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Highly sensitive and selective dual-emission ratiometric fluorescence detection of dopamine based on carbon dots-gold nanoclusters hybrid

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ABSTRACT

In this work, a novel fluorescence resonance energy transfer (FRET)-based ratiometric fluorescent probe, carbon dots-gold nanoclusters hybrid (CDots-AuNCs), was fabricated for selective, sensitive and reliable sensing of dopamine (DA). This FRET probe is comprised of a two-fluorophore, where carbon dots (CDots) serve as the energy donor and gold nanoclusters (AuNCs) as the acceptor, with dual emission peaks at 420 nm and 610 nm under a single excitation wavelength of 380 nm. The addition of DA to this probe solution resulted in the fluorescence at 610 nm quenching, while the blue fluorescence at 420 nm recovering. By monitoring the change of ratiometric fluorescent intensity at 420 and 610 nm, the DA could be detected with the range from 5 to 180 nM and a limit of detection around 2.9 nM. Finally, the developed sensing method was successfully applied to DA determination in serum samples with satisfactory recoveries in the range of 95%–105%.

1. Introduction

Dopamine (DA) is an important hormone and neurotransmitter in the catecholamine and phenethylamine families. It plays a number of significant roles in the human brain and body and controls many biological functions such as motivation, emotion, endocrine regulation, and locomotion [1,2]. Many diseases, such as Parkinson's disease, schizophrenia, and anorexia are associated with abnormal DA levels [3]. However, the concentration of DA in living system ranges from 0.1 mM to 1.0 mM, which is very low [4,5]. Therefore, sensitive detection of DA is still challenging.

Up to date, many techniques have been developed for the detection of DA including high performance liquid chromatography, mass spectrometry, spectrophotometry, and electrochemical techniques [6–9]. However, these techniques have a lot of drawbacks. For example, the chromatographic and mass spectrometric approaches rely on expensive equipment and specific sample pretreatment procedures [10,11]; the spectrophotometric method has relatively low sensitivity [12]; electrochemical method often suffers from the interferences of ascorbic acid owing to the similar oxidation potential [13].

Fluorescent method is a better alternative than those mentioned above due to its outstanding features such as low cost, simple, high sensitivity, practicability and good selectivity. Moreover, it has the advantage of detecting the DA in complex biological matrixes without the separation procedure [14]. Recently, several interesting fluorescent probes such as organic dyes and single-walled carbon nanotubes have been developed to selectively, sensitively and directly detect neurotransmitters, including DA [15–18]. However, currently, fluorescence-based probes for DA are mainly single wavelength intensity modulation type sensors.

As we all know, the emission intensity may be influenced by many factors, such as the drifts of the optoelectronic system (lamps and detectors), the probe concentration, autofluorescence in complicated biosystems, which are prone to disturbance in quantitative detection [19,20]. Ratiometric fluorescence (RF) sensors can avoid these problems by measure the ratio of two emission intensities at different wavelengths [21]. Moreover, this sort of sensors have been demonstrated as visual sensing platforms and widely applied for the detection of various targets such as ions, protein, DNA, and so on [22–25]. Fluorescence resonance energy-transfer (FRET) is a commonly used sensing mechanism in the design of RF probes, in which there are two fluorophores, one act as a donor and another act as an acceptor, excited donor energy is transferred to an accep-

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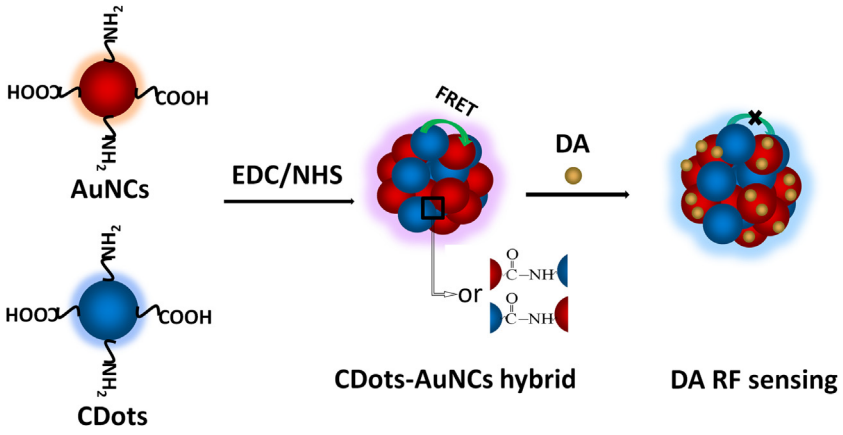

Scheme 1. Schematic illustration of the CDots-AuNCs RF assay of DA.

tor without any photon-emission. FRET-based RF probes, calculated the intensities at two different emission wavelengths, provide a built-in correction for environmental effects and can also increase the dynamic range of fluorescence measurement [26]. In particular, FRET has the advantage of remarkable emission shifts with fixed excitation wavelengths [27]. For FRET-based RF sensors, the design and development of a donor-acceptor pair is very critical.

