 0.75, $\text{pH} = (31.87 \pm 2.1) D - 16.89 \pm 1.3$ with
 293 $R^2 = 0.99$. At the same wavelength, the UV–vis spectra of
 294 FON-CNPs solutions also showed a linear response, in
 295 the D range of 0.71–0.8, to the pH ranged from 8 to 11:
 296 $\text{pH} = (28.11 \pm 1.56) D - 11.65 \pm 1.2$ with $R^2 = 0.99$.

297 The prepared FON-CNPs in solutions showed high toler-
 298 ance to possible changes in the ionic strength. In fact, the
 299 PL intensity showed good stability in solutions with up to
 300 1.0 mol L^{-1} NaCl. These solutions have good resistance to
 301 photobleaching, and the PL intensity remains constant under
 302 continuous irradiation for 2 h. We suggest that FON-CNPs
 303 can find potential applications in bio-labeling/bio-imaging.
 304 Moreover, the hydrogen bonds of the shell and steric protec-
 305 tion of C–F bonds reduce photoluminescence quenching at
 306 room temperature.

307 On the other hand, the PL features of the prepared FON-
 308 CNPs are highly pH-dependent (Fig. 5). This observation
 309 indicates that PL species in the FON-CNPs should have
 310 basic/acidic sites taking part in reversible protonation and

311 responsible for the PL intensity variation. We assume that
 312 the pH level increasing caused the negative surface charging;
 313 the de-protonation can dissociate hydrogen bonds. It will be
 314 a reason for the dissociation of both amide groups and car-
 315 boxylic groups, in the background of possible deprotonating
 316 of nitrogen-containing groups (Long et al. 2018).

317 As shown in Fig. 4, as pH increased from 3.0 to 10.0, a
 318 gradient increase of the PL intensity of FON-CNPs centered
 319 at 510–525 nm can be seen. This increase of the PL
 320 intensity remained relatively steady in the 9.0–10.0 pH range
 321 (Fig. 5a–e). However, the PL signal peak is slightly red-
 322 shifted from 510 to 525 nm when the pH values increased
 323 from 3.0 to 11.0. The specific features, the blue shift to
 324 475 nm and the PL signal quenching was registered when pH
 325 values in the colloid solutions increased from 10.0 to 12.0
 326 (see Fig. 5e–g). As can be seen from Fig. 5, the prepared
 327 FON-CNPs could be sensitive pH indicators due to their
 328 pH-dependent PL intensity. Additionally, there is a good
 329 linear relationship between the PL intensity and the pH of
 330 solutions in the range of 3.0–9.0, the relationship between
 331 the PL intensity and pH values was fitted as a linear equation
 332 of $\text{PL}(\text{a.u.}) = (16.76 \pm 2.2)[\text{pH}] + 769.0 \pm 20$ with $R^2 = 0.99$.
 333 But the PL response deviates from linearity in the higher
 334 and lower ranges.

335 An alternative view on the pH-sensing mechanism could
 336 be formulated considering the chemistry of FON-CNPs. If
 337 judging by the TG data, the prepared FON-CNPs are rich in
 338 carboxyl groups and other oxygen functionality (phenolic
 339 and carbonyl groups).

340 With an increase in pH, the carboxyl groups are first
 341 deprotonated. This de-protonation can increase the lumi-
 342 nescence with the concentration of ionized particles in the
 343 solution. At high basic pH levels, we observe some quench-
 344 ing of luminescence. One can explain this observation by
 345 the ionization of the carbonyl functional group. The latter
 346 is typical for dyes at such high pH values. Apparently, the
 347 ionization of the carbonyl groups leads to the destruction
 348 of conjugated systems inside the matrix and, accordingly,
 349 results in the quenching of the PL signal.

350 Conclusion

351 The core–shell FON-CNPs prepared using trifluoromethyl-
 352 ated derivatives were found to be excellent PL probes for
 353 pH measurements. We consider possible reasons for the pH-
 354 sensitive PL enhancement and PL subsequent quenching in
 355 the solutions of FON-CNPs. It has been demonstrated that
 356 the FON-CNPs have a good linearity range in the detection
 357 of pH levels. The reported sensing system based on the PL
 358 response of FON-CNPs shows many advantages, includ-
 359 ing rapid detection, high sensitivity, and medium–low pro-
 360 duction costs of the probe FON-CNPs. Potentially, as high

