Solution plasma: new synthesis method of N-doped carbon dots as ultra-sensitive fluorescence detector for 2,4,6-trinitrophenol

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Abstract

Herein, we report the synthesis of nitrogen-doped carbon dots (NCDs) through solution plasma (SP) for the first time. The SP method occurs a rapid dissociation of molecules, such as organic compounds, caused by an electrical discharge between electrodes immersed in a solution. The dissociation can result in the creation of various radicals such as -C2·, -CN, and -H which enable the rapid synthesis of carbon dots (CDs). The unique reaction of radicals allowed the formation of CDs with high N concentration and functionalization of the surface in a short time. In this study, by using the SP method, a very fine NCDs with size of 6 nm were synthesized from a pyridine/water mixture in just 10 min. Bright blue fluorescence (410 nm) with a high quantum yield (61%) was observed due to the high N concentration and the surface passivation. From the potential application point of view, the synthesized NCDs showed an excellent detection property for 2,4,6-trinitrophenol (TNP) by fluorescence quenching effect. It was due to rich amino-functional groups which act as a reaction pathway to TNP. This phenomenon was caused by the synergetic effect of a photo-induced electron transfer with the assistance of proton transfer-assisted electron transfer.

1. Introduction

Among nitroaromatic compounds, 2,4,6-trinitrophenol (TNP) is a popular choice for the utilization of industrial and agricultural purposes [1]. However, direct exposure to TNP has serious effects on human health, such as skin/eye irritation, liver, or kidney damage [2, 3]. Early detection can prevent these problems. Thus, several methods have been introduced and developed. For example, gas chromatography [4], surface-enhanced Raman spectroscopy [5], and surface plasmon resonance [6] have been successfully used for detecting TNP. Unfortunately, the mentioned methods are expensive, time-consuming, and generally require a complicated labeling procedure [1, 7]. Therefore, finding more simple and reliable methods for TNP detection is still a big challenge.

In recent years, fluorescence-based materials have been intensively investigated for detection of TNP, due to their portability and easy operation [1]. Recently, carbon dots (CDs) were also introduced as promising materials for application in the fluorescence-based detectors [8, 9]. The CDs in the range of a few nanometers show fluorescence property due to the quantum confinement effect [10–12]. Moreover, their excellent biocompatibility and nontoxicity make them strong candidates for use in many bio-related applications [13–15]. However, the quantum yield of pristine CDs for the fluorescence efficiency is quite low about 10%.
| Detector          | Synthesis method       | Precursor                                         | Q.Y (%) | Linear range (μM) | LOD (nM) | References |
|-------------------|------------------------|---------------------------------------------------|---------|-------------------|----------|------------|
| P doped CDs       | Solvothermal treatment | Sucrose                                           | 21.8    | 0.2–17.0          | 16.9     | [18]       |
| N,B doped CDs     | Hydrothermal treatment | Citric acid anhydrous, ethylenediamine, borate     | 68.3    | 0.02–0.16         | 1400     | [19]       |
| Amorphous CDs     | Ultrasound             | Dextrose                                          | 39.5    | 0.5–50            | 200      | [20]       |
| N doped CDs       | Thermal treatment      | o-Phenylenediamine                                | 13.2    | n/a               | 2000     | [21]       |
| N doped CDs       | Solvothermal treatment | Citric acid, urea                                 | 43.0    | 0–0.5             | 127      | [22]       |
| Ammonium functionalized CDs | Hydrothermal treatment | Carboxymethyl cellulose sodium                  | 8.9     | n/a               | 700      | [23]       |
| N doped graphene quantum dots | Pyrolysis              | Citric acid, tris(hydroxymethyl)aminomethane     | 59.2    | 1–60              | 300      | [24]       |
| N doped CDs       | Hydrothermal treatment | Spermine, m-phenylenediamine                      | 11.7    | 0.1–100           | 28       | [25]       |
| N doped CDs       | Hydrothermal treatment | 4-(diethylamino) salicylaldehyde                  | 19.0    | 1–100             | 480      | [26]       |
| CDs               | Potassium hydroxide-assisted reflux | Dextrin                                         | 13.1    | 0–50              | 19       | [27]       |
| Mn doped CDs      | Hydrothermal treatment | 1-(2-pyridylazo)-2-naoithaleno, MnCl₂             | 83.2    | 0.1–200           | 19       | [28]       |
| N doped CDs       | Solution plasma        | Pyridine, water                                   | 61      | 0–50              | 10       | This work  |
Also, an absence of functional groups, that can enhance to detect the target molecule, is a critical problem. Therefore, the recent studies of CDs have been focusing on introducing heteroatoms, which causes specific changes in the electronic band structure, and adding functional groups to enhance their performance, as shown in table 1 [16, 17].

