



Paper Strip Embedded Graphene Quantum Dots as a “turn off” Luminescence Sensor for Fe²⁺ Ions

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Abstract

The surrounding environment is significantly contaminated with heavy metal ions. Consequently, the qualitative and quantitative determination of these ions in water has become a matter of great interest. In this context, we have developed an easy-to-use and cost-effective paper-based sensor for detecting Fe²⁺ ions in aqueous solutions. This sensor utilizes blue luminescent graphene quantum dots (GQDs) embedded into cellulose paper. The GQDs were synthesized through a pyrolysis method using citric acid, resulting in uniform particles with an average size of 5 nm. These GQDs exhibited blue luminescence with a peak centered at 460 nm when excited at 360 nm. We validated the potential of GQD-embedded paper as a sensing probe by observing a significant fluorescence quenching effect in the presence of Fe²⁺ ions at varying concentrations in the low range, from 0.2 to 0.8 mM. The calculated limit of detection for Fe²⁺ ions was 0.08 mM. This innovation opens up new possibilities for simple and rapid screening of heavy metal ions, making it especially valuable in remote settings where sophisticated analytical tools may not always be readily available.

Keywords: Graphene quantum dots, Fluorescence, Paper sensor, Fe²⁺ detection

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1. Introduction

Heavy metal ions are categorized as a typical class among water pollutants, which are extremely harmful to the biosphere if exposure limit is exceeded [1]. Currently, various analytical methods have been utilized in heavy metal ion sensing such as atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, mass spectrometry, etc. Although these methods provide accurate and reliable results, yet they are not suitable for on-site measurements and they need expensive instruments and expertise to operate [2]. Compared with different detection methods, fluorometric approach attracted great attention due to its unique potential like high sensitivity and short response time. Nowadays, fluorescent graphene quantum dots (GQDs) have emerged as one of the potential materials to be used in optical sensor, as supported by various studies in sensing, for example to detect presence of anions or cations by monitoring change in photoluminescence (PL) intensity [3-4]. GQDs have attracted the attention of numerous researchers due to their stable luminescence properties, high photo stability, low production cost, high emission quantum yield, long fluorescence lifetime and good biocompatibility [5-6].

Moreover, recently, paper has been developed as valuable substrate for sensor fabrication with potential for real time monitoring. Paper-based sensor arises as a promising sensing platform due to the low-cost, ease of use, portability, great biodegradability, and disposability [7]. Paper based sensors fabricated with different types of nanomaterials utilized as either colorimetric, electrochemical, or fluorescence-based sensing tool to quantitatively determine the toxic metal ions that present in various environmental and biological samples [8]. Iron (Fe) is an essential element, but excessive or uncontrolled levels of Fe²⁺ ions can be harmful to the environment and human health. Therefore, in this work, a highly sensitive fluorometric paper-based sensor for the determination of Fe²⁺ ion in water samples was reported. The blue luminescent GQDs obtained from direct pyrolysis of citric acid embedded into filter paper to be used as sensing tool. It was found that the GQDs based paper sensor could be a promising tool for screening Fe²⁺ ions in the low range from 0.2 mM to 0.8 mM. The obtained quantitative data enable new prospects for a rapid, simple, and real time monitoring of such metal ions in aqueous medium.

2. Materials and methods

2.1. Materials

Citric acid was purchased from Sigma. The metal ion solutions used in the study were sourced from various suppliers as follows: Iron (II) chloride tetrahydrate was obtained from Acros Organics Belgium, magnesium chloride hexahydrate from Chemiz, sodium chloride from System, lead (II) nitrate from Friendemann Schmidt Chemical, zinc chloride from Friendemann Schmidt Chemical, potassium sulfate from Emsure in Germany, cobalt (II) chloride from Chemie GmbH in the UK, magnesium sulfate, aluminum sulfate hexahydrate, and calcium nitrate tetrahydrate from R & M Chemicals. Hydrochloric acid and sodium hydroxide were purchased from J.T. Baker (Thailand). Deionized (DI) water was used throughout the study.

2.2. Methods

2.2.1. GQDs synthesis

The GQDs were synthesized via direct pyrolysis of citric acid according to with no modification [9]. Briefly, 2 g of citric acid was pyrolyzed at 225°C for 15 minutes. Then, the orange liquid slowly transferred into 50 mL of DI water and naturally cooled at room temperature. Once completely cooled to room temperature, the solution was filtered using membrane filter (0.22 μm) to remove any insoluble precipitates. The synthesized GQDs solution was stored at a temperature of 4°C for further analysis.

2.2.2. Paper strip preparation

Whatman Filter papers with diameter of 5 mm were prepared. Then, 4 μL of GQDs solution were added separately on each paper strips and let it dry at room temperature for 45 minutes.