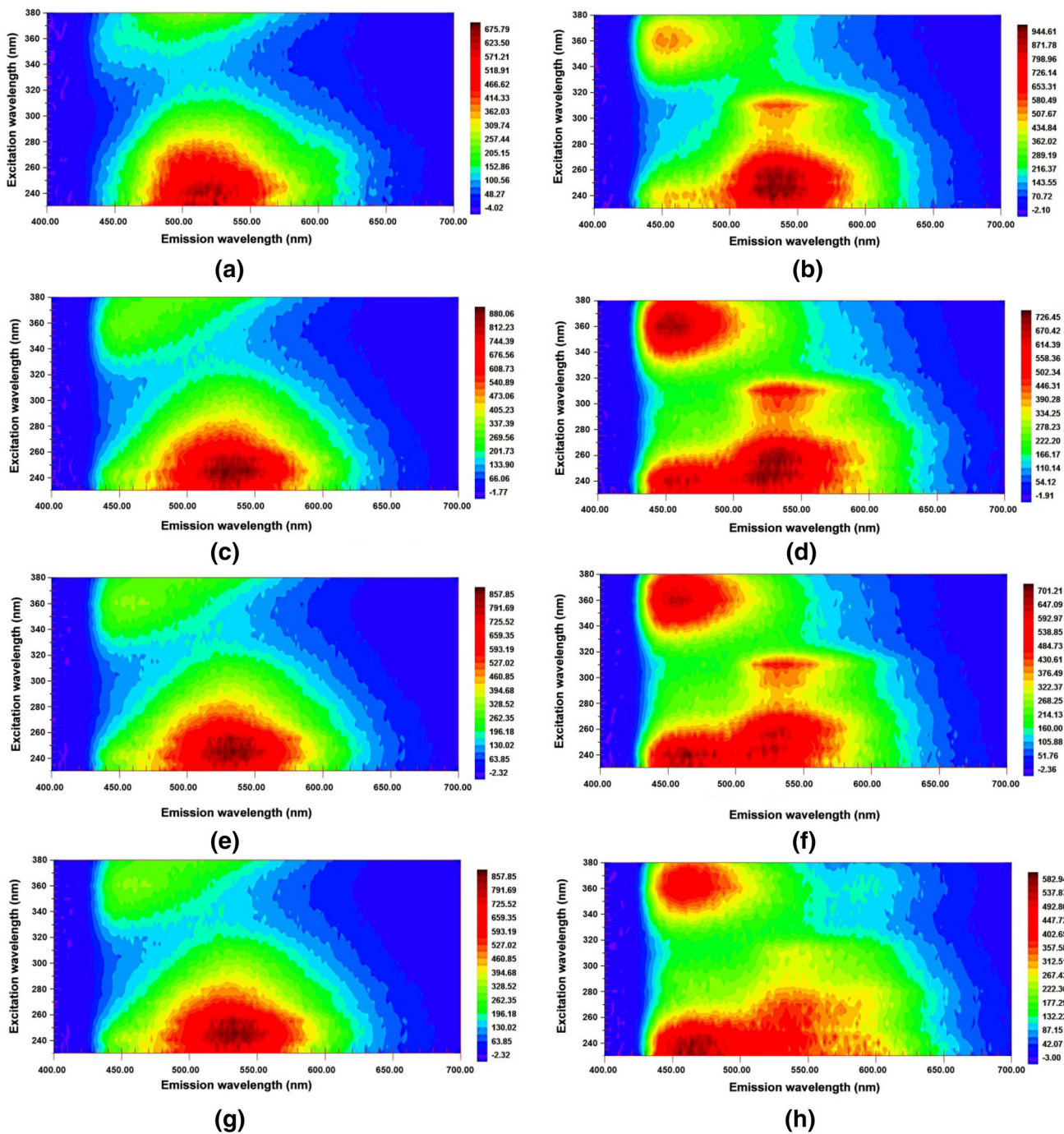


Fig. 5 3D PL plots of selected aqueous solution of FON-CNPs in different pHs: **a** 1.07, **b** 5.32, **c** 6.17, **d** 9.03, **e** 9.81, **f** 10.13, **g** 10.73, and **h** 12.03

361 selective probes, they can be applied to measure pH levels
362 in aqueous solutions and cells.

363 **Acknowledgements** G.K. Mussabek, Y.T. Taubayev, and V.V. Lisnyak
364 acknowledge the support of Grant No AP08856579 of the Ministry of
365 Education and Science of the Republic of Kazakhstan. G.K. Mussa-
366 bek is grateful to Al-Farabi Kazakh National University for a Scholar-
367 ship in the Postdoctoral Fellowship program. A.N. Zaderko and V.A.