In general, heteroatom-doped CDs can be successfully prepared by hydrothermal and pyrolysis methods [29–32]. However, these methods require a high operating temperature and are considered time-consuming. Hence, new synthesis methods should be considered. Recently developed in-liquid plasma technology, so-called solution plasma (SP), has become an alternative method for synthesis of carbon nanomaterials under mild condition (i.e., room temperature and atmospheric pressure) [33]. During the SP process, plasma can be generated between electrodes, submerged in the solution, by using a bipolar-pulsed power supply, as shown in figure 1. Molecules nearby the electrodes are continuously collided by the electrons coming out from the electrodes. Those collisions cause the excitation and dissociation of the molecules. Thus, the SP can induce the formation of various highly reactive species (e.g., H₂O → H⁻, ·OH, H⁺, OH⁻ and C₆H₆ → ·C₆H₅, ·H, H⁺, ·OH, C₂) which can lead to a rapid synthesis reaction for the carbon nanomaterials [34–36]. According to the previous work, a pyridine monomer, which has a similar structure to benzene with one methine group (=CH−) replaced by a nitrogen atom, could be converted to a pyridine oligomer functionalized by a nitrile group in a few seconds [37]. This evidence gave a clue for the rapid synthesis of the nitrogen-doped carbon dots (NCDs) with rich functional groups.

In this study, a successful formation of NCDs from pyridine by the SP method has been shown. The fabricated NCDs were shown to have high N concentration and abundant amino-functional groups due to the unique reaction at the plasma/liquid interface.

2. Experimental section

2.1. Materials

Pyridine, 2,4,6-trinitrophenol (TNP), nitro-benzene (NB), nitronaphtalene (NN), nitroanthracene (NA), nitrofluorene (NF), and distilled water were purchased from Kanto chemicals. Distilled water was used in all experiments.

2.2. Synthesis of nitrogen-doped carbon dots (NCDs)

The mixture of pyridine (70 ml) and water (30 ml) was used for the synthesis of the NCDs. The homogeneous solution was assured using a magnetic stirrer for 30 min. After that, the SP was generated for 10 min by a bipolar power supply (MPP-HV02, Kurita, CO., Ltd) between the tungsten electrodes (diameter = 1 mm, Nilaco CO., Ltd) covered with insulating ceramic tubes (inner diameter = 1 mm, outer diameter = 2 mm, Nilaco CO., Ltd) as shown at figure 1. The electrodes were placed at the center of the reactor leaving a gap of 0.5 mm. During the plasma discharge, the voltage and current were fixed at 2 kV and 1A, respectively. The pulse width and pulse repetition frequency were fixed at 1.0 μs and 50 kHz. After the discharge, the color of the pyridine and water solution changed to dark brown. The solution was purified by a PTFE membrane filter (pore size = 0.1 μM, Merck Millipore). The pale brown solution was obtained after filtration and some black carbon powder was separated on the membrane filter. At last, the solution was dried in the vacuum oven at 70 °C to get the NCDs powder.
2.3. Characteristics
The size and size distribution of NCDs were analyzed by transmission electron microscopy (TEM, JEM-2500SE, JEOL). To obtain information about atomic composition, the elemental analysis (EA, CHNS/O2400-2, PerkinElmer) was performed. The x-ray diffraction patterns of the samples were obtained using an x-ray diffractometer (XRD, SmartLab, Rigaku). The molecular vibration was confirmed by Raman spectroscopy (Invia Raman microscope, Renishaw). The absorption spectra were recorded by the UV–vis spectrophotometer (UV-3600, Shimadzu). The Fourier transform infrared spectroscopy (FT-IR, Nicolet 8700, Thermo Fisher) was carried out to confirm the functional groups. The fluorescence spectra of NCDs were measured using a spectrophotometer (FP-6600, JASCO).

2.4. Quantum yield
The quantum yield of CDs was calculated by the following equation (1)

$$Q_a = Q_{st} \frac{I_a}{I_{st}} A_a \frac{\eta_a}{\eta_{st}}^2,$$

where the subscript \(st\) refers to a standard molecule of known quantum yield (Rhodamine B in this study) and refers to the studied NCDs sample. \(Q\) is the quantum yield and \(Q_{st}\) of Rhodamine B is 0.31. The \(\eta\) is the refractive index of the used solvent. In both measured and reference solutions water was used, therefore the values of \(\eta_a\) and \(\eta_{st}\) are equal to 1.333. \(I\) means fluorescence peak integrated area and \(A\) represent the corresponding absorbance value.