2.2.3. Sensing experiments

10 μL of the analyte solution was added to the as prepared fluorescent paper strip. After drying at room temperature, the paper strip was placed under the UV lamp (365 nm wavelength) and all the pictures were taken with a Redmi Note 10.

2.2.4. Characterization of GQDs

The microscopic images and sizes of GQDs were obtained by transmission electron microscope (TEM) using Thermo Fisher- Talos 120C (USA). To identify the surface functional groups of CDs, Fourier transform infrared spectroscopy (Nicolet 6700, Germany) was used. Measurements for absorption spectra under UV radiation were obtained from UV-vis spectroscopy (Perkin Elmer-Lambda 35, UK). The PL intensity of the synthesized CDs was recorded with single beam spectrofluorophotometer (Edinburg Instrument, United Kingdom) at room temperature. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a Japan Kratos Axis Ultra-DLD spectrometer using a monochromatic Al K α source at 1486.6 eV. All pH measurements were made using digital pH-meter (827 PH LAB, Switzerland).

3. Results and Discussions

The size and morphology of GQDs were observed by TEM. The TEM image (**Fig. 1a**) clearly confirmed that GQDs were well dispersed quasi-spherical nano dots. The size distribution (**Fig. 1b**) showed that the aqueous distribution of GQDs had a narrow size distribution with average diameters of 5 nm. Furthermore, the aqueous dispersion of GQDs appeared yellowish in daylight and emitted strong blue luminescence upon excitation under a 365 nm UV lamp. The UV-vis absorption and PL emission spectra obtained from the aqueous dispersion of GQDs are showed in **Fig 2**. A strong absorption peak at 282 nm together with a shoulder around 320 nm was observed in the UV-vis absorption spectrum. The peak at 282 nm was ascribed to the blue-shifted π - π^* transition of the conjugated C=C units from the carbon core, whereas the shoulder was due to the n - π^* transition of C=O groups on the surface of GQDs [10-11]. Upon excitation at 360 nm, the PL emission spectrum of GQDs verified the blue luminescence as the appearance of a peak centered at 460 nm.

3.1. Sensing Measurements

After synthesis and characterization, the GQDs were placed on top of the Whatman cellulose paper strips for subsequent sensing measurements. The features of cellulose-based sensor strip such as light weight, portable, cost effective, high surface area to volume ratio and higher capabilities of GQDs confinement were responsible for its selection [15]. For optimal sensing platform, 10 μL of GQDs solution is deposited on the paper strips which results in a homogeneous dispersion of GQDs in the sensing area. Moreover, GQDs pH value showed to be crucial parameter to be controlled. At pH 2, the fluorescence of GQDs is quenched, whereas the fluorescence of GQDs is nearly maintained from pH 5 to pH 11, as shown in **Fig. 4**. The luminescence of GQDs in solution of different pH values varied with the ionization states of either acidic or alkaline solutions. The reduction of PL intensity of GQDs in extremely acidic solution (pH 2) might be caused by formation hydrogen bonds on surface of GQDs which led to aggregation induced PL quenching [16-17].

In pH 2 conditions, numerous hydrogen ions are present and can interact with electronegative groups on the GQD surface, such as oxygen-containing functional groups. This interaction leads to the formation of hydrogen bonds. Moreover, this pH-dependent behavior provided additional evidence that the PL of GQDs might originate from the emissive traps on the surface of GQDs [13]. For optimal detection process, response time of 1 min, pH value of 7.0 and room temperature (25°C) were adopted. The luminescence is turned on when the GQDs are encapsulated within cellulose paper strip and the fluorescence quenching to an "off" state observed upon addition of the Fe²⁺ ions. To validate the selective response of GQDs paper strip as a fluorescence sensor to iron ion, the fluorescence response of GQDs has been researched in the different metal cation solutions, including Cu²⁺, Al³⁺, Ca²⁺, Co²⁺, Fe²⁺, K⁺, Mg²⁺, Na⁺, Pb²⁺ and Zn²⁺. The peak position of the maximum emission was not affected upon addition of metal ion. Therefore, the normalized PL intensities of GQDs in the presence of different metal ions were plotted (**Fig. 5**).