In the merits of large Stokes shift, long lifetime, biocompatibility, ease of conjugation, gold nanoclusters (AuNCs) have popularized as a promising class of fluorescence materials for biosensing and imaging [28]. On the other hand, carbon dots (CDots) have attracted much attention due to their low cost, green synthesis, good biosafety, and environmental friendliness [29]. Especially, their outstanding photoluminescence properties, such as a lack of optical blinking and low photobleaching, make them perfect substitutes of traditional fluorophores as fluorescence donors and have been widely used in sensing fields [30]. Several groups have recently described CDots-AuNCs-based probes for RF sensing chemicals [31–34]. However, their application is still scarce. Additionally, most of them are not based FRET strategy. Seeking suitable fluorescence CDots and AuNCs to construct FRET-based RF sensors and expanding their applications are still of interest.

Herein, we proposed an effective FRET-based RF sensor for the detection of DA by combining CDots and AuNCs to form CDots-AuNCs hybrid. Scheme 1 schematically illustrates the principle of sensing. In this sensor, CDots act as an energy donor, AuNCs as an acceptor. The latter fluorescence can be quenched by DA, resulting in the emission from CDots recovering. Consequently, the ratio of two fluorescence intensities gradually changed corresponding to the concentrations of DA, which could be easily observed by the naked eyes under an UV lamp, resulting in visualization detection. This sensor demonstrates several advantages: First, since it is a RF probe toward DA, the influence of environmental effects can be avoided, which can ensure more accurate detection. Second, it is a highly sensitive and selective method with a very low detection limit of 2.9 nM DA. Moreover, the toxicity of both donor and acceptor is very low, which benefit the bioanalysis more desirable.

2. Experimental

2.1. Chemicals and materials

Bovine serum albumin (BSA, fraction V) was purchased from Sangon (Shanghai, China). 1-ethyl-3-(3-(dimethylamino)propyl)-carbodii-mide (EDC) and N-hydroxy-sulfosuccinimide (NHS) were obtained from Sigma-Aldrich (Shanghai, China). L-dopamine hydrochloride (DA), chloroauric acid ($HAuCl_4{\cdot}4H_2O$), L-cysteine (L-Cys), citric acid (CA), and sodium borohydride ($NaBH_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

All other reagents were of analytical grade. Ultra-pure water was used in all experiment. Unless otherwise stated, the detection solution was 10 mM pH = 9.0 phosphate buffer solution (PBS 10 mM, Na_2HPO_4, 2 mM KH_2PO_4, 137 mM NaCl, 2.7 mM KCl).

2.2. Instruments and measurements

X-ray photoelectron spectroscopy (XPS) measurements of CDots were performed on a ESCALAB250Xi spectrometer (ThermoFisher Scientific). The morphology of CDots, AuNCs, CDots-AuNCs were analyzed using a JEM-2100 transmission electron microscope (HRTEM, JEOL). The mean particle sizes of the nanoparticles were analyzed using a ZetaPALS laser particle size analyzer (Brookhaven). The X-ray diffraction (XRD) analysis was performed using a D8 Advance diffractometer (Bruker). FT-IR spectra were recorded on Nicolet 6700 spectrometer (Nicolet). All fluorescence spectra were measured on a Shimadzu RF-5301PC. UV–vis absorption spectra were measured using a UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu).

2.3. Preparation of CDots

The CDots were prepared by a hydrothermal method [35]. Briefly, 2 g CA and 1 g L-cysteine were sufficiently dissolved in 5 mL water. The mixed solution was evaporated at 70 °C until dry. Then, the resulted thick syrup was transferred to a Teflon-sealed autoclave and heated at 200 °C for 3 h. The obtained black syrup product was dispersed in 100 mL ultrapure water and neutralized with 1 M NaOH solution. After centrifugation at 6000 rpm for 5 min, the optically transparent sample was further dialyzed with a dialysis membrane (1000 Da) for purification. The purified CDots were preserved at 4 °C for further use.

2.4. Preparation of AuNCs

The BSA-stabilized AuNCs were synthesized according to a previously reported method with minor modification [36]. Briefly, 5 mL $HAuCl_4$ (10 mM) and 5 mL BSA (50 mg/mL) were mixed and stirred at 800 rpm in the dark for 30 min. After added 500 μL NaOH (1 M), the mixture was heated at 50 °C for 7 h under vigorous stirring. After centrifugation at 6000 rpm for 5 min, the transparent sample was further dialyzed with membrane (1000 Da) for purification. Finally, the AuNCs powder was obtained by freeze drying the solution.