2.5. Procedure for detection of nitro group molecules
TNP with various concentrations (i.e., 0, 1, 5, 10, 50, 100, and 500 \(\mu\)M) were added into the NCDs solution (conc. 150 mg l\(^{-1}\)) to confirm the sensitivity. The experiment for selectivity was also performed with the 100 \(\mu\)M of NB, NN, NA, and NF in the NCDs solution. The change of fluorescence of NCDs solutions was revealed with 340 nm of excitation wavelength at room temperature. The quenching constant value \((K_{sv})\) was calculated as the slope \((S)\) of the calibration plot and the limit of detection \((LOD)\) equals to \(3\sigma / S\), where \(\sigma\) is the standard deviation of the blank signal calculated from the Stern-Volmer plots. The Stern-Volmer equation is shown as following:

$$F_0 / F = 1 + K_{sv} C,$$

where \(F_0\) and \(F\) are intensities of fluorescence in the absence and presence of a quenching molecule, respectively. \(K_{sv}\) is the quenching constant of the quencher, and \(C\) is concentration.

3. Result & discussion
The NCDs were successfully synthesized from the pyridine–water mixture by SP in just 10 min. The TEM image (figure 2(a)), clearly shows that the obtained NCDs were well monodispersed and had a spherical shape. The size of the NCDs was in the range of 4–8 nm measured with a calculated mean size of 6 nm (figure 2(b)).
The crystalline structure of the obtained NCDs was observed by HRTEM measurements, as shown in figure 2(a) inset.

To confirm the doped nitrogen contents in NCDs, the atomic composition was carried out and the results are presented in table 2. The carbon and nitrogen were found to be the main atomic constituents of NCDs, which were derived from the pyridine as the organic monomer. Since the radicals from plasma were the main resources to assemble the NCDs, an understanding of radical information was necessary. A signal from the SP-induced radicals was detected as shown in the optical emission spectroscopy (OES) spectrum in figure 3(a). The C2 and CN radicals originating from the dissociation of pyridine molecules by the plasma discharge were also confirmed. Reactive species, such as OH and O, coming from water molecules were also revealed in the measurement (figures 3(a) and (b)). The OH band was visible in the vicinity of 306 to 320 nm and the peak from O radical was found at 777 nm. This data was in agreement with the previous work [36]. The presence of oxygen-containing radicals in the solution might lead to introducing oxygen onto the surface of the NCDs obtained via SP synthesis, which could give an advantage for the improvement of fluorescence efficiency at the desired wavelength [38].

Table 2. The atomic composition of the NCDs.

| Sample | C [at.%] | H [at.%] | N [at.%] | O [at.%] |
|--------|----------|----------|----------|----------|
| NCDs   | 54.89    | 28.66    | 12.43    | 4.03     |

Powder x-ray diffraction analysis was conducted to investigate the crystalline structure of NCDs. The XRD pattern, as shown in figure 4(a), exhibited two broad peaks. The bigger one was visible in the vicinity of 24°, associated with (002) plane, and a small peak around 43° corresponded to (111) plane [39]. This result indicated that an intermediate structure, between graphite and amorphous states, could be observed in the obtained NCDs. Such a structure is referred to as a turbostratic structure [39]. The Raman spectrum measurement could provide the evidence that the heteroatoms are contained in the carbon frameworks. Figure 4(b) shows the Raman spectrum of the obtained NCDs. The peaks at 1330 and 1550 cm⁻¹ corresponded to the D and G bands. In general, the D band is associated with structural defects, disorder, or edge, while the G band corresponds to the E₂g vibration in the sp² carbon, referring to graphitization [40]. The graphitization degree of carbon materials is commonly confirmed by the intensity ratio of two bands (I_D/I_G ratio). The I_D/I_G ratio calculated for the studied NCDs equaled to 0.99, which could imply that the heteroatoms in the carbon framework caused relatively high defect density in the structure of NCDs.