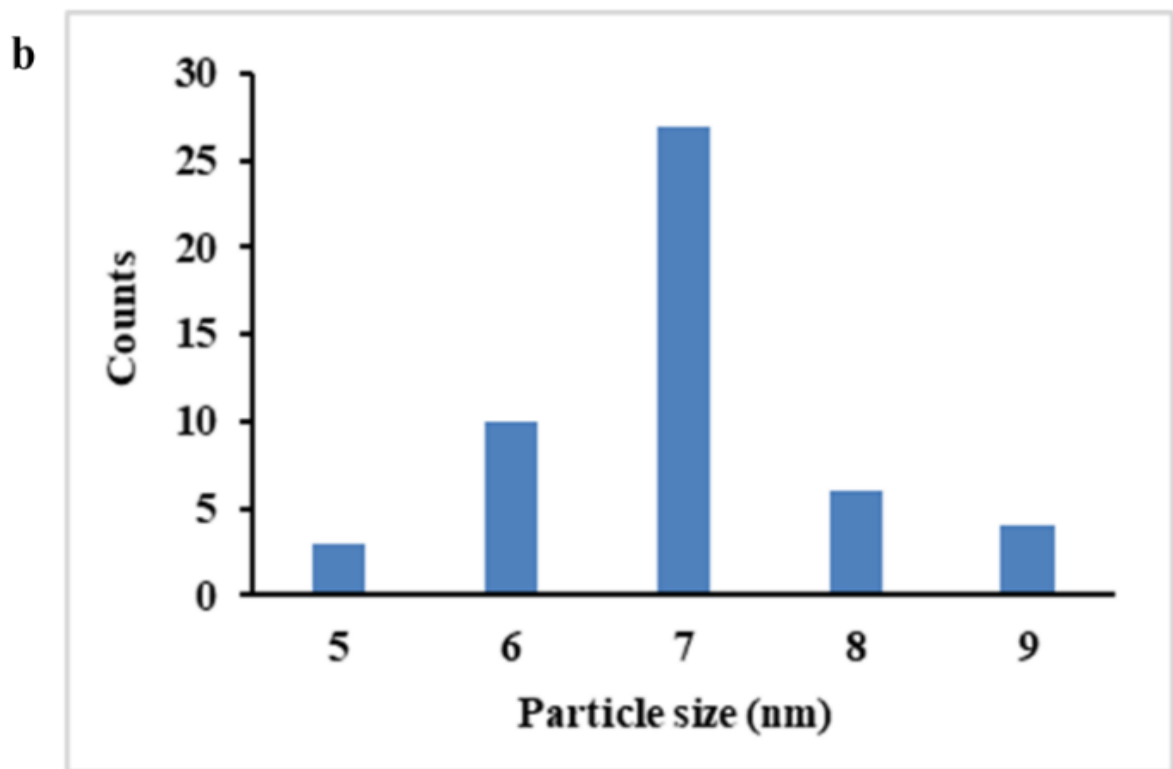
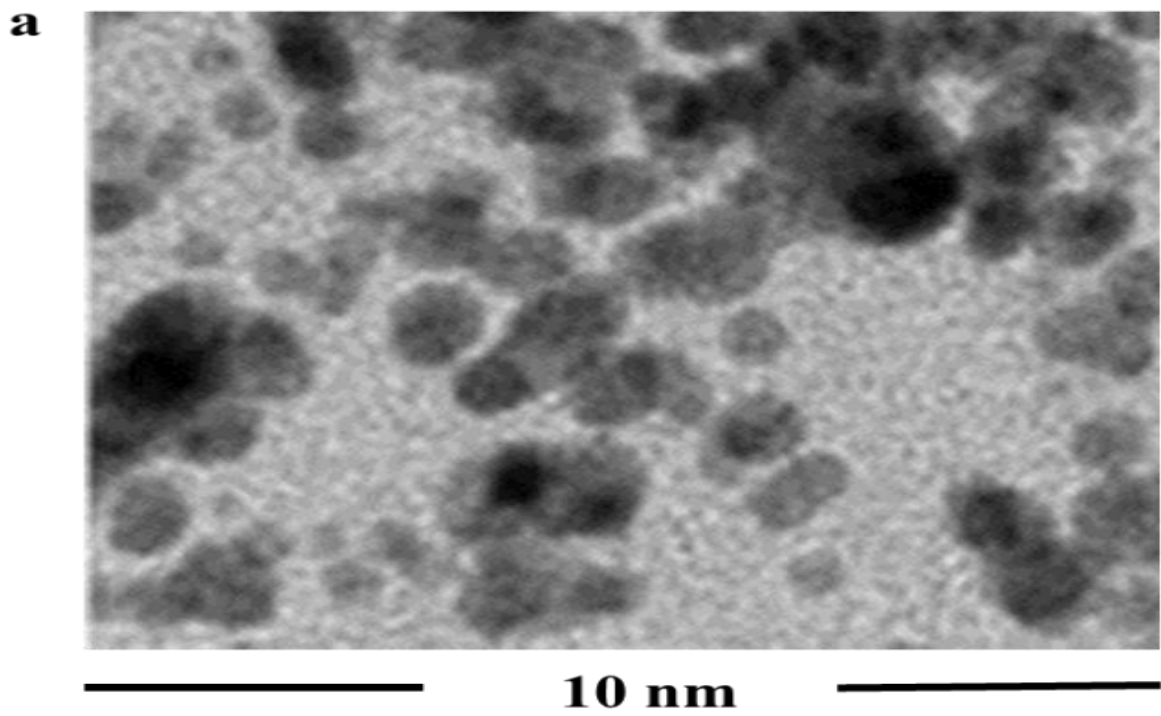


Fig. 1 (a) TEM image of GQDs (Magnification factor: 20 nm); (b) Size distribution.

