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A fluorescent sensor for detecting dopamine and tyrosinase activity by dual-emission carbon dots and gold nanoparticles

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ABSTRACT

In this work, we report a fluorescence strategy for detecting dopamine (DA) and sensing tyrosinase (TYR) activity on the basis of the dual-emission carbon dots (DECDs), which contain two emitters: the blue emitters (BE, maximum emission at 385 nm) and yellow emitters (YE, maximum emission at 530 nm). Gold nanoparticles (AuNPs) can effectively quench the two emissions of DECDs. The addition of DA aggregates AuNPs effectively, leading to the fluorescence recovery of dual emitters gradually. This strategy exhibits a high selectivity toward DA and shows good linear ranges, such as 0.5–3 μM for BE and 0.1–3 μM for YE. Additionally, the proposed method is successfully applied to the determination of DA in real samples with satisfactory recoveries. Subsequently, this DECDs-AuNPs platform is further taken advantage to assess TYR activity by the aid of TYR's capability for oxidation of DA into dopaquinone, which will not induce the agglomeration of AuNPs, so the fluorescence quenching of DECDs is associated with TYR activity. Finally, the mechanism of the reaction is discussed in detail, and the results suggest that both amine and phenolic hydroxyl groups of DA bring the aggregation of AuNPs.

1. Introduction

Dopamine (3, 4-dihydroxyphenylethylamine, DA), a catecholamine neurotransmitter, is ubiquitous in a variety of animals with a series of functions in the central nervous system [1]. The disorder levels of DA are considered to be the indicator of some neurological syndromes, such as schizophrenia [2] and Parkinson's disease [3]. Tyrosinase (TYR), which can catalyze DA to dopaquinone [4], is a copper-containing polyphenol oxidase and widespread in nature [5]. In the human body, an abnormally elevated level of TYR is associated with several diseases, including melanoma cancer and vitiligo [6]. Therefore, there is an urgent demand for the development of simple, selective, and sensitive assays for DA and TYR activity.

Up until now, a large variety of analytical methods have been employed to determine DA and TYR successfully including electrochemical analysis [7,8] and the fluorescence method [9–13]. Although the sensitivity of electrochemical methods is satisfactory, the repeatability and the anti-interference ability of these sensors should be further improved. While the fluorescence detection of DA is usually established by the direct interaction between DA and nano-probes, for instance, DA could effectively quench the emissions of β-cyclodextrin functionalized gold nanoclusters [9], adenosine capped CdSe/ZnS quantum dots [10] and graphene quantum dots [11]. Furthermore, the detection of TYR is always based on the catalyze reaction between DA and TYR. For example, when DA was transformed to dopaquinone under the catalysis of TYR, the dopaquinone could quench the fluorescence of the gold/silver nanoclusters [12] and glutathione protected gold nanoclusters [13]. Consequently, the fluorescence change was directly correlated to the concentration of TYR by taking advantage of the different effect of DA and dopaquinone.

Recently, our group has developed a green and simple synthesis of dual-emission carbon dots (DECDs), which contain two different emitters: the blue emitters (BE, λex = 315 nm, λem = 386 nm) and the yellow emitters (YE, λex = 365 nm, λem = 530 nm) [14]. The fluorescence of dual emitters can be quenched effectively by gold nanoparticles (AuNPs) within 5 min. After addition of DA, the aggregation of AuNPs occurs, causing the dual emissions restore rapidly. The mechanism study reveals that both the amine and phenolic