To further identify the functional groups, presented in the studied materials, FT-IR was carried out and the results are gathered in figure 4(c). The broad absorption band between 3680 and 3150 cm⁻¹, which related to OH and NH stretching, respectively, were observed [41, 42]. The presence of OH and NH could contribute to making water-soluble NCDs. The band associated with sp² CH stretching was visible at 3072 cm⁻¹, and sp³ CH stretching was found at 2919 and 2850 cm⁻¹ [43]. However, the C–H band almost disappeared when compared with the FT-IR results of pyridine (figure S1 is available online at stacks.iop.org/NANOX/1/020043/mmedia), as a main precursor. It was due to the decrease in the number of C–H bands at the edges through the polymerization process. The band of nitrile (C≡N) functional group was clearly visible as a sharp peak at 2200 nm.
The formation of the nitrile-functional group was possible due to the reaction of cyano radicals generated from the dissociation of the pyridine molecule by plasma discharge [37]. The bands positioned at 1647 and 1504 cm\(^{-1}\) were assigned to the stretching vibration of aromatic C=\(\text{C}\), while the bands contributing to C–O and C=O were observed in the range of 1400 to 1200 cm\(^{-1}\) [44]. Based on the evidence obtained from the EA and FT-IR studies, a presence of oxygen-based functional groups on the surface of the NCDs was confirmed. These oxygen-based functional groups can result in surface oxidation, which plays an important role in improving the quantum yield of the NCDs. The relationship between surface oxidation and quantum yield is described further in text, in the section devoted to fluorescence. The bands related to the amino-functional group appeared in the range from 700 to 800 cm\(^{-1}\) [45]. In our previous report about plasma discharge in pyridine solvent, a formation of nitrile functional group was confirmed as deriving from cyano radical, generated in the dissociation of pyridine [37]. However, in this work, the formation process of functional groups was slightly different due to the dissociation of water molecules when the SP was generated in the mixture of pyridine and water. Therefore, some nitrile-functional groups could be converted to amino-functional groups due to the relatively high concentration of H radicals in pyridine aqueous solution in comparison with pure pyridine. The analysis of transition band in NCDs was conducted by UV–vis absorbance measurement. The absorbance spectrum of the SP-induced NCDs in the aqueous solution is presented in figure 4(d). The absorption band appearing at 250 nm was associated with \(\pi-\pi^*\) transition from C=\(\text{C}\), while the broad shoulder bands at 330 nm, related to \(n-\pi^*\) transition bands, were observed. The typical absorption spectrum of colloidal CDs solution generally shows the \(\pi-\pi^*\) transition band [46]. In this work, the presence of the broad \(n-\pi^*\) transition band in the CDs containing heteroatoms was expected. Therefore, the appearance of the absorption band around 330 nm proved successful doping of nitrogen on the obtained CDs.

The chemical state of N in the carbon framework of the NCDs was confirmed by using XPS. In the spectrum presented in figure 5(a), three main peaks associated with C 1s, N 1s, and O 1s were observed at 284.5, 399.5, and 532.5 eV, respectively. The nitrogen configuration was further investigated using a high-resolution scan in the vicinity of N 1s peak (395–405 eV) and the results are shown in figure 5(b). The N 1s spectrum was deconvoluted and four constituents could be obtained, including pyridinic-N (N\(_{\text{p}}\)) at 399.0 ± 0.5 eV, pyrrolic-N (N\(_{\text{pp}}\)) at 400.0 ± 0.5 eV, cationic-N (N\(_{\text{c}}\)) at 401.0 ± 0.5 eV, and pyridinic-N oxide (N\(_{\text{ox}}\)) at 402.5 eV. The composition percentages of N\(_{\text{p}}\), N\(_{\text{pp}}\), N\(_{\text{c}}\), and N\(_{\text{ox}}\) were equaled to be 42.2%, 22.3%, 29.6%, and 5.9%, respectively.
Consequently, the NCDs configuration could be constructed, and the model is shown in figure 5(c). In general, three main kinds of N bonding configurations can be distinguished, when the nitrogen atoms are doped in the planar carbon framework, such as pyridinic N, pyrrolic N, and graphitic N (or quaternary N). Introduction of N atoms, due to their five valence electrons, can lead to a deterioration of the planar carbon structure, hindering the preparation of CDs or graphene. However, the SP synthesis of the NCDs, presented in this work, enabled the successful introduction of a cationic type of N-dopant, NC, with four valence electrons (same as carbon) into the NCDs and the preservation of planar carbon structure [39]. Furthermore, to reveal functional groups on the surface, the peak analysis of C1s and O1s peaks were conducted. The high-resolution XPS spectrum of C1s, as shown in figure S2(a), was deconvoluted into two peaks centered at 284.6, and 286.1 eV, respectively, corresponding to C=C, and C–N/C–O bonds. Also, figure S2(b) exhibited the high-resolution XPS spectrum of O1s. The peak at 531.2 eV can be related to C=O. The peak at 532.6 eV is assigned with C–O. It can be inferred that oxygen has connected to the carbon surface through the above chemical bonds, which can be estimated from the XPS and FT-IR results.

