Synthesis of Highly Fluorescent Nitrogen-Doped Graphene Quantum Dots for Selective Detection of Cu (II)

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ABSTRACT

Graphene quantum dots (GQDs) are a kind of 0D material with characteristics derived from both graphene and carbon dots (CDs). Combining the structure of graphene with the quantum confinement and edge effects of CDs, GQDs possess unique properties. In this review, we focus on the application of GQDs and N-GQDs in electronic, photoluminescence sensor. We have summarized different techniques and given future perspectives for developing smart sensing based on GQDs.

1 INTRODUCTION

Graphene quantum dots (GQDs), as defined, are a kind of 0D material with characteristics derived from both graphene and CDs, which can be regarded as incredibly small pieces of graphene [1,4]. By converting 2D graphene sheets into 0D GQDs, the GQDs exhibit new phenomena due to quantum confinement and edge effects, which are similar to CDs [4]. Compared with organic dyes and semiconductive quantum dots (QDs), GQDs are superior in terms of their excellent properties, such as high photostability against photobleaching and blinking, biocompatibility, and low toxicity [1,2,4]. Unlike their cousins, CDs, GQDs clearly possess a graphene structure inside the dots, regardless of the dot size, which endows them with some of the unusual properties of graphene [3,4]. For these reasons, GQDs have attracted significant attention from researchers.

In the early research on GQDs, tremendous effort was devoted to developing methods for the preparation of GQDs and exploring their properties [1,4]. Their application in the analytical field has not been explored until very recently. Due to their novel properties, sensors based on GQDs can achieve a high level of performance. In this review, we primarily focus on sensors and analytical systems that utilize GQDs as a key component.

In this work, we develop a simple and low-cost synthetic strategy to prepare N-GQDs by hydrothermal treatment of GQDs with hydrazine. The obtained N-GQDs show blue photoluminescence with a high Quantum Yield. Meanwhile, to the best of our knowledge, although carbon quantum dots have been used to detect metal ions, no attention has been paid to the use of nitrogen-doped GQD as a fluorescent sensing platform for label-free detection of metal ions, especially Cu^{2+}. Here we found that the as-prepared N-GQDs can serve as a very effective fluorescent sensing platform for label-free sensitive and selective detection of Fe (III) ions with detection limit as low as 90 nM. The successful application of the N-GQDs in the detection of Cu^{2+} ions in real water samples is also demonstrated.

2. EXPERIMENTAL SECTION

2.1. Materials

Citric acid, NaOH and C_2H_5OH were purchased from Scientific companies such as Modern Scientific and Universal Scientific.

2.3. Preparation of GQDs

GQDs were synthesized by pyrolyzing citric acid(CA), 2 g of CA was put into a 5 mL beaker and heated to 200 °C by a heating mantle for about 30 min until the citric acid changed to an orange liquid. The liquid was then dissolved in 100 mL of 10 mg mL^{-1}NaOH with continuous vigorous stirring. The pH of the obtained GQDs solution was adjusted to 8 by using 1 mg mL^{-1} CA and the sample was stored in a refrigerator.

2.4. Preparation of N-GQDs

N-GQDs were prepared by hydrothermal treatment of GQDs with hydrazine (30%). In a typical synthesis, 0.30 mL hydrazine (30%) was added into 20 mL GQDs (20 mg mL^{-1}). The mixture was then transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The N-GQDs were collected by removing the large dots though centrifugation at 10,000 rpm for 10 min in aqueous ethanol solution (3:1). The N-GQDs were collected by rotary evaporation after being washed with aqueous ethanol solution several times.
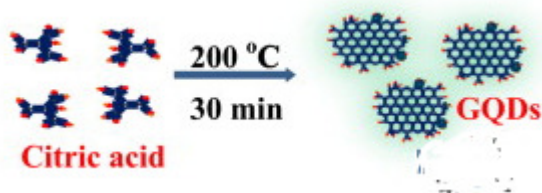
Fig.1 Scheme diagram of GQDs Preparation

3.4 Sensing

Metals like Cobalt, Chromium, Copper, Zinc, Nickel and Ascorbic acid were added to various GQDs at 50mM to detect sensing effects. Copper has an effective sensing, compared to other metal compounds, particularly on copper sensing with all GQDs, N-GQDs has ever more better sensing comparative to others.