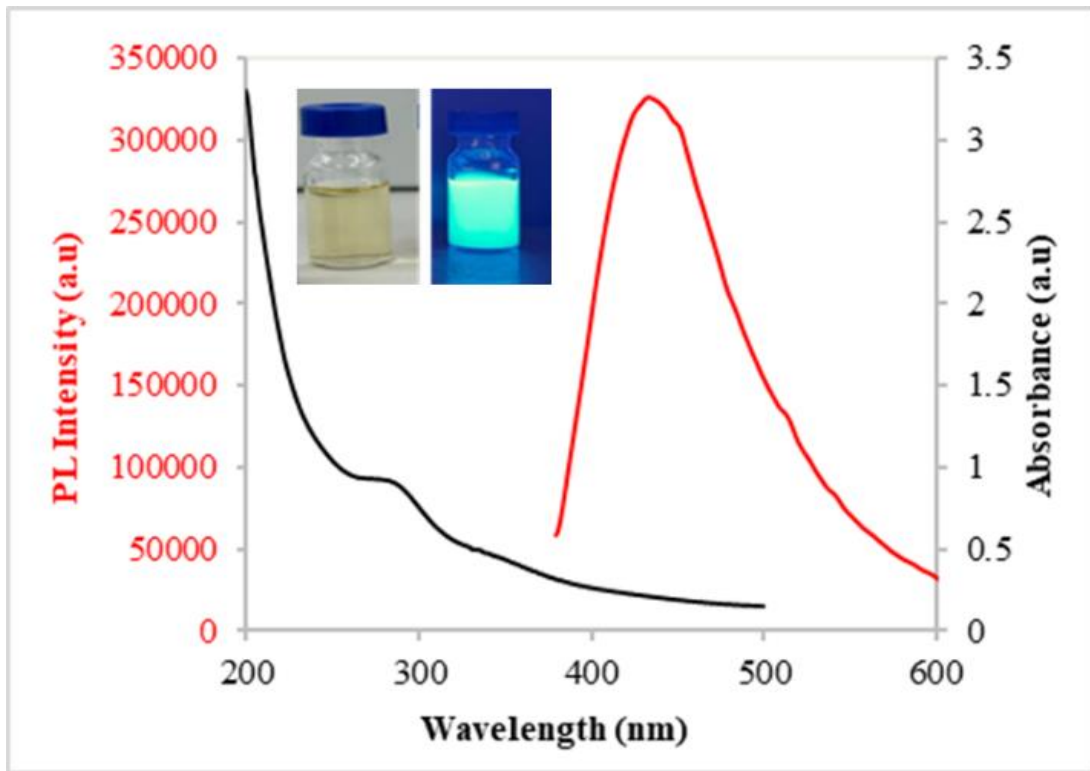
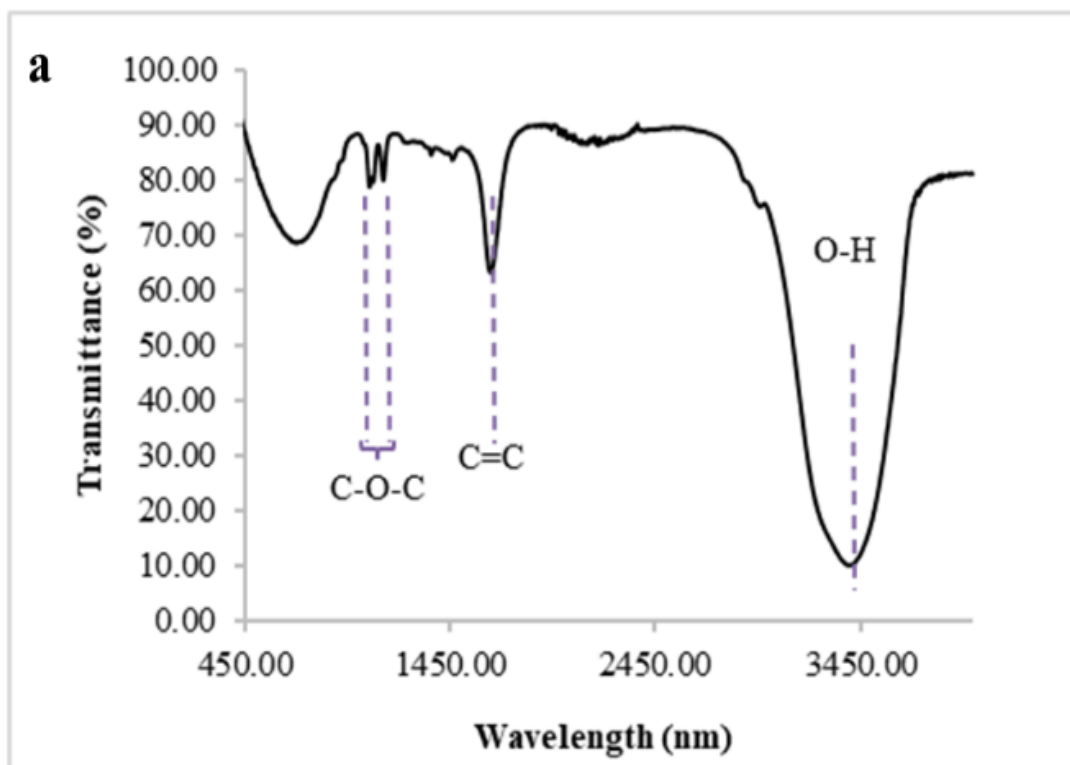