Figure 6(a) shows the digital images of the NCDs solution under daylight and UV light. The results showed that the NCDs solution emitted a strong blue light under the UV-light. To understand their fluorescence property, the fluorescence spectra were measured using different excitation wavelengths, as shown in figure 6(b). The stoke shift of emission wavelength from the excitation wavelength indicated that the emission of NCDs was

![Figure 5. (a) XPS survey spectrum, (b) high-resolution XPS N1s spectrum of NCDs (NP: pyridinic N, NPR: pyrrolic N, NC: cationic N, NOX: oxidized N, and (c) schematic representation of N atom configurations in the carbon structure.](image)
The quantum yield of the NCDs obtained in this work is comparable or higher than the results reported for other heteroatom-doped CDs, as presented in table 3. The high quantum yield is an important feature of CDs, considering energy efficiency. Generally, it can be controlled by two factors, the presence of heteroatom and surface passivation [47]. Firstly, the lone pair electrons of introduced nitrogen heteroatoms generate \( n \)-orbital as a HOMO level between existing \( \pi \) and \( \pi^* \)-orbital in the carbon structure. The relatively narrow bandgap of \( n-\pi^* \) transition is much favorable for visible light emission compared with that of \( \pi-\pi^* \) transition. Therefore, NCDs can emit visible light efficiently. For the NCDs, presented in this work, the \( n-\pi^* \) transition band was confirmed in the range of 300 to 350 nm. Furthermore, the light absorbed in this range, especially at 340 nm, was converted into blue fluorescence of the maximum intensity (figure 6(b)). Secondly, surface passivation of NCDs by oxygen, which could remove dangling bonds of the NCDs, contributed to the improvement of quantum yield, achieved in this work. In general, the presence of dangling bonds corresponds to numerous energy levels interferes with the excitation and recombination of electrons for fluorescence [38]. Therefore, the removal of dangling bonds leads to reinforcement of the efficiency of fluorescence at the desired wavelength. As a result, NCDs studied in this work, are characterized by a high quantum yield of over 60% at the blue light range. Additionally, the photostability and effect of pH on the NCDs were evaluated. As shown in figure S3(a), the fluorescence intensity was maintained until 120 min of UV light exposure. The fluorescence intensity gradually decreased as pH increasing (figure S3(b)). The results might be attributed to the protonation of the functional groups on the NCDs surface in the acidic condition [48]. The enhancing of intensity is considered the affection of improving hydrophilic properties, stability, and dispersibility by protonation.

To evaluate the property of NCDs toward TNP detection, the fluorescence response of the NCDs with the addition of various concentrations of TNP solutions was tested under 340 nm of excitation wavelength. As shown in figure 7(a), the fluorescence intensity of NCDs slightly dropped with the addition of 1 \( \mu \)M of TNP. It was further gradually decreasing as the concentration of TNP was increasing. Finally, the peak of fluorescence almost completely disappeared when the concentration of TNP reached 500 \( \mu \)M. Figure 7(b) represents the calibration of the NCDs with a low concentration of TNP. The high coefficient of determination \((R^2 = 0.9978)\) demonstrated that the reliability of NCDs as an excellent molecular detector below 50 \( \mu \)M of TNP. The quenching constant value and the limit of detection (LOD) of the NCDs were \( 9.1 \times 10^4 \) M\(^{-1}\) and 10.1 nM.

![Figure 6](image1.png)

**Figure 6.** (a) Digital images of NCDs solution (20 mg/200 ml) under daylight and UV light (340 nm) and (b) fluorescence spectra of NCD with different excitation wavelengths.

| Sample       | Absorbance value (A) | Integrated area (I) | Quantum yield [%] |
|--------------|----------------------|---------------------|-------------------|
| NCDs         | 0.82                 | 76124               | 61                |
| Rhodamine-B  | 0.27                 | 12750               | 31                |