Result and Discussion

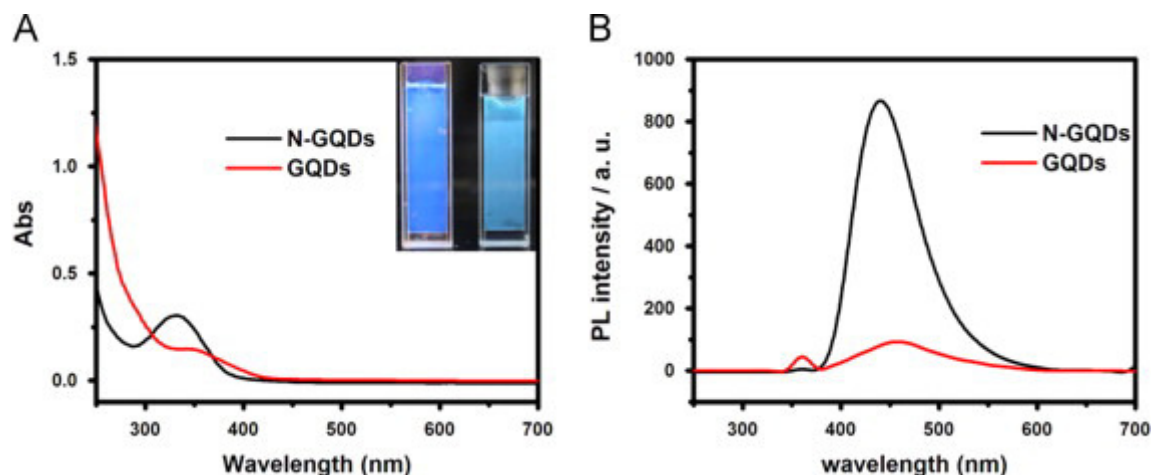**3.1 Characterization of CuO NPs by UV-Visible Spectroscopy**

Fig.2. (A) UV–vis absorption spectra of the GQDs (red line) and N-GQDs (black line). Insets show the photographs of the as-prepared GQDs (right) and N-GQDs (left) aqueous solutions taken under UV light (365 nm). (B) PL spectra of the GQDs (red line) and N-GQDs (black line) aqueous solutions with excitation at 360 nm.

Fig 2 shows the UV–vis absorption (A) and photoluminescent (PL) emission spectra (B) of the aqueous dispersion of GQDs and N-GQDs. It can be seen that the UV–vis spectrum of GQDs exhibits a typical absorption at 360 nm. However, the N-GQDs shows a broadened absorption band centered at 332 nm which has a blue-shift of 28 nm compared to that of the GQDs. The inset of Fig 2A shows the photograph of aqueous solutions of GQDs (right) and N-GQDs (left)

collected under excitation with a 365 nm laser. The GQDs exhibit green color, whereas the N-GQDs show blue color. Fig 2B presents the PL emission spectra of the aqueous solutions of GQDs and N-GQDs with excitation at 360 nm; the GQDs and N-GQDs show emissions at 458 and 440 nm, respectively. Moreover, the PL intensity of N-GQDs is considerably greater than that of GQDs. The highly efficient PL emission possibly results from the N-doping-induced modulation of the chemical and electronic characteristics of the GQDs.