Fig. 2. Absorbance spectra (black line) and PL spectra (red line). Inset, image of GQDs under UV (right) and daylight (left), respectively.



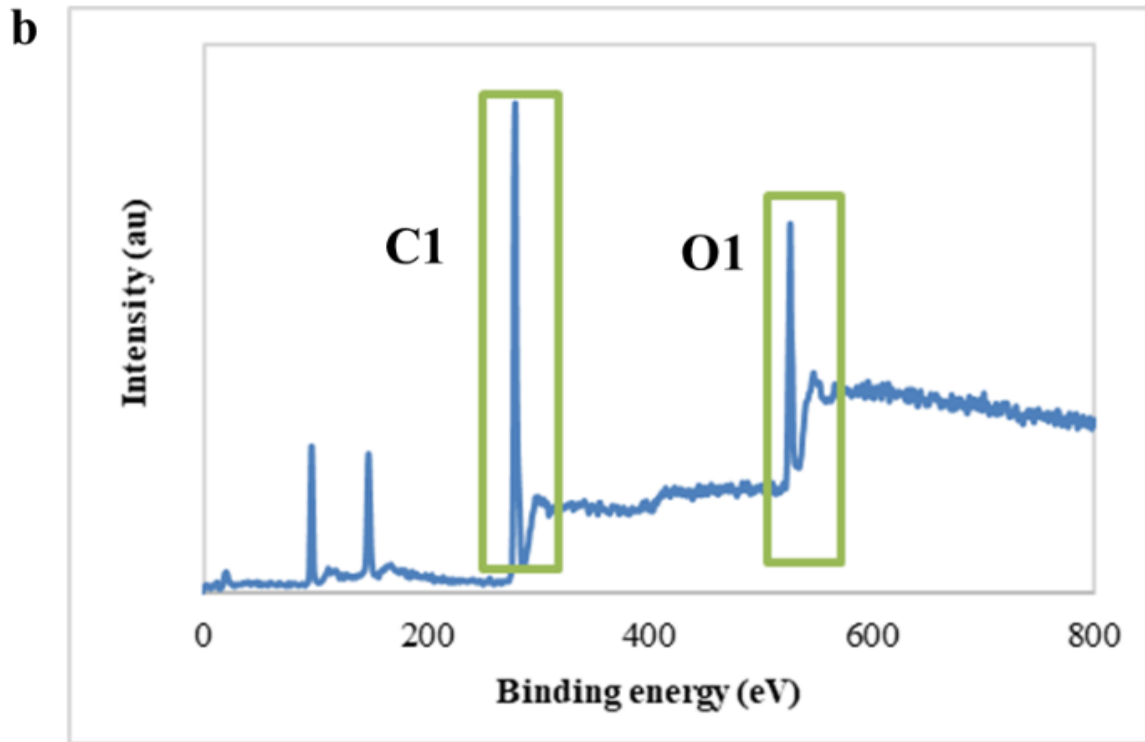


Fig. 3 (a) FTIR spectrum of GQDs; (b) XPS spectra of the GQDs.

