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A simple and convenient fluorescent strategy for the highly sensitive detection of dopamine and ascorbic acid based on graphene quantum dots

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ABSTRACT

In this paper, a simple and convenient fluorescent "turn off-on" strategy for the highly sensitive detection of dopamine (DA) and ascorbic acid (AA) based on graphene quantum dots (GQDs) was developed. DA and GQDs can form the DA-GQDs complex due to the electrostatic interaction and hydrogen bonding. The interaction between Cu^{2+} and the catechol moiety of DA-GQDs complex could lead to strong fluorescence quenching of GQDs. When AA is introduced into the system, AA can reduce Cu^{2+} to Cu^{+}, disturbing the interaction between Cu^{2+} and DA-GQDs complex and resulting in the fluorescence recovery of GQDs. Thus, a sensitive and convenient sensor for the detection of DA and AA was developed. Under the optimized experimental conditions, the fluorescence intensity was linearly correlated with the concentration of DA and AA in the range of 0.5–120 μmol L^{-1} and 0.05–6 μmol L^{-1} with a detection limit of 0.16 μmol L^{-1} and 0.021 μmol L^{-1}, respectively. Meanwhile, the proposed method has potential applications on the detection of DA and AA in human urine and serum samples.

1. Introduction

Dopamine (DA), one of catecholamine neurotransmitters, is used for message transfer between neurons, which is closely related to human's motivation, sleep, attention span, learning and neuronal plasticity [1,2]. Abnormal levels of DA in blood are associated with a variety of diseases, including attention deficit hyperactivity disorder, anorexia, schizophrenia, Parkinson's diseases and Alzheimer's disease [3–5]. Similarly, ascorbic acid (AA) also plays an extremely important role in maintaining human health. Elevated levels of AA in blood are often accompanied by diarrhea, hyperacidity, coronary heart disease and other diseases [6,7]. In contrast, lower AA levels can cause scurvy and immunocompromised [8,9]. Thus, it is important to develop a rapid, convenient and accurate method to monitor DA and AA in blood.

Up to now, many methods, such as colorimetry [10,11], electrochemical methods [12,13], liquid chromatography [14,15] and mass spectrometry [16,17], have been successfully developed for the detection of DA and AA. However, some disadvantages of these methods limit their practical applications, such as the requirement for complex synthesis or complicated extraction, sophisticated instrumentation, time-consuming and cumbersome [18–20]. Electrochemical assay requires complex electrode modification procedures. Liquid chromatography is time-consuming and requires complicated sample preparation processes such as derivatization, liquid-liquid extraction, ion pair extraction and etc. Owing to some advantages including high sensitivity, rapid response and operational simplicity, fluorescence methods draw more attentions [21,22]. Tian's group developed a fluorescence method to detect DA based on the redox reaction between Cr(VI) and DA [23]. Niu et al. reported the detection of AA based on the formation of cadmium oxalate polymeric species in the presence of AA using CQDs/AuNCs nanohybrid as an efficient ratiometric fluorescent probe [24].

In recent years, semiconductor quantum dots and organic dyes are greatly limited by some disadvantages, including high toxicity, low biocompatibility, high cost and low chemical inertness, in bioimaging and sensing applications [25,26]. As a newly emerging fluorescent material, graphene quantum dots (GQDs) have attracted increasing interests in catalysis, photovoltaics, bioimaging, light-emitting and sensing applications, owing to their overwhelmingly superior in terms of low toxicity, high biocompatibility, good chemical inertness and solubility, tunable optical properties and ease of functionalization [27–29].

Studies have shown that GQDs can be rapidly quenched by both of quinone and o-semiquinone, which can be generated by the specific interaction between catecholates with Cu^{2+} [30–32]. Moreover, several studies demonstrated that Cu^{2+} could be reduced by AA, resulting in the fluorescence recovery of the quenched GQDs [33,34]. Based on the

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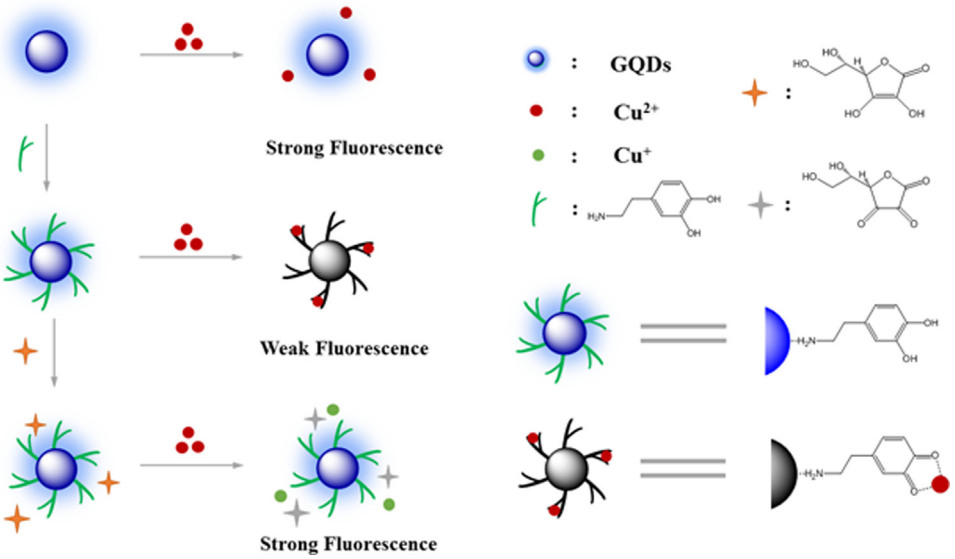