368 Skryshevsky recognize a support from the Ministry of Education and
369 Science of Ukraine, Grant No 0119U100326. A.N. Zaderko is also
370 thankful for the scholarship of the National Scholarship Programme
371 of the Slovak Republic, Grant No 32492. This work was partially sup-
372 ported by EU Horizon 2020 Research and Innovation Staff Exchange
373 Programme (RISE) under Marie Skłodowska-Curie Action (project
374 101008159 “UNAT”).

375 **Compliance with ethical standards**

376 **Conflict of interest** A.N. Zaderko is the inventor of the WO2020121119
377 international patent publication. A.N. Zaderko is the owner of the
378 trademark Fluocar® Nano UA213198 and US5479088. All authors
379 declare that they have no conflict of interest.

380 **References**

381 Bellamy LJ (1980) Carbonyl Frequencies. In: Bellamy LJ (ed) The
382 infrared spectra of complex molecules. Springer, Dordrecht, pp
383 128–194

384 Benilov A, Gavrilchenko I, Benilova I, Skryshevsky V, Cabrera M
385 (2007) Influence of pH solution on photoluminescence of porous
386 silicon. *Sens Actuators A* 137:345–349. <https://doi.org/10.1016/j.sna.2007.02.032>

387

388 Cañado LG, Takai K, Enoki T, Endo M, Kim YA et al (2006) Gen-
389 eral equation for the determination of the crystallite size La of
390 nanographite by Raman spectroscopy. *Appl Phys Lett* 88:163106.
391 <https://doi.org/10.1063/1.2196057>

392 Coates J (2006) Interpretation of infrared spectra a practical approach.
393 In: Meyers RA, McKelvy ML (eds) *Encyclopedia of analytical*
394 *chemistry*. Wiley, Hoboken

395 Soc C, Inc. (2018) *Evaluated Infrared Reference Spectra*. In: Linstrom
396 PJ, Mallard WG (eds) *NIST chemistry webbook, nist standard*
397 *reference database number 69*. National Institute of Standards and
398 Technology, Gaithersburg

399 Ding H, Yu SB, Wei JS, Xiong HM (2016) Full-color light-emitting
400 carbon dots with a surface-state-controlled luminescence
401 mechanism. *ACS Nano* 10:484–491. <https://doi.org/10.1002/adma.201704740>

402

403 Feng S, Mu Z, Liu H et al (2019) A novel application of fluorine doped
404 carbon dots combining vortex-assisted liquid-liquid microextrac-
405 tion for determination of 4-nitrophenol with spectrofluorimetric
406 method. *J Fluoresc* 29:1133–1141. <https://doi.org/10.1007/s10895-019-02427-8>

407

408 He J, Chen Y, He Y, Xu X (2020) Anchoring carbon nanodots onto
409 nanosilica for phosphorescence enhancement and delayed fluores-
410 cence nassence in solid and liquid states. *Small* 16:49. <https://doi.org/10.1002/sml.202005228>

411

412 Jiang L, Ding H, Lu S, Geng T et al (2019) Photoactivated fluorescence
413 enhancement in F, N-doped carbon dots with piezochromic behav-
414 ior. *Angew Chem* 132:10072–10077. <https://doi.org/10.1002/ange.201913800>

415

416 Kauffman KL, Culp JT, Goodman A, Matranga C (2011) FT-IR study
417 of CO₂ adsorption in a dynamic copper (II) benzoate-pyrazine
418 host with CO₂-CO₂ interactions in the adsorbed state. *J Phys*
419 *Chem C* 115:1857–1866. <https://doi.org/10.1021/jp102273w>

420 Larkin PJ (2011) *Infrared and Raman spectroscopy principles and spec-*
421 *tral interpretation*. Elsevier, Amsterdam, pp 61–62

422 Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG (1991) *The hand-*
423 *book of infrared and Raman characteristic frequencies of organic*
424 *molecules*. Academic Press, San Diego, pp 479–481

425 Lin C-K (2018) Pyridine vs. N-Hydrogenated pyridine moieties: theo-
426 retical study of stability and spectroscopy of nitrogen-contained
427 heterocyclic aromatic compounds and graphene nanoflakes. *ACS*
428 *Omega* 3:12312–12319. <https://doi.org/10.1021/acsomega.8b01759>

429

430 Liu L, Anwar S, Ding H, Xu M (2019) Electrochemical sensor based
431 on F, N-doped carbon dots decorated laccase for detection of cat-
432 echol. *J Electroanal Chem* 840:84–92. <https://doi.org/10.1016/j.jelechem.2019.03.071>