3.2 Characterization of CuO NPs by UV-Visible Spectroscopy

FT-IR spectra were used to identify the functional groups presenting on GQDs. The absorption band at (Fig 3A) 1643 cm-1 shows the C=C stretching vibration, at 2978 cm-1 refers the C-H stretching vibration, the band at 938 cm-1 shows C-H bending vibration and the band between 2500-3500 it refer a O-H stretching vibration it shows a lot of hydroxyl group present in the compound
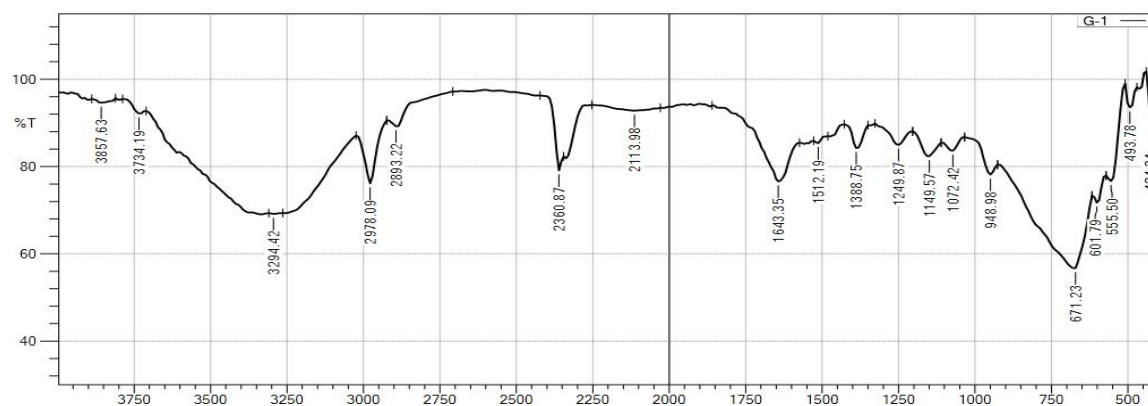
Figure: 3A FTIR – Spectra for N-GQDs

The absorption bands at (Fig 3B) 3000-3500 cm-1 are assigned to stretching vibrations of O-H and N-H. Those indicate that there are amino and hydroxyl groups on the surface of GQDs, which results the GQDs have high hydrophilic property.The bands at 1693 cm-1 shows the N-H bending vibration and the band at 1388 cm-1 shows the N-O symmetrical and assymmetrical stretching vibration.
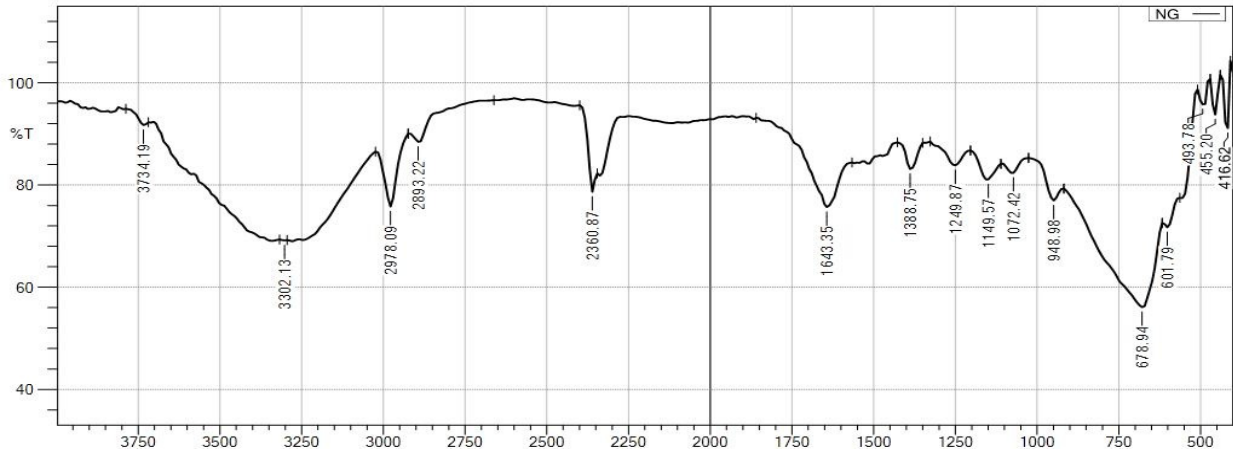
Figure: 3B FTIR – Spectra for N-GQDs

