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Starch (Tapioca) to carbon dots: an efficient green approach to on-off-on photoluminescence probe for fluoride ion sensing

Aniruddha Basu, Anil Suryawanshi, Begraj Kumawat, Anshu Dandia, Debanjan Guin and Satishchandra B Ogale

Photoluminescent carbon dots with size 4-5 nm are prepared from starch (Tapioca Sago) through solution method using mild conditions. The as-prepared carbon dots are used as photoluminescence probe for highly anion selective fluoride ion detection in water solutions. A ready-to-use device is also demonstrated.

Since last decade the luminescent carbon dots (C-dots) are gaining importance in the scientific field because of their unique and novel properties. The most notable properties are their high stability, high solubility in water, low toxicity, high bio-compatibility, different photoluminescence (PL) behaviour etc. All these properties make this new member of the carbon family extremely interesting to the scientific community.

C-dots have a wide range of applications in different fields of science and technology. In device science, they have been used in optoelectronics, chemo-sensors etc. While in bio-medical applications, they have found use in bio-imaging, bio-labelling, drug delivery etc. Most of these applications are based on the photoluminescence (PL) property of C-dots. The details of the PL behaviour of C-dots are associated with several aspects such as the quantum confinement effect, trap states at the surface, charge transfer, radiative exciton recombination, particle size distribution etc. The generalised theory behind the PL of C-dots is yet to be established.

The PL property of C-dots has a very interesting and rather unique characteristic, i.e. easy ‘turn off’ and ‘turn on’. Addition of electron acceptor or donor moiety on the surface of C-dot causes quenching of the PL intensity (‘turn off’ state). On removal of the said moiety, the PL intensity can be restored (‘turn on’ state). Based on this property, chemo-sensor using C-dots have developed to detect environmental pollutant. Normally, in such application inorganic quantum dots (QD) have been vastly studied and used. But their inherent toxicity limits their applicability as environmental pollutant detectors. Recently, C-dots have emerged as extremely promising candidate in this field due their low toxicity. Till date most of the C-dot based chemo-sensors are developed to detect the cation pollutants like Hg, Pb, Be, Ag etc. There are also a few sensors to detect anion pollutants such as NO, PO, etc. To the best of our knowledge, however, till date there is only one report wherein C-dots are used for the detection of fluoride (F) ions, but using an entirely different scheme.

F ions are considered as one of the major water pollutants. Although F is necessary for our biological system its excess intake can severely harm different organs. According to world health organization (WHO), excess F intake can permanently damage bones, teeth and kidney. It has most adverse effect on children. Prolonged exposure to F can inhibit IQ development of children. Hence selective detection of F in water is extremely important. Many studies have already been done on this topic. However, most such studies on the optical or PL based detection of F ions have been carried out with organic molecules. The synthesis of the corresponding organic molecules generally involves more than one step. Hence the overall production cost is very high. Importantly, many of these molecules are mostly water insoluble. Hence, the detection of F ion in water samples cannot be done directly by their use.

In this paper, we have introduced for the first time a simple ‘on-off-on’ strategy to develop a PL based ultrafast chemo-sensor using C-dots, which is not only highly sensitive and selective to F but is also environmental friendly and cost effective. In order to develop the chemo-sensor we have first focused on the synthesis of water soluble C-dots. Towards this end, we have developed a green strategy to synthesize C-dots from low cost and easily available precursor such as a starch. The source of the starch used here is a very common Indian food product, Sabudana (Tapioca Sago). As mentioned earlier, the working principle of this chemo-sensor is based on ‘on-off-on’ mechanism. Here, we have used Fe ion to turn off the PL of C-dots. The Fe ions attached to the surface of C-dots effectively quench the PL intensity through charge transfer process (“turn off”). Subsequently, F ions added to the solution remove the Fe from the surface. On removal of Fe the PL intensity is restored to its original, leading to the “turn on” state.
The response of the chemo-sensor toward the F ions is extremely fast and selective. Further we have developed a gel-based device which is very convenient for qualitative detection of F ions in water.

We have used a novel green approach for the synthesis of water-soluble C-dots using starch and mild base. The starch was treated with hot (80-90°C) water. Then, this hot starch solution was stirred with 0.1M potassium hydroxide (KOH) for 12 h to form C-dots, and the solution was subsequently neutralised (pH-7) by 0.1M hydrochloric acid. The as-synthesized C-dots are highly water soluble (dispersible).

To confirm the surface functionalization of the C-dots, infrared spectroscopy was performed. The FTIR spectrum (ESI figure S1) confirms the presence of the carboxylic –OH group (broad absorption peak at 3250 cm\(^{-1}\)) and the carboxylic C=O group (weak absorption at 1693 cm\(^{-1}\)). These indicate the presence of –COOH as the surface functional groups on C-dots which facilitate its solubility in water. The FTIR spectrum also showed the characteristic C=C stretching vibration (1579 cm\(^{-1}\)) and sp\(^2\) C-H bending vibration (1012 cm\(^{-1}\)) of C-dots. Along with the C-H stretching (2913 cm\(^{-1}\)) and C-H rocking (1379 cm\(^{-1}\)) vibrations which indicate the presence of sp\(^3\) carbon in the C-dot.