433

434 Long P, Feng Y, Cao C, Li Y et al (2018) Self-protective room-tem-
435 perature phosphorescence of fluorine and nitrogen codoped car-
436 bon dots. *Adv Funct Mater* 28:1800791. <https://doi.org/10.1002/adfm.201800791>

437

438 Mermoux M, Crisci A, Petit T, Girard HA, Arnault J-C (2014) Surface
439 modifications of detonation nanodiamonds probed by multiwave-
440 length Raman spectroscopy. *J Phys Chem C* 118:23415–23425.
441 <https://doi.org/10.1021/jp507377z>

442

443 Mochalin V, Osswald S, Gogotsi Y (2009) Contribution of functional
444 groups to the Raman spectrum of nanodiamond. *Chem Mater*
21:273–279. <https://doi.org/10.1021/cm802057q>

445

446 Nevar A, Tarasenko N, Nedelko M, Tarasenko N (2020) Carbon nano-
447 dots with tunable luminescence properties synthesized by elec-
448 trical discharge in octane. *Carbon Lett*. <https://doi.org/10.1007/s42823-020-00147-9>

449

450 Novoa De León IC, Johny J, Vázquez-Rodríguez S, García-Gómez
451 N, Carranza-Bernal S, Mendivil I, Shaji S, Sepúlveda-Guzmán
452 S (2019) Tuning the luminescence of nitrogen-doped graphene
453 quantum dots synthesized by pulsed laser ablation in liquid and
454 their use as a selective photoluminescence on-off-on probe
455 for ascorbic acid detection. *Carbon* 150:455–464. <https://doi.org/10.1016/j.carbon.2019.05.057>

456

457 Pal A, Sk MP, Chattopadhyay A (2020) Recent advances in crystal-
458 line carbon dots for superior application potential. *Mater Adv*
1:525–553. <https://doi.org/10.1039/D0MA00108B>

459

460 Rap DB, Marimuthu AN, Redlich B, Brünken S (2020) Stable isom-
461 eric structures of the pyridine cation (C₅H₅N⁺) and proto-
462 nated pyridine (C₅H₅NH⁺) elucidated by cold ion infrared spec-
463 troscopy. *J Mol Spectrosc* 373:111357. <https://doi.org/10.1016/j.jms.2020.111357>

464

465 Serdiuk T, Skryshevsky VA, Ivanov II, Lysenko V (2011) Storage
466 of luminescent nanoparticles in porous silicon: toward a solid
467 state “golden fleece.” *Mater Lett* 65:2514–2517. <https://doi.org/10.1016/j.matlet.2011.05.033>

468

469 Shahravan A, Desai T, Matsoukas T (2012) Controlled manipulation
470 of wetting characteristics of nanoparticles with dry-based plasma
471 polymerization method. *Appl Phys Lett* 101:251603. <https://doi.org/10.1063/1.4772544>

472

473 Shen L, Zhang L, Chen M, Chen X, Wang J (2013) The production
474 of pH-sensitive photoluminescent carbon nanoparticles by the
475 carbonization of polyethylenimine and their use for bioimaging.
476 *Carbon* 55:343–349. <https://doi.org/10.1016/j.carbon.2012.12.074>

477

478 Sim Y, Seung Kim SJ, Janani G, Chae Y et al (2019) The synergistic
479 effect of nitrogen and fluorine co-doping in graphene quantum dot
480 catalysts for full water splitting and supercapacitor. *Appl Surf Sci*
50:145157. <https://doi.org/10.1016/j.apsusc.2019.145157>

481

482 Singh NP, Yadav RA (2001) Vibrational studies of trifluoromethyl
483 benzene derivatives 1: 2-amino, 5-chloro and 2-amino, 5-bromo
484 benzotrifluorides. *Indian J Phys* 75B:347–355

485

486 Smith DC, Godard G (2009) UV and VIS Raman spectra of natural
487 lonsdaleites: towards a recognised standard. *Spectrochim Acta A*
73:428–435. <https://doi.org/10.1016/j.saa.2008.10.025>

488

489 Socrates G (1994) *Infrared characteristic group frequencies*. Wiley,
490 New York

491

492 Su Q, Lu C, Yang X (2019) Efficient room temperature phosphores-
493 cence carbon dots: Information encryption and dual-channel pH
494 sensing. *Carbon* 152:609–615. <https://doi.org/10.1016/j.carbon.2019.06.061>