3.3 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is a useful technique for the study and characterization of materials and dynamical processes occurring in materials, specifically the optical properties of the materials. GQDs emit visible light at different wavelengths depending on the wavelength of the excitation radiation. Fig.4A & 4B shows the emission spectra of GQDs and N-GQDs at different excitation wavelengths. The emission intensity was gradually increased while the excitation wavelength was increased from 300 to 400 nm. GQDs maximum emission was observed at 365nm,420nm while exciting at 320 nm, 350nm
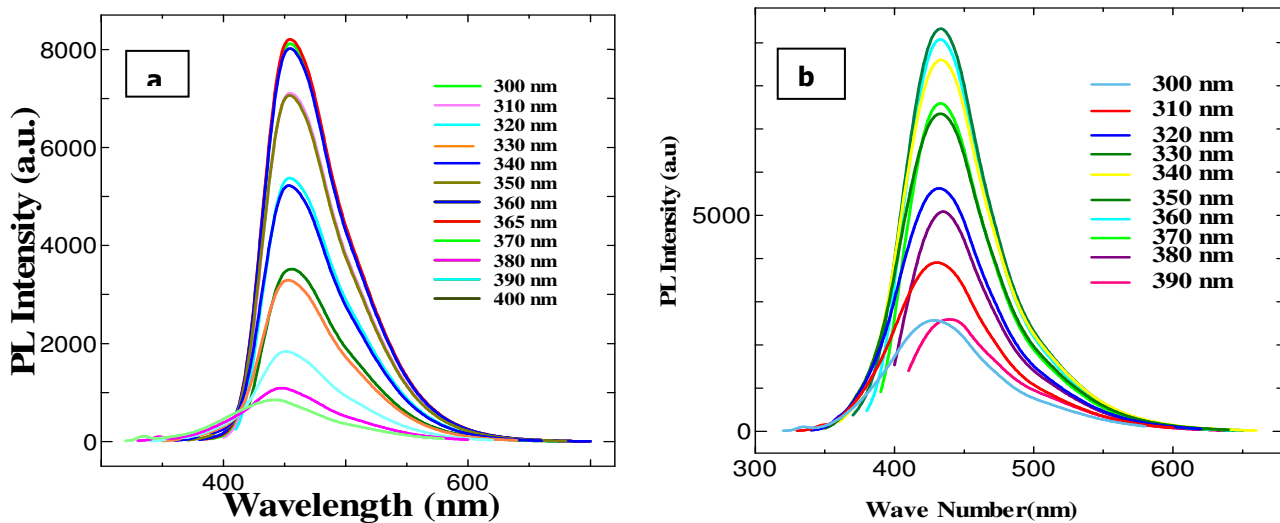

Figure: 4 (A) PL spectroscopy for GQDs and B) PL spectroscopy for N-GQDs

3.4 Colorimetric graph with different metals on GQDs

Selective determination of Cu^{2+} was studied by adding possible interferences of 50 mM Zinc, Cobalt, Chromium, Ascorbic acid and Copper to the colloidal solution of Various GQDs. The yellow color of GQDs remains unaltered while adding the above said interferences. On the other hand, addition of 200 μM Cu^{2+} to various GQDs solution leads to the formation of a greenish blue color. These results indicate that selective determination of Cu^{2+} is possible by visual detection. Calorimetric is taken for GQDs and other doped GQDs with the addition of some compounds such as Zinc, Cobalt, Chromium, Ascorbic acid and Copper to detect the sensing effect, among all N-GQDs shows good sensing effect while compared to all other GQDs.
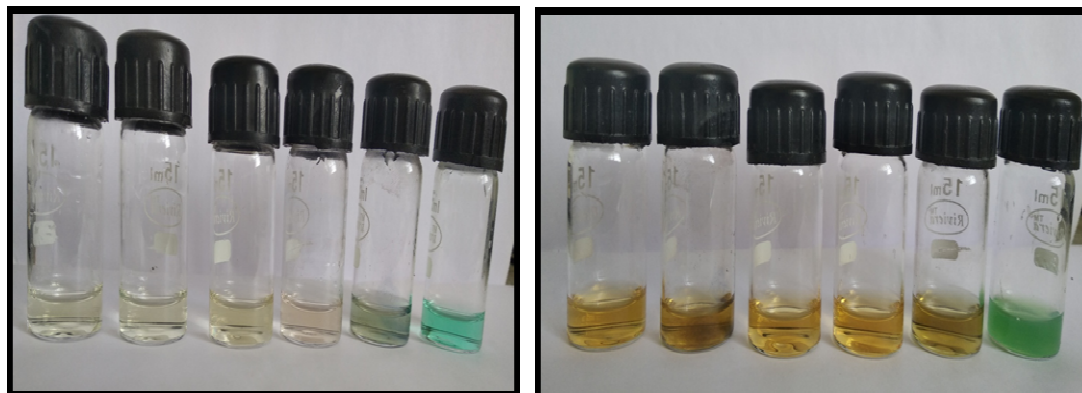