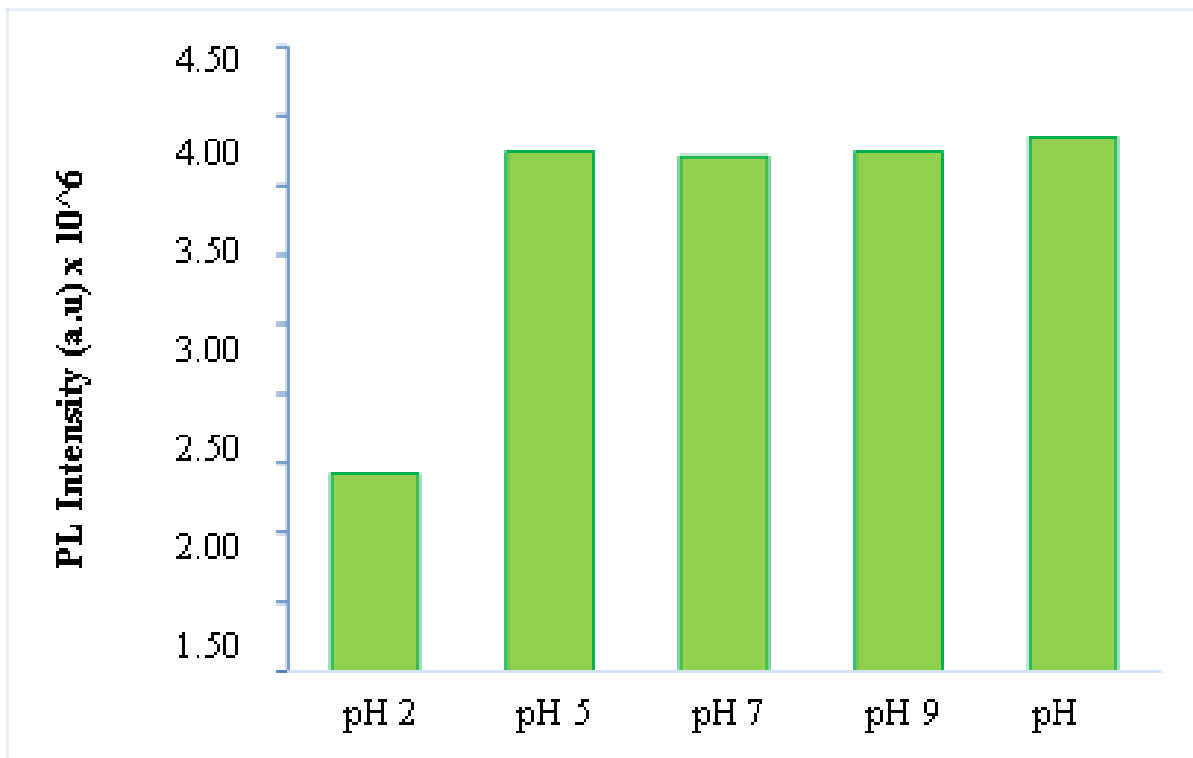


Fig. 4. PL intensity of GQDs in different pH

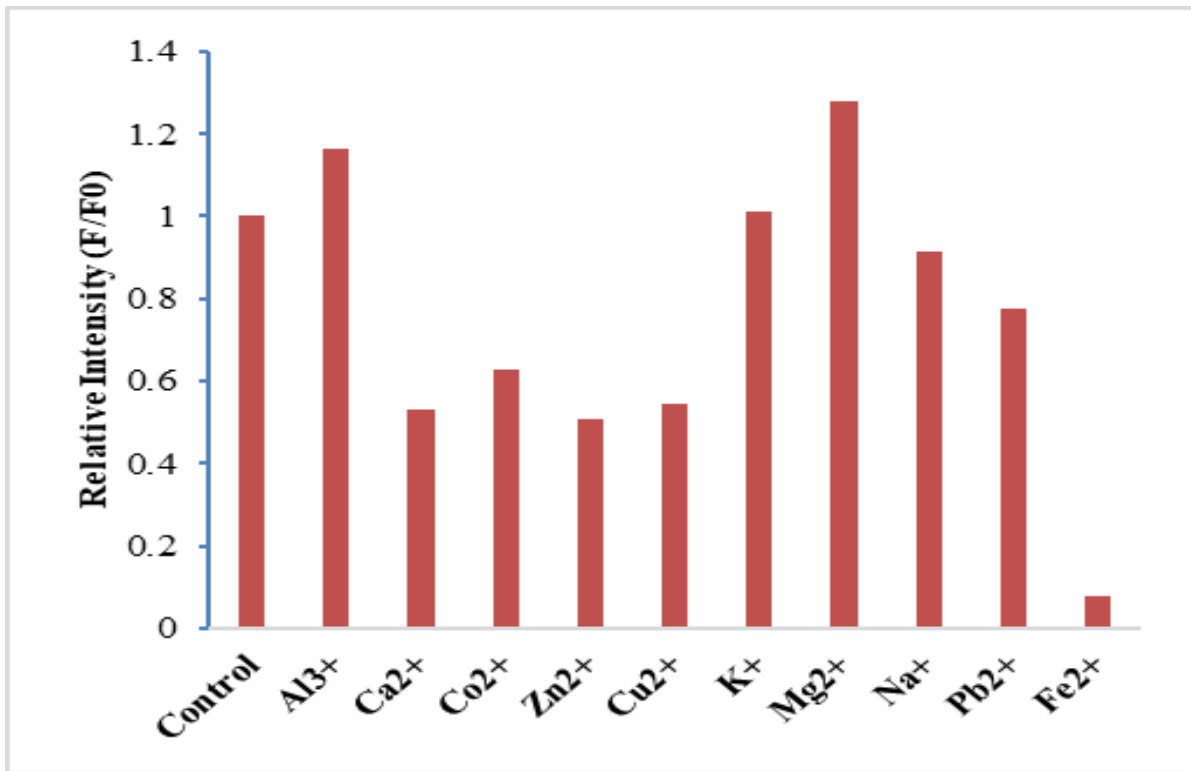