Table 3. The absorbance value (A) of UV-vis spectra at 340 nm, the integrated area (I) of emission under 340 nm, and quantum yield of the NCDs and Rhodamine-B.
respectively. Accordingly, it could imply that the NCDs obtained in this work had high selectivity toward TNP. The possible mechanism of fluorescence quenching could be described as a photo-induced electron transfer (PET) that prohibits the emission due to the transfer of an excited electron from donor to acceptor. When the amino-functional groups of NCDs (donor) and nitro-functional groups of TNP (acceptor) came close, the excited electron from the NCDs could transfer to TNP without recombination, resulting in the lack of light emission from the NCDs. Thus, the efficiency of electron transfer could affect the sensitivity of the NCDs. Since the amino-functional group is a strong electron donor among the functional groups, it could potentially enhance the efficiency of the donation process. Therefore, the NCDs, containing rich amino-functional groups, showed potential as a high-sensitive detector for TNP even at the low concentration. For checking the selectivity of the NCDs toward TNP, the quenching efficiency of the NCDs with other nitro group molecules (NB, NN, NA, NF) was also investigated. As shown in figure 7(c), the quenching efficiency of the SP-synthesized NCDs in this work was 91% at 100 μM of TNP, which is significantly higher than that of NCDs with other molecules (NB: 0.1%, NN: 1.3%, NA: 2.9%, NF: 12%). The digital image in figure 7(d) shows that the addition of TNP significantly weakened the fluorescence of NCDs solution. The hydroxyl groups of TNP and amino-functional groups of NCDs were reported to show a proton transfer-assisted electron transfer [21]. The kinetic energy of this method of transfer is lower than that of transferring only electron [49]. As a result, it showed that the better quenching efficiency for TNP than for other nitro-functional group molecules. Furthermore, the effect of the nitro group was revealed by the quenching efficiency of nitrophenol and dinitrophenol which have different numbers of nitro-functional groups, as shown in figure S4. The quenching efficiency was gradually increased as increasing the number of nitro-functional groups. Accordingly, both the photo-induced electron transfer and the proton transfer-assisted electron transfer contribute to the excellent selectivity of NCDs for TNP.

4. Conclusion

In this work, the synthesis of the nitrogen-doped carbon dots (NCDs) was conducted successfully by the solution plasma (SP) method. The SP method enabled the quick synthesis of NCDs (10 min) under mild condition (i.e., room temperature and atmospheric pressure). High rate of reaction was achieved owing to the radicals
generated from the solution taking part in the reaction via the plasma discharge. High quantum yield (61%) achieved for the studied NCDs, which makes them an energy-efficient fluorescent molecular detector. This enhancement was possible due to the high N concentration and the surface passivation by radicals generated by the plasma discharge. Further, rich amino-functional groups on the surface offered an effective pathway of electron transfer to TNP. As a result, TNP as a target molecule can be detected with high sensitivity (LOD of 10.1 nM). Excellent selectivity of the NCDs for TNP was confirmed by a high quenching efficiency of 91% as compared with the other nitro group molecules (0.1%–12%). Consequently, the SP method offers a simple manufacturing process for not only NCDs but also other hetero-atom doped CDs. Broader use of this method is recommended to facilitate the commercialization of fluorescence-based materials for ultrasensitive detection and other related application.