Fig.3.9. Photographs of GQDs, N-GQDs in the presence of Zn, Co, Cr, Ascorbic acid,(50 mM) and in the presence of Cu^{2+} (250 μM)

3.5 Characterization of GQDs by FE-SEM

FESEM is the abbreviation of Field Emission Scanning Electron Microscope. FESEM is microscope th works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. A FESEM is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometer (= billion of a millimeter). The particles prent in the size of 5 μm.
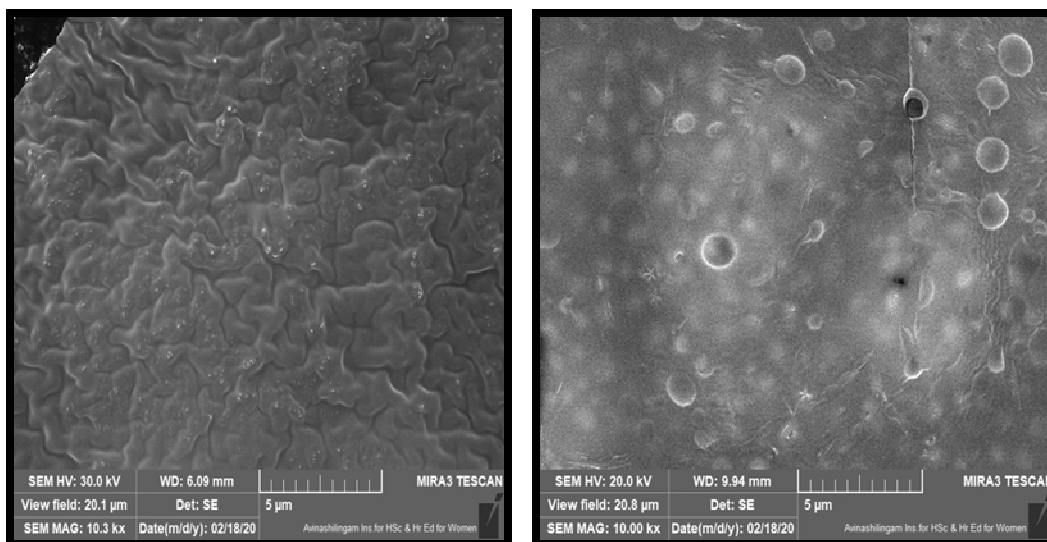
Figure: 5.14 (a) FE-SEM for N-GQDs and (b) FE-SEM for Cu^{2+} on N-GQDs

4. CONCLUSION

We have developed a simple hydrothermal method for the preparation of N-doped graphene quantum dots with hydrazine as nitrogen source. The as-synthesized N-GQDs exhibited an enhanced fluorescence compared to the un-doped GQDs. Such N-GQDs have been further used as a novel sensing platform for label-free sensitive and selective detection of Cu^{2+} ion. Also we found that both dynamic and static quenching mechanisms are present for the quenching effect of Cu^{2+}ions on the fluorescence of N-GQDs. However, a surface process occurs for the Cu^{2+}quenching on the fluorescence of un-doped GQDs. The present study provides a simple, low-cost route toward production of N-GQDs for sensing, bioimaging, optical imaging and other applications.

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