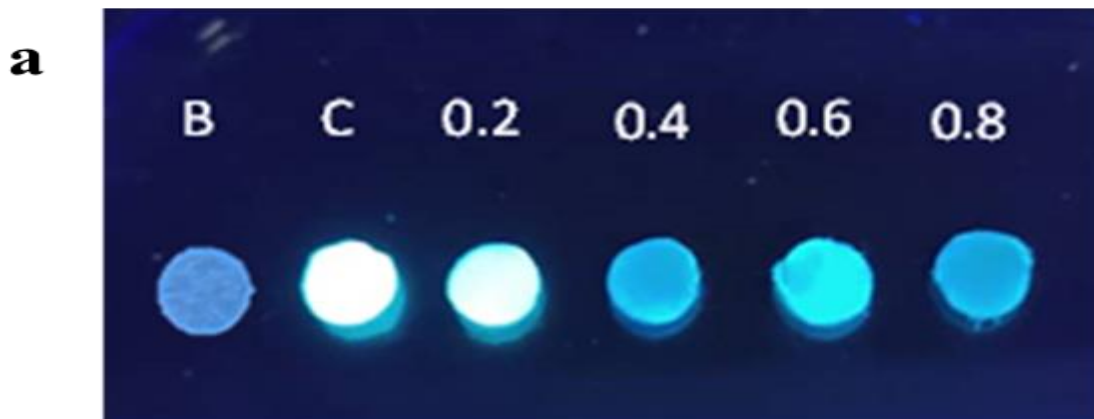


Fig. 5. PL response of GQDs paper strip towards different metal ions (0.5 mM)