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References

[1] Zhang C, Zhang S, Yan Y, Xia F, Huang A and Xian Y 2017 Highly fluorescent polyimide covalent organic nanosheets as sensing probes for the detection of 2,4,6-trinitrophenol ACS Applied Materials & Interfaces, 9 13415–21
[2] Li Z, Wang Y, Ni Y and Kokot S 2015 A sensor based on blue luminescent graphene quantum dots for analysis of a common explosive substance and an industrial intermediate, 2,4,6-trinitrophenol Spectrochim. Acta, Part A 137 1213–21
[3] Chan K K, Yap S H K and Yong K T 2018 Biogreen synthesis of carbon dots for biotechnology and nanomedicine applications Nano-Micro Letters, 10 72
[4] Gaude E et al 2019 Targeted breath analysis: exogenous volatile organic compounds (EVOC) as metabolic pathway-specific probes J. Breath Res. 13 032001
[5] Abu Bakar N, Mat Salleh M, Ali Umar A and George Shapter J 2017 Design and measurement technique of surface-enhanced Raman scattering for detection of bisphenol A Adv. Nat. Sci.: Nanosc. Nanotechnol, 8 025008
[6] Shankaran D R, Gobi K V and Miura N 2007 Recent advancements in surface plasmon resonance immunosensors for detection of small molecules of biomedical, food and environmental interest Sensors Actuators B 121 158–77
[7] Chen B B, Liu Z X, Zou H Y and Huang C Z 2016 Highly selective detection of 2,4,6-trinitrophenol by using newly developed turbid-doped blue carbon dots Analyst 141 2676–81
[8] Jiao X-Y, Li-L-S, Qin S, Zhang Y, Huang K and Xu L 2019 The synthesis of fluorescent carbon dots from mango peel and their multiple applications Colloids Surf., A 577 306–14
[9] Ganguly S, Das P, Banerjee S and Das N C 2019 Advancement in science and technology of carbon dot-polymer hybrid composites: a review Functional Composites and Structures, 1 022001
[10] Zhu S et al 2013 Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging Angew. Chem. Int. Ed. 52 3953–7
[11] Zheng X T, Ananthanarayanan A, Luo K Q and Chen P 2015 Glowing graphene quantum dots and carbon dots: properties, syntheses, and biological applications Small. 11 1620–36
[12] Miao X et al 2018 Synthesis of carbon dots with multiple color emission by controlled graphitization and surface functionalization Adv. Mater. 30 1704741
[13] Mandal D, khatun S, Gupta A N and Chandra A 2019 DNA supported graphene quantum dots for Ag ion sensing Nanotechnology 30 255501
[14] Cruz R A T et al 2019 Functionalized carbon-based quantum dots: optical characterisation and potential application as Bio-fluorophore IOP Conf. Ser.: Mater. Sci. Eng. 559 012003
[15] Das P, Ganguly S, Banerjee S and Das N C 2019 Graphene based emergent nanolights: a short review on the synthesis, properties and application Res. Chem. Intermed. 45 3823–53
[16] Li H et al 2015 Fluorescent N-doped carbon dots for both cellular imaging and highly-sensitive catechol detection Carbon 91 66–75
[17] Xu Q et al 2015 Preparation of highly photoluminescent sulfur-doped carbon dots for Fe(iii) detection J. Mater. Chem. A 3 542–6
[18] Shi D, Yan F, Zheng T, Wang Y, Zhou X and Chen L 2015 P-doped carbon dots act as a nanosensor for trace 2,4,6-trinitrophenol detection and a fluorescent reagent for biological imaging RSC Adv. 5 98492–9
[19] Ye Q et al 2016 N, B-doped carbon dots as a sensitive fluorescence probe for Hg2+ ions and 2,4,6-trinitrophenol detection for bioimaging J. Photochem. Photobiol., B 162 1–13
[20] Siddique A B, Pramanick A K, Chatterjee S and Ray M 2018 Amorphous carbon dots and their remarkable ability to detect 2,4,6-trinitrophenol Sci. Rep. 8 9770
[21] Ju B et al 2018 Photostable and low-toxic yellow-green carbon dots for highly selective detection of explosive 2,4,6-Trinitrophenol based on the dual electron transfer mechanism ACS Applied Materials & Interfaces. 10 13040–7
[22] Ren G et al 2018 Orange emissive carbon dots for colorimetric and fluorescent sensing of 2,4,6-trinitrophenol by fluorescence conversion RSC Adv. 8 16095–102.

[23] Gao K, Guo Y, Niu Q, Han L, Zhou L and Wang L 2018 Quaternary ammonium-functionalized carbon dots for sensitive and selective detection of 2,4,6-trinitrophenol in aqueous medium. Sensors Actuators B 268 298–305

[24] Lin L et al 2015 A facile synthesis of highly luminescent nitrogen-doped graphene quantum dots for the detection of 2,4,6-trinitrophenol in aqueous solution Nanoscale. 7 1872–8

[25] Liu ML, Chen BB, Liu ZX and Huang CZ 2016 Highly selective and sensitive detection of 2,4,6-trinitrophenol by using newly developed blue-green photoluminescent carbon nanodots Talanta 161 873–80

[26] Chen B et al 2019 2,4,6-Trinitrophenol detection by a new portable sensing gadget using carbon dots as a fluorescent probe Anal. Bioanal. Chem. 411 2291–300

[27] Xu J et al 2018 A dual spectroscopic fluorescence probe based on carbon dots for detection of 2,4,6-trinitrophenol/Fe (III) ion by fluorescence and frequency doubling scattering spectra and its analytical applications Spectrochim. Acta, Part A 200 150–7

[28] Fan H et al 2018 Manganese-doped carbon quantum dots-based fluorescent probe for selective and sensitive sensing of 2,4,6-trinitrophenol via an inner filtering effect Spectrochim. Acta, Part A 205 221–6

[29] Xu Q et al 2016 Heteroatom-doped carbon dots: synthesis, characterization, properties, photoluminescence mechanism and biological applications Journal of Materials Chemistry B 4 7204–19

[30] Chandra S, Chowdhuri AR, Laha D and Sahu SK 2018 Fabrication of nitrogen- and phosphorous-doped carbon dots by the pyrolysis method for iodide and iron (III) sensing Luminescence. 33 336–44.