Scheme 1. Schematic illustration of the strategy for the detection of DA and AA.

specific interaction between catechol moiety of DA-GQDs complex and Cu^{2+} and the reduction of AA, we developed a simple and convenient fluorescent strategy for sensing DA and AA using GQDs as fluorescent probe (Scheme 1). When GQDs were mixed with DA, DA could be adsorbed on the surface of GQDs to form the DA-GQDs complex due to the electrostatic interaction and hydrogen bonding [18,32]. After Cu^{2+} was added into the system, the catechol moiety of DA-GQDs complex would complex with Cu^{2+} and be oxidized to o-semiquinone, which lead to significant fluorescence quenching of GQDs. However, AA could reduce Cu^{2+} to Cu^{+} and disturb the generation of complex containing o-semiquinone because of the strong reduction property of AA, resulting in the fluorescence recovery of GQDs. Thus, a simple and convenient fluorescent "turn off-on" sensor for the detection of DA and AA was developed. To the best of our knowledge, it is the first time to detect DA and AA based on the complexation and oxidation principles of DA on the surface of GQDs and Cu^{2+}.

2. Experimental section

2.1. Materials

All chemicals used were at least of analytical reagent grade and used without further purification. Citric acid, NaOH, DA, AA, glucose, alanine, aspartic acid, threonine, serine, lysine, resorcin, hydroquinone, cysteine, glutamic acid and glycine were obtained from Beijing Dingguo Biotechnology Co. Ltd. $CuCl_2$, NaCl, KCl and $CaCl_2$ were purchased from Sinopharm Group Chemical Regent Co. Ltd. All other chemicals were purchased from Huacheng Biological Co., Ltd (Changchun). The water used in all experiments had a resistivity higher than 18 MΩ cm.

2.2. Apparatus

All fluorescence measurements were carried out by an F-2700 fluorescence spectrophotometer using a 1 cm path length quartz cuvette. UV–vis absorption spectra were measured by a Varian GBC Cintra 10e UV–visible Spectrophotometer. FT-IR spectra were recorded with a Bruker IFS66V FT-IR spectrometer equipped with a DGTS detector (32 scans). Fluorescence decay was obtained by a Fluorescence Lifetime and Steady State Spectroscopy (FLS920, Edinburgh Instrument). All pH measurements were performed on a PHS-3C pH meter. All the optical measurements were conducted at room temperature under ambient conditions.

2.3. Synthesis of GQDs

GQDs were prepared from citric acid according to the previous work with minor modification [32]. In brief, 1 g of citric acid monohydrate was added into a 100 mL beaker and heated in an oven at 200 °C. During the heating, citric acid was liquated and the color gradually turned from colorless to yellowish and finally orange, depicting the formation of GQDs. After the heating of 20 min, 50 mL NaOH (10 mg mL^{-1}) solution was added into the beaker and a yellowish solution appeared. After cooling down, the pH of the solution was adjusted to neutral and the resulting GQDs solution were stored in 4 °C for further use. The quantum yield was 9.7%, calculated by using quinine sulfate in 0.1 mol L^{-1} H_2SO_4 solution (quantum yield = 0.54) as a reference.

2.4. Procedure for DA and AA determination

For the detection of DA, 100 μL GQDs solution, different concentrations of DA (0–10 mmol L^{-1}, 100 μL) and 1220 μL deionized water were added to a series of 2.0 mL calibrated test tubes. After ten minutes, Tris-HCl buffer solution (40 mmol L^{-1}, 500 μL; pH 7.8) and a certain concentration of $CuCl_2$ solution (1 mmol L^{-1}, 80 μL) were added and then the mixtures were mixed thoroughly for 60 min at room temperature before fluorescent measurement.

For the detection of AA, 100 μL GQDs solution, a certain concentration of DA (2 mmol L^{-1}, 120 μL) and 1100 μL deionized water were added to a series of 2.0 mL calibrated test tubes. After ten minutes, Tris-HCl buffer solution (40 mmol L^{-1}, 500 μL; pH 6.2), different concentrations of AA (0–200 μmol L^{-1}, 100 μL), and a certain concentration of $CuCl_2$ solution (1 mmol L^{-1}, 80 μL) were added, successively. After the solution shaken thoroughly for 60 min at room temperature, the fluorescence spectra were recorded in the 390–650 nm emission wavelength range at an excitation wavelength of 370 nm.

2.5. Real sample assay

For serum samples detection, healthy blood samples were collected from the Hospital of Changchun China-Japan Union Hospital. In order to remove large molecules and proteins, acetonitrile was added to the blood samples (the volume of acetonitrile and blood was 1.5:1) and the product centrifuged at 10,000 rpm (the centrifugal force was 6820 g) for 10 min after shaking for 2 h at room temperature. The supernatant was stored in − 20 °C until testing.

Serum samples were diluted with Tris-HCl buffer solution before