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A Short Review on Fluorimetric Sensing with Graphene Quantum Dots

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ABSTRACT

Graphene quantum dots (GQDs) are the zero dimensional particles, which show completely different properties from their bulk structure. When GQDs are illuminated underultra-violet-visible light, electronsare excited to a state of higher energy and after that, these excited electrons come back to lower energy states by emitting light. This is a very interesting property of GQDs, which is known as fluorescence. Depending on the fluorescence property of GQDs, they have been implemented for the sensing of various metal ions, biomolecules, toxic chemical, etc.This short review mainly focuses on the fluorescence property of GQDs. Moreover, by using fluorescence property of GQDs,the sensing of various metal ions are pointed out by showing a continuous progress in this fluorometric sensing process by modifying the structural properties of GQDs. Later, the future scope in the same filed and their further implementation in the real life.

Keywords - GQDs, fluorescence, metal ions, sensing, turn on/ turn off signal

1. INTRODUCTION

Graphene quantum dots (GQDs) is one the most interesting derivatives of graphitic material due to their optical and electric properties. The optical property of GQDs is one of the most interesting properties of GQDs. When the GQDs are excited with sufficient energy, the valance band electrons get excited to the conduction band. After that, the excited state electrons come back to lower energy states. Due to the present of enormous number of defect states, vacancy, function groups, a large number of states are generated in between the conduction band and valance band. As a result, the excited states electrons come to that defect induced states and produce a broad band emission spectrum with a maxima. Depending on the excitation, the position of maxima may vary.[1]There is various studies on the synthesis of GQDs. Mainly two methods have been adopted : top down[2] and bottom up[3].Doping a very powerful method to engineer the structural and optical properties of GQDs.The morphological analysis was also reported GQDs as circular in shaped. By using X-ray Powder Diffraction (XRD), Raman spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, the structural analysis was reported.[2, 4]. A broad XRD peak around $2\theta \sim 26^0$ signified that present of graphenetic component. Raman analysis specifies the graphitic contribution by characteristic G and D band around 1580 cm^{-1} and 1380cm^{-1}. The G band arises due to in-plane phonon vibration of C=C graphitic carbon and D band comes from defect states.[2]FTIR confirms the present of various functional groups like OH, COOH, C=O, etc.Optical properties of GQDs werereported based on UV-vis absorption and photoluminescence (PL) spectroscopy studies. The UV-vis absorption spectrum of GQDs shows two different types of electronic transitions, namely $\pi-\pi*$and $n-\pi*$ transition.$\pi-\pi*$ transition is corresponding to band to band transition and $n-\pi*$ transition corresponding to functional groups and defect states.PL is basically the emission of the photons through the relaxation of excitons to the lower energy levels.The sources of fluorescence emission are mainly defect states, vacancy, functional groups. With change of these sites, fluorescence signal may change. Using this mechanism, metal ions have been detected with various concentrations. Notably, the doping in GQDs changes the fluorescence emission colour as well as intensity also. Due to high surface area, enormous number of oxygen functional groups, unique fluorescence emission, high charge density, water solubility properties of GQDs, they have been implemented in optical sensing, bio imaging, fabrication of optoelectroic devices, etc.[5, 6]

In this short review, the sensing of various metal ions presented with a step by step progress in this sensing method along with the future scope for further implementation in real life.