[31] Das P et al 2019 Converting waste Allium sativum peel to nitrogen and sulphur co-doped photoluminescence carbon dots for solar conversion, cell labeling, and photobleaching dilegences: a path from discarded waste to valuable-added products J. Photochem. Photobiol., B 197 111545

[32] Das P et al 2019 Surface quaternized nanosensor as a one-arrow-two-hawks approach for fluorescence turn ‘on–off–on’ bifunctional sensing and antibacterial activity New J. Chem. 43 6205–19

[33] Saito N, Bratescu MA and Hashimi K 2017 Solution plasma: a new reaction field for nanomaterials synthesis Japan. J. Appl. Phys. 57 01024A

[34] Morishita T et al 2016 Fastest formation routes of nanocarbons in solution plasma processes Sci. Rep. 6 36880

[35] Kim D-W, Li OL, Pootawang P and Saito N 2014 Solution plasma synthesis process of tungsten carbide on N-doped carbon nanocomposite with enhanced catalytic ORR activity and durability RSC Adv. 4 16813–9

[36] Chokradjaroen C, Theeramunkong S, Yui H, Saito N and Rujiravanit R 2018 Cytotoxicity against cancer cells of chitosan oligosaccharides prepared from chitosan powder degraded by electrical discharge plasma Carbohydrate Polym. 201 20–30

[37] Kim K, Hashimi K, Bratescu MA and Saito N 2018 The Initial Reactions from Pyridine to Hetero-Carbon Nanomaterials Through Solution Plasma Nanoscale and Nanotechnology Letters. 10 814–9

[38] Wolkin MV, Jorje F, Fauchet PM, Allan G and Delerue C 1999 Electronic states and luminescence in porous silicon quantum dots: the role of oxygen Phys. Rev. Lett. 82 197–200

[39] Chae S, Panomusawan G, Bratescu MA, Teshima K and Saito N 2019 p-Type doping of graphene with cationic nitrogen ACS Appl. Nano Mater. 2 11350–5

[40] Kaufman JH, Metin S and Saperstein DD 1989 Symmetry breaking in nitrogen-doped amorphous carbon: infrared observation of the Raman-active G and D bands Phys. Rev. B 39 13053–60.

[41] Ramanathan T, Fisher FT, Ruoff RS and Brinson LC 2005 Amino-functionalized carbon nanotubes for binding to polymers and biological systems Chem. Mater. 17 1290–5

[42] Yuen SM, Ma CC-M, Lin Y-Y and Kuan HC 2007 Preparation, morphology and properties of acid and amine modified multiwalled carbon nanotube/polyimide composite Compos. Sci. Technol. 67 2564–73

[43] Huang HG, Huang YJ, Ning YS and Xu GQ 2004 Selective bonding of pyrazine to silicon(100)–2 × 1 surfaces: the role of nitrogen atoms J. Chem. Phys. 121 4820–5

[44] Travlou NA, Giannakoudakis DA, Algarra M, Labella AM, Rodriguez-Castellon E and Bando ZJ 2018 S- and N-doped carbon quantum dots: surface chemistry dependent antibacterial activity Carbon 135 104–11

[45] Tamilselvan S et al 2013 Growth, thermal, dielectric and mechanical properties of L-phenylalanine–benzoic acid: a nonlinear optical single crystal Spectrochim. Acta, Part A 114 19–26

[46] Jiang K, Wang Y, Gao X, Cai C and Lin H 2018 Facile, quick, and gram-scale synthesis of ultralong-lifetime room-temperature-phosphorescent carbon dots by microwave irradiation Angew. Chem. Int. Ed. 57 6216–20.

[47] Li LN and Dong T 2018 Photoluminescence tuning in carbon dots: surface passivation or/and functionalization, heteroatom doping J. Mater. Chem. C 6 7944–70

[48] Liu Y et al 2015 One-step synthesis of robust nitrogen-doped carbon dots: acid-evoked fluorescence enhancement and their application in Fe3+ detection J. Mater. Chem. A 3 17747–54

[49] Warren J, Tronic TA and Mayer JM 2010 Thermochromistry of proton-coupled electron transfer reagents and its implications Chem. Rev. 110 6961–7001