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GSH-doped GQDs using citric acid rich-lime oil extract for highly selective and sensitive determination and discrimination of Fe^{3+} and Fe^{2+} in the presence of H_2O_2 by a fluorescence "turn-off" sensor

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Synthesis and characterization of graphene quantum dots (GQDs) simultaneously doped with 1% glutathione (GSH-GQDs) by pyrolysis using citric acid rich-lime oil extract as a starting material. The excitation wavelength (λ_{max} = 337 nm) of the obtained GSH-GQD solution is blue shifted from that of bare GQDs (λ_{max} = 345 nm), with the same emission wavelength (λ_{max} = 430 nm) indicating differences in the desired N and S matrices decorating the carbon based nanoparticles, without any background effect of both ionic strength and masking agent. For highly Fe^{3+}-sensitive detection under optimum conditions, acetate buffer at pH 4.0 in the presence of 50 μM H_2O_2, the linearity range was 1.0–150 μM (R^2 = 0.9984), giving its calibration curve: $y = 34.934x + 169.61$. The LOD and LOQ were found to be 0.10 and 0.34 μM, respectively. The method's precisions expressed in terms of RSDs for repeatability ($n = 3 \times 3$ for intra-day analysis) were 2.03 and 3.17% and for reproducibility ($n = 5 \times 3$ for inter-day analysis) were 3.11 and 4.55% for Fe^{2+} and Fe^{3+}, respectively. The recoveries of the method expressed as the mean percentage (n = 3) were found in the ranges of 100.1–104.1 and 98.08–102.7% for Fe^{2+} and Fe^{3+}, respectively. The proposed method was then implemented satisfactorily for trace determination of iron speciation in drinking water.

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1. Introduction

Iron (Fe) is a metal of biological, clinical, environmental, and industrial importance. It is one of the most essential trace elements in living biosystems and plays indispensable and versatile roles in many physiological and pathological processes, including enzyme catalysis, oxygen transport, cellular metabolism, electron transfer, and DNA and RNA synthesis.[1–5] Speciation of iron, an occurrence of the element in two oxidation states (II and III), is mostly found in nature. Different biological activities of $Fe^{2+}$and Fe^{3+} are well known. Fe^{2+} is favored for absorption by biological cells. To treat clinical symptoms of iron deficiency some medicaments containing Fe^{2+} can be administrated to eliminate complications. The low stability of Fe^{2+} caused by its easy oxidation to Fe^{3+} by oxygen in the air can result in a decrease in the real Fe^{2+} concentration in pharmaceuticals.[6] However, both a deficiency and an excess accumulation of iron in the human body can induce serious disorders such as anaemia, intelligence decline, arthritis, heart failure, diabetes and cancer.[7–9] Thus, the determination of iron speciation is of fundamental importance for the early identification and diagnosis of these diseases. In addition, the measurement of iron concentration in water samples is also crucial for environmental safety.[10]

Currently, several analytical techniques for determination of Fe^{2+} and Fe^{3+} ions have been applied including solid phase extraction,[11] fiber-optic chemosensor,[12] voltammetric methods,[13] high performance liquid chromatography,[14] capillary electrophoresis,[15] inductively coupled plasma mass spectrometry,[16] flow injection analysis[17] and chemiluminescence.[18] Although these techniques are highly sensitive and selective, they require tedious sample preparation and preconcentration procedures, expensive instruments, and professional personnel.

In recent years, several fluorescence sensors have been widely investigated for the selective detection of iron speciation in biological systems because of their ability to provide a simple, sensitive, and selective method for monitoring without the need for any pretreatment of the sample; these techniques also have the advantages of spatial and temporal

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