2.1. Detection of Fe^{3+} ions:

$Fe^{3+}$is one of the important metal ions in the human body, and it is responsible for cellular metabolism, oxygen transport, enzyme catalysis as well as nucleic acid synthesis processes.[7-9] The dysfunction of Fe^{3+}concentration in the human blood can be originof several diseases, such as anemia, Parkinson's illness, malaria,cancer Alzheimer’s disease, etc.[9, 10] Therefore, actual sensing of Fe^{3+} ion is highly desirable for healthy living. Considerable research has been devoted to constructing different analysis methods for quantitative and quantitative detection of Fe^{3+}.Kim et al. reported the detection of Fe^{3+}ions with a lower limit ~7.22μM at pH 4 by using fluorescence GQDs synthesized by exfoliation.[11] In this detection process, the fixed concentration of GQDs (50 μg/mL) was mixed with different concentration of Fe^{3+}ions and then the mixed solution was excited with 365 nm UV light to get the changes in the PL intensity. With the increasing concentration of Fe^{3+}ions from 20 μM to 360 μM, a monotonic reduction of the PL intensity was observed. For the detection purpose, the liner region was selected, as shown in the Fig. 1. Xu et al. reported the sensing of Fe^{3+}ions with higher efficiency by nitrogen doped GQDs (N-GQDs).[10] This group reported limit of detection (LOD) as low as ~0.06 μM and the range of detection was 1-80 μM. Note that, the whole range of the detection is a linear region as shown in Fig.2. Here, N-GQDs were synthesized by top-down method and the excitation wavelength is ~365 nm. Due to the doping of nitrogen, it increases the sensitivity and selectivity towards Fe^{3+}ions due to the formation of N-GQDs-Fe complex. Sulfur-doped GQDs (S-GQDs) was further used in the purpose of sensing of Fe^{3+}ions, which showed very high sensitivity with LOD in nM level.[7] The LOD value was 4.2 nM with the range of the detection 0-0.72 μM. In this literature, S-GQDs was prepared by one-step electrolysis of graphite in sodium p-toluenesulfonateaqueous solution. In the detection process S-GQDs was excited under excitation 380 nm. In this sensing process, when Fe^{3+} ionsare added into the S-GQDs solution, they get attached withphenolic hydroxyl groups on the edge of S-GQDs, and the electrons in the excited state of S-GQDs will transfer tothe half-filled 3d orbits of Fe^{3+}, which occurs non-radiative recombination leading to PL quenching.

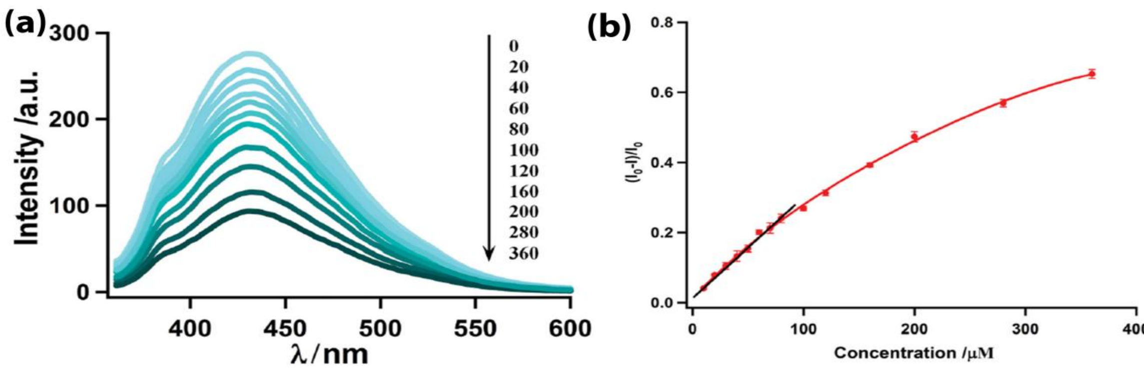

Fig. 1: (a) PL emission spectra of GQDs with different concentrations of Fe^{3+} ions. (b)Concentration-dependent fluorescence response. Adopted from Ref.[11]