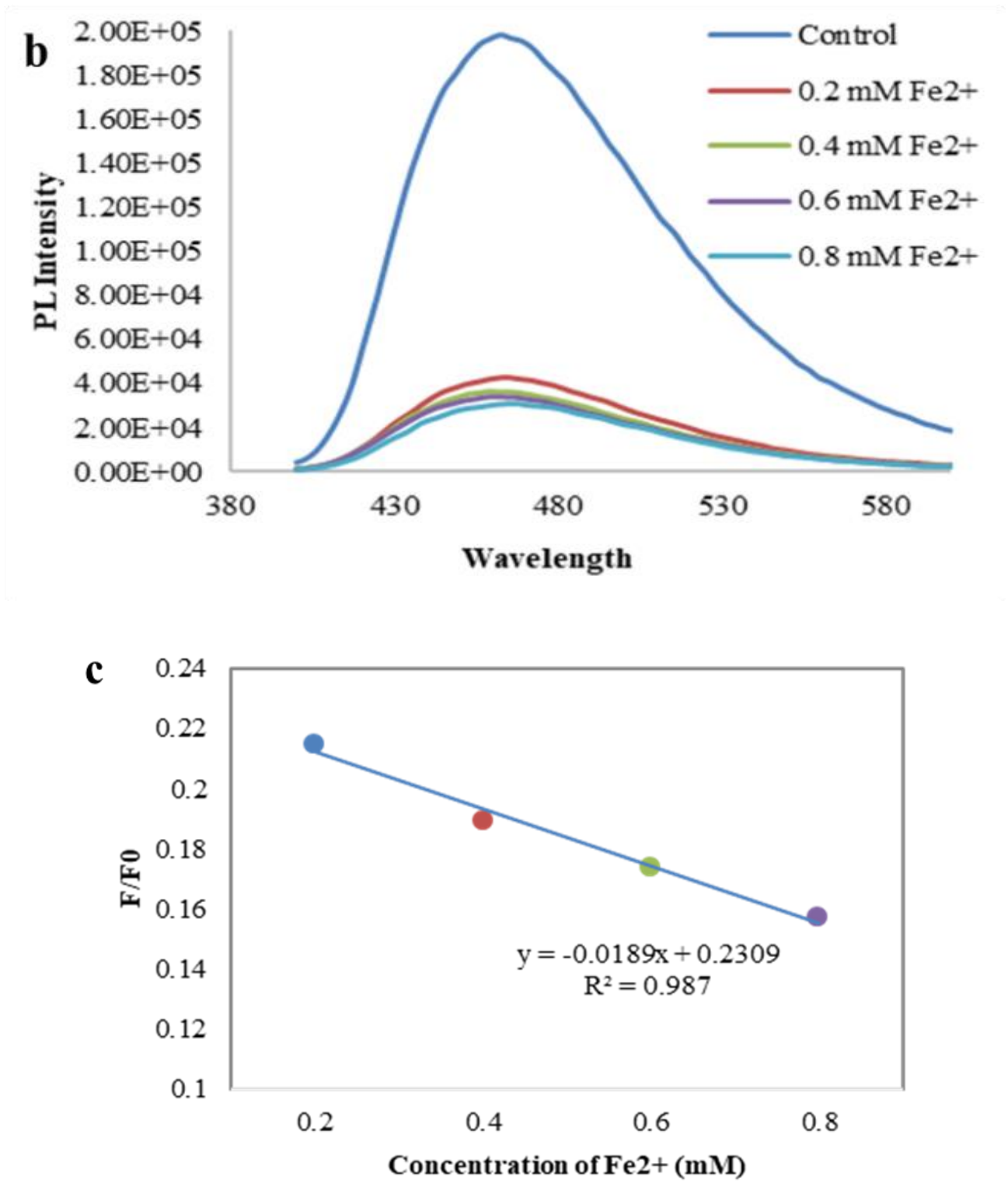


Fig. 6 (a) Visual observations of the paper strips; (b) PL spectroscopy of GQDs paper strips in presence of different concentrations of Fe²⁺ ions; (c) The linear response of the PL quenching and the Fe²⁺ ions concentration.

Notably, there was a tremendous decrease in PL intensity upon addition of Fe^{2+} . Such dramatic quenching of PL by Fe^{2+} might be due to that Fe^{2+} ion has higher affinity with oxygen atoms on the surface of GQDs [13]. However, small reduction in PL intensity was observed upon addition of other metal ions and the exact cause for the increased fluorescence of metal ions, namely Al^{3+} and Mg^{2+} , is not known, but the working hypothesis is that it is due to the formation of some new bonds by the metal ions on the GQDs surface and then forming new energy levels, leading to more fusion radiation between the holes and electrons [18]. Thus, led to enhanced PL intensity of GQDs. The sensitivity of the GQDs paper strip was assessed by varying different concentration of Fe^{2+} ion. **Fig. 6a** illustrates that no fluorescence is observed in the blank paper strip (B), and the blue fluorescence gradually diminishes as the concentration of Fe^{2+} ions increase from 0 mM (C) to 0.8 mM. To further validate the visual observation, the PL intensity of the paper strips measured by PL spectroscopy as shown in **Fig. 6b**. The PL intensity decreases as the concentration of Fe^{2+} ions increased from 0 mM to 0.8 mM. In **Fig. 6c**, the ratio between the PL intensity of the probe before and after adding Fe^{2+} ions linearly decreased with Fe^{2+} ions concentration. Strong electrostatic interaction between Fe^{2+} ions and GQDs causes the decline in PL intensity of the GQDs, which could be supported by zeta potentials.

The Fe^{2+} ions have high affinity to the carbonyl groups on GQDs with the result of increasing positive charges on GQDs, and the zeta potentials of GQDs without and with Fe^{2+} at pH 7.0 are -16.8 and -4.1 mV, suggesting that many Fe^{2+} ions were bonded to GQDs [19]. The active adsorption site on cationic Fe^{2+} promotes adhesion of GQDs, thus resulting in blocking of radiative recombination of electron holes through an effective electron transfer process, and subsequently leading to quenching of fluorescent GQDs [11]. Furthermore, the limit of detection (LOD) was calculated according to $\text{LOD}=3\sigma/S$, where S is the slope of the regression equation and σ is the standard deviation of the y-intercept. In this case, the LOD for Cu^{2+} ions are about 0.08 mM. At this point, we successfully demonstrated that the GQDs embedded paper strip has sensing properties that able to quantify Fe^{2+} ions in aqueous medium.

4. Conclusions

This study demonstrated that the GQDs embedded fluorescence paper strip can be used to detect Fe^{2+} ions, which is easy to use and low cost. The fluorescence of GQDs was dramatically quenched by interaction with the Fe^{2+} ions. A remarkable color change of the sensor strips from bright blue to darker depends on the nature and concentration of the Fe^{2+} ions. Thus, highly fluorescent GQDs along with paper platforms were exploited in the development of presented probe, towards new generation of simple and inexpensive paper-based sensor with versatile applications.

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