495

496 Sun Y, Liu S, Sun L, Wu S et al (2020) Ultralong lifetime and efficient
497 room temperature phosphorescent carbon dots through multi-
498 confinement structure design. *Nature Commun* 11:1. <https://doi.org/10.1038/s41467-020-19422-4>

499

500 Tarasenko N, Stupak A, Tarasenko N, Chakrabarti S, Mariotti D (2017)
501 Structure and optical properties of carbon nanoparticles gener-
502 ated by laser treatment of graphite in liquids. *ChemPhysChem*
18:1074. <https://doi.org/10.1002/cphc.201601182>

- 500 Tsapyuk GG, Diyuk VE, Mariychuk R et al (2020) Effect of ultrasonic
501 treatment on the thermal oxidation of detonation nanodiamonds.
502 Appl Nanosci 10:4991–5001. [https://doi.org/10.1007/s13204-020-](https://doi.org/10.1007/s13204-020-01277-2)
503 [01277-2](https://doi.org/10.1007/s13204-020-01277-2)
- 504 Wang H, Sun C, Chen X, Zhang Y et al (2017) Excitation wavelength
505 independent visible color emission of carbon dots. Nanoscale
506 9:1909–1915. <https://doi.org/10.1039/C6NR09200D>
- 507 Wang Y, Yue Q, Hu Y, Liu C et al (2019) Synthesis of N-doped car-
508 bon dots and application in vanillin detection based on collisional
509 quenching. RSC Adv 9:40222–40227. [https://doi.org/10.1039/](https://doi.org/10.1039/C9RA08352A)
510 [C9RA08352A](https://doi.org/10.1039/C9RA08352A)
- 511 Xia C, Zhu S, Feng T, Yang M, Yang B (2019) Evolution and synthesis
512 of carbon dots: from carbon dots to carbonized polymer dots. Adv
513 Sci 6:23. <https://doi.org/10.1002/advs.201901316>
- 514 Xiang M, Dan Q, Dongxue Y, Bing N, Yikang Z, Hongyou F, Zaicheng
515 S (2018) Synthesis of carbon dots with multiple color emission by
516 controlled graphitization and surface functionalization. Adv Mater
517 30:1704740. <https://doi.org/10.1021/acsnano.5b05406>
- 518 Yadav RA, Singh IS (1985) Vibrational spectra and normal coordi-
519 nate analysis for substituted trifluoromethyl benzenes. Proc Indian
520 Acad Sci (Chem Sci) 95:471–487. [https://doi.org/10.1007/BF028](https://doi.org/10.1007/BF02840446)
521 [40446](https://doi.org/10.1007/BF02840446)
- 522 Yang P, Zhu Z, Chen W, Luo M et al (2020) Nitrogen/sulfur Co-
523 doping strategy to synthesis green-yellow emitting carbon dots
derived from xylose: toward application in pH sensing. J Lumin
232:117489. <https://doi.org/10.1016/j.jlumin.2020.117489>
- Zaderko A (2020) The process for obtaining of fluoralkylated carbon
quantum dots. WO2020121119 Patent. [https://patentscope.wipo.](https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2020121119)
[int/search/en/detail.jsf?docId=WO2020121119](https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2020121119). Accessed 25 Jan
2021
- Zaderko AN, Shvets RYa, Grygorchak II et al (2019) Fluoroalkylated
nanoporous carbons: testing as a supercapacitor electrode. Appl Surf Sci 470:882–892. <https://doi.org/10.1016/j.apsusc.2018.11.141>
- Zan M, Li C, Liao F, Rao L et al (2020) One-step synthesis of green
emission carbon dots for selective and sensitive detection of nitrite
ions and cellular imaging application. RSC Adv 10:10067–10075.
<https://doi.org/10.1039/C9RA11009G>
- Zuo G, Xie A, Pan X, Su T, Li J, Dong W (2018) Fluorine-doped
cationic carbon dots for efficient gene delivery. ACS Appl Nano
Mater 1(5):376–2385. <https://doi.org/10.1021/acsnm.8b00521>
- Publisher's Note** Springer Nature remains neutral with regard to
jurisdictional claims in published maps and institutional affiliations.

UNCORRECTED PROOF

Journal:	13204
Article:	1725

Author Query Form

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your article, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query	Details Required	Author's Response
AQ1	Author names: Please confirm if the author names are presented accurately and in the correct sequence (given name, middle name/initial, family name). Also, kindly confirm the details in the metadata are correct.	

Author Proof