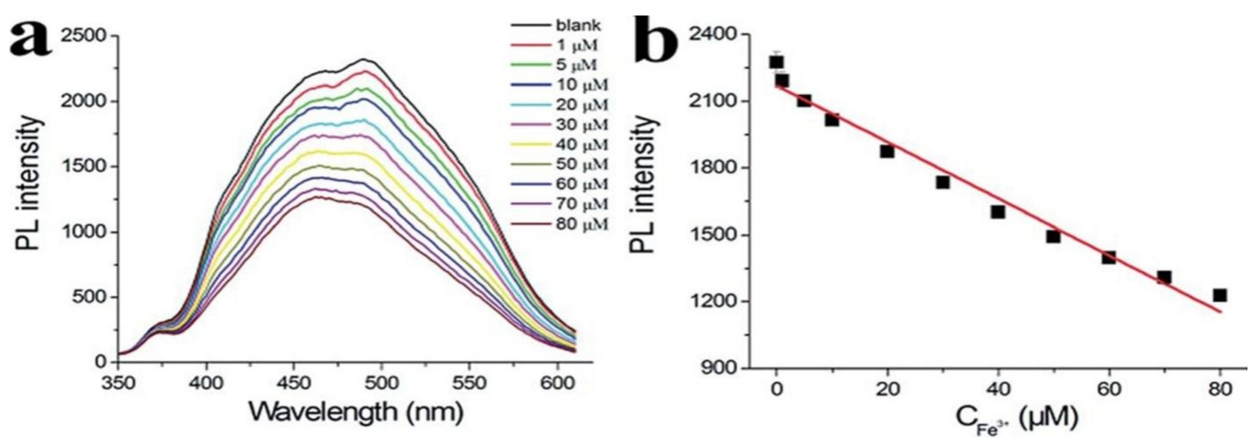

Fig. 2: (a) PL emission spectra of N-GQDs with different concentrations of Fe^{3+} ions. (b)Concentration-dependent fluorescence response. Adopted from Ref.[10]

2.2. Detection of Cu^{2+} ions:

As essential an element in the human body,Cu^{2+} plays an important role in many physiological processes. Low concentrationof $Cu^{2+}$is an essential micronutrient.However, high concentration of Cu^{2+} would cause serious harm in human body. Excessive Cu^{2+} may cause a variety of difficulties, such as high blood pressure, sleepiness, neurological diseases like Alzheimer's and Parkinson's diseases, etc. So the sensitive detection of Cu^{2+} ions important. Liu et al. reported the detection of Cu^{2+} ions using novel GQDs-based fluorescent probe.[12]Cu^{2+} is paramagnetic ion with an unfilled d shell and quenches the fluorescence via electron or energy transfer.The proposed sensor works in the concentration range 50–150μM with LOD 50μM.Wang et al. showed the detection of Cu^{2+} ions using blue fluorescent GQDs.[13] Addition of Cu^{2+} ions with different concentrations, the fluorescent quenching of GQDs occur due to ground state complex formation. They reported the LOD as low as .023 μM and the linear detection range~0.2–300μM.The excitation wavelength was320 nm and emission wavelength was 430 nm.Wang et al. reported the detection of Cu^{2+} ions with LOD 72.2 nM using N-GQDs as the sensing probe.[14] The range of detection is 0.0–35.0μM. In this sensing process, COOH functional group on the surface of N-GQDs was deprotonated with the present of Cu^{2+} and as a result, sensitivity of detection process enhances.

2.3. Detection of Al^{3+} ions:

Aluminum (Al) metal and its compounds exist in environment and human daily life, such as aluminum alloy has been used as cookware, the compounds of aluminum also can serve as clinical drugs. However, the excessive intake of Al is harmful to liver, kidney, and bones of human body, especially can induce Alzheimer's disease and osteoporosis. Fang et al. detected Al^{3+} ions as low as 1.3μM concentration using N-GQDs as sensing platform.[15]

3. Conclusion and Future Perspectives:

In conclusion, an over view of fluorometric sensing method is discussed here. In this process, various types of GQDs were implemented for the detection of different metal ions. The detection mechanism is also elucidated here along with their detection range and limit of detection. In the purpose of medical implementation, the requirement of detection of various metal ions is also discussed here.

The possibilities of using GQDs as a platform for sensing, and therapy are vast. Due to low toxicity nature of GQDs, they can be further implemented for in vivo sensing.

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