To confirm the size and shape of the as synthesized C-dots high resolution transmission electron microscope (HR-TEM) imaging was employed. The HR-TEM image (figure 1) confirm the presence of 4-5 nm sized mostly spherical C-dots. The d-spacing obtained from HR-TEM is approximately 0.22 nm which matches with the characteristic d-spacing of C-dots as per literature.\(^{28}\) The UV-visible spectrum (ESI figure S2) also shows the characteristic absorption of C-dots around 260 nm which arises due to \(\pi\)-\(\pi^*\) transition.\(^{28}\)

Figure 1 a) TEM image of C-dot, b) HRTEM image of C-dot, inset shows the lattice parameter.

Further we performed detailed PL intensity analysis of C-dots with different excitation wavelengths (ESI figure S3). We used 300 nm to 500 nm excitation ranges with 25 nm increment. In this study, we have found that as the excitation wavelength increases the PL intensity peak shifts to the higher wavelength i.e. these C-dots show excitation dependent PL. Going from lower to higher excitation wavelength the PL intensity increases initially till 375 nm and then decreases progressively. In our sensing studies we performed all the experiments at 350 nm excitation wavelength. The as-synthesized C-dots have PL intensity around 450 nm for 350 nm excitation.

To develop the PL based chemo-sensor we have used the concept of PL intensity quenching through charge transfer process by attaching electron acceptor or donor to the surface of C-dot, followed by the PL recovery by removing the same. Here we have used cations as the electron acceptor which get readily attached to the C-dot surface with the help of –COOH groups and quench the PL intensity of C-dots. Further to remove the cations from the C-dot surface we have used F ions. The PL in the C-dot arises due to radiative recombination of the electron hole pair. Addition of an electron acceptor in the solution leads to the quenching of PL intensity due to the non-radiative electron/hole recombination.

In sensing study, ferric chloride (FeCl\(_3\)), nickel nitrate (Ni(NO\(_3\))\(_2\)), cobalt nitrate (Co(NO\(_3\))\(_2\)), cadmium nitrate (Cd(NO\(_3\))\(_2\)), cupric chloride (CuCl\(_2\)) and manganese chloride (MnCl\(_2\)) were used as the sources of Fe\(^{3+}\), Ni\(^{2+}\), Co\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\) and Mn\(^{2+}\) respectively, and ammonium fluoride (NH\(_4\)F), ammonium chloride (NH\(_4\)Cl), sodium sulphate (Na\(_2\)(SO\(_4\))\(_2\)) and sodium nitrate (NaNO\(_3\)) as the sources of F\(^-,\) Cl\(^-\), SO\(_4^{2-}\) and NO\(_3^+\) respectively. The concentration of the stock solution for all the cations was 1mM. For the PL intensity quenching study 100µl from the stock solution was used. The concentration of the stock solution of the anions was 10mM.

The PL intensity quenching study was done using different cations having the same concentration (ESI figure S4). In this study we found that Cd\(^{2+}\) has least PL intensity quenching ability with only 2%. Mn\(^{2+}\) also showed low quenching of about 13%. Somewhat better result was obtained in case of Ni\(^{2+}\) and Co\(^{2+}\) where they showed 30% and 36% quenching. The best result however obtained for the Fe\(^{3+}\) and Cu\(^{2+}\) cases. These cations were found to be more effective in this process than the other cations used, with quenching of 67% and 69%. As we have discussed earlier, the effective quenching of C-dot PL intensity occurs due to the formation of charge transfer complex with the metal ions through its –COOH functional group. The better the charge transfer complex the greater will be the PL quenching. Fe\(^{3+}\) and Cu\(^{2+}\) are well known for stable metal-complex formation as compared to other transition metals. The stability of the complexes can be explained by hard-soft-acid-base (HSAB) principle. The carboxylic acid group is a hard base. Now to form an effective metal-complex, the metal should also be hard. Among the metals used in our experiment, Fe\(^{3+}\) is hard acid and rest fall in the borderline region.\(^{30}\) Again amongst the borderline metals, Cu\(^{2+}\) forms the most stable complex.\(^{30}\) Hence, in this case, Fe\(^{3+}\) and Cu\(^{2+}\) bind effectively to the –COOH group of C-dot to form better charge transfer complex which in turn shows better PL quenching. Thus we continued our PL intensity recovery experiment with F\(^-\) with these two specific cations.

In the PL intensity recovery study Fe\(^{3+}\) was found to be more responsive than Cu\(^{2+}\) (ESI figure S5). In this experiment, we first quenched the PL intensity with Fe\(^{3+}\) and Cu\(^{2+}\) solutions having equal concentrations and then added equal amount (200µl from the stock) of F\(^-\) solution in both these to recover the PL intensity. From this study we have found that the PL intensity recovery in the case of Fe\(^{3+}\) ions was 59% which is more pronounced than that for Cu\(^{2+}\) case (47%). We therefore have performed a detailed PL recovery study with the Fe\(^{3+}\) case (Figure 2). To study the sensing property of the chemo-sensor we first quenched the PL intensity of C-dots up to 20% of its original with Fe\(^{3+}\) ions and then examined the recovery of the same using different F concentrations: i) 0.29 mg/ml, ii) 0.57 mg/ml iii) 1.13 mg/ml, iv) 2.19 mg/ml and v) 4.14 mg/ml. In the recovery study, over 75% PL recovery was noted for 4.14mg/ml F\(^-\) ion concentration.
Further to check the selectivity of the chemo-sensor for different anions we performed a comparative study using F-, chloride (Cl⁻), nitrate (NO₃⁻) and sulphate (SO₄²⁻), which are mostly present in water (ESI figure S6). From this study, it is quite clear that the chemo-sensor is highly selective towards F⁻ ion. The reason for this selectivity can be explained by considering the stability of the compounds formed in water solution upon addition of the anions. The stability of an ionic compound in water depends upon its lattice energy and hydration energy. If the hydration energy of an ionic compound is less than its lattice energy, then it will be stable in water i.e. it will not be in the ion state. In our experiment, the products formed upon anion addition should be stable (insoluble) in water solution to remove Fe³⁺ effectively from the C-dot surface. If they are not, such as in the case of FeCl₃ (which is soluble) the Fe³⁺ ions thus formed in the solution can again get re-associated on the C-dot surface (kinetic equilibrium) and quench the luminescence. The product formed on addition of F⁻ ion is FeF₂ which is quite stable in water solution. This is because the lattice energy of FeF₂ is very high (5870 kJ/mol) than its hydration energy (4953 kJ/mol). Hence a large amount of energy (917 kJ/mol) is required to ionize it in water. In the case of NO₃⁻ and SO₄²⁻ due to their large size they cannot approach the Fe³⁺ attached on the C-dot surface. Hence, Fe³⁺ removal does not take place. This can also be inferred from the PL recovery study with different anions. In this recovery study, initially we quenched the PL intensity up to 23% of its original. Addition of F⁻ caused PL intensity to rise over 75%. In case of Cl⁻ ion, just 25% of the actual intensity was observed. NO₃⁻ (19%) and SO₄²⁻ (20%) could also not take part in the PL intensity recovery. This in turn strongly confirms the selectivity of the chemo-sensor toward F⁻ ions.

For further confirmation confocal microscopy was performed (figure 3). In this study, we found that the dispersed pristine C-dots (figure 3 a) have intense PL under 482 nm (± 18 nm) excitation (figure 3 d). After addition of Fe³⁺, not much change is observed in the dispersion of the C-dots (figure 3 b) but the PL intensity got quenched dramatically (figure 3 e). Further, with the addition of F⁻ ions the C-dots started to agglomerate (Figure 3 e), but more importantly they regained their PL intensity (Figure 3 e). Thus considering these images we can say that PL intensity quenching occurs due to the attachment of Fe³⁺ ions on the surface of C-dots and the recovery results due to Fe³⁺ removal by F⁻ ions.

We also could demonstrate a practical application of the C-dots as chemo-sensors. Towards this end, we developed a ready-to-use agarose gel based off/on type chemo-sensor device (figure 4). Initially the C-dot solution was taken and agarose gel was added to make a 3 mg/ml solution. It was then heated at 80°C till the agarose dissolved completely and then put in the container of a desired shape and cooled to room temperature for gelation. We prepared beads of agarose gel with C-dots confined inside (figure 4 a). Under UV light (365 nm) the beads exhibited very intense PL uniformly in all beads (figure 4 d), which confirms the confinement as well as homogeneous distribution of C-dots inside agarose gel matrix. Then we put the bead in Fe³⁺ solution for 30 seconds. On removal, no notable colour change could be detected under visible light (figure 4 b). However, under UV light (365 nm) drastic quenching of PL intensity was observed for these beads (figure 10 e). Further, for F⁻ sensing these beads were immersed in water containing F⁻ ions (4.14mg/ml) for 1 minute. Again no notable visual change was detected (figure 4 c), but the PL intensity of the beads was found to recover when irradiated under UV light (figure 4 f).
extremely selective, sensitive and spontaneous. This can be used as a handy tool for quick checking of water samples for F− pollutant.

Conclusions

To summarize the work, we have developed C-dot based PL chemo-sensor for F− ion detection in water. The C-dots used to develop the PL chemo-sensor are synthesized in one step from very cheap starch source, using mild reaction conditions. The as-synthesized C-dots are -COOH functionalised which not only helps their uniform dispersion in water but also enables cation attachment on their surface. A chemo-sensor is developed using the as-synthesized C-dots without further modification. The sensing procedure involves two steps, first, quenching of PL intensity of C-dots with Fe3+ followed by PL intensity recovery by the addition of F− ions. This chemo-sensor is highly selective and spontaneous toward F− ion detection. We have also developed ready to use agarose gel based sensor for practical application. The device is very spontaneous in F− ion detection and can easily be used for quick detection of F− in water. The advantages of the chemo-sensor developed in this work are low cost, fast response and highly selectivity.

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Notes and references

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