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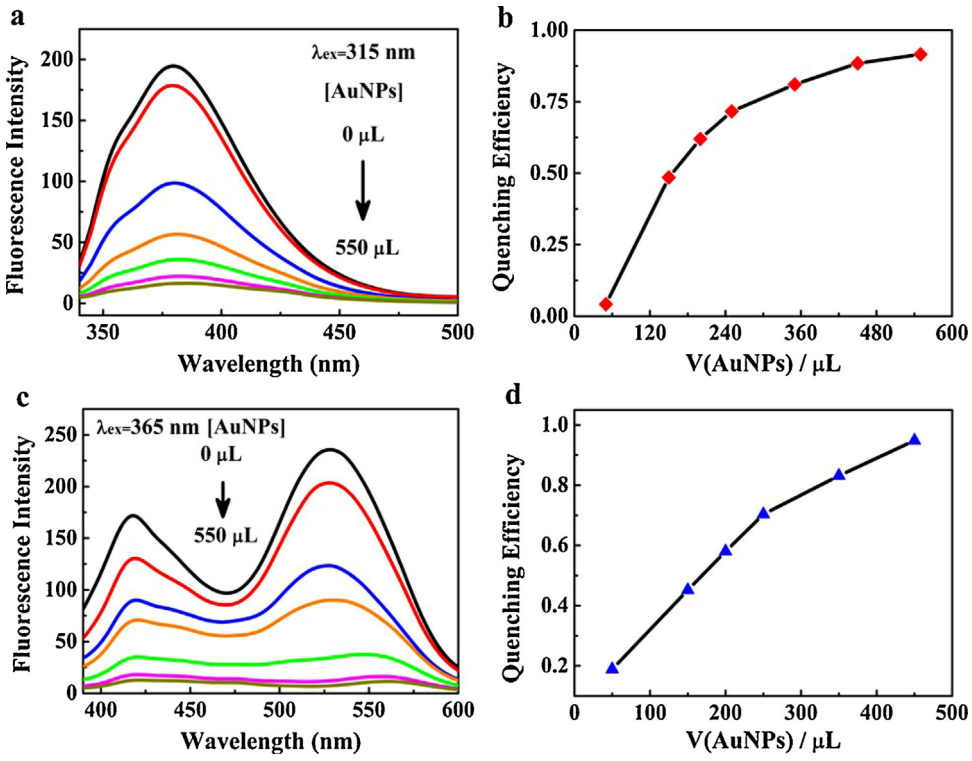

Fig. 1. Fluorescence spectra (a, BE; c, YE) of DECDs upon addition of different concentrations of AuNPs and the quenching efficiency of DECDs in the presence of different volumes of AuNPs (b, BE; d, YE).

hydroxyl groups of DA together bring the aggregation of AuNPs. Hence, when DA is oxidized to dopaquinone by TYR, AuNPs keep the dispersed state rather than agglomeration, and the fluorescence of two emitters is quenched again. Importantly, this DECDs-AuNPs system paves a new way to detect DA and TYR simultaneously, and the determination is simple, rapid and convenient. The limits of detection (LOD) are 0.037 μM and 0.0098 U/mL for DA and TYR, respectively. Benefiting from the superior sensitivity and selectivity, this DECDs-AuNPs system is successfully applied for the detection of DA in human plasma samples.

2. Experimental section

2.1. Chemicals and materials

Ascorbic acid, ethylene glycol, sodium citrate, dopamine hydrochloride, tyrosinase from mushroom, chloroauric acid, glucose, L-tryptophan, heparin, p-nitrophenol, hydrochloric acid, nitric acid, Na_2HPO_4 and NaH_2PO_4 were purchased from Aladdin (Shanghai, China). Levodopa, epinephrine, L-phenylalanine and catechol were purchased from Xiya Reagent (Shandong, China). The 58-mer dopamine-binding aptamer (DBA) with the sequence of 5′-GTC TCT GTG TGC GCC AGA GAA CAC TGG GGC AGA TAT GGG CCA GCA CAG AAT GAG GCC C-3′ was designed by the reported study [15] and synthesized by Sangon Biotech Co. Ltd. (Shanghai, China). All reagents were of analytical grade and without any further purification. Deionized water (18 MΩ cm) was used throughout the experiments.

2.2. Instruments

The fluorescence spectra were recorded by a Hitachi F-7000 fluorescence spectrophotometer. The ultraviolet-visible (UV–vis) absorption spectra were performed on a Cary 300 Bio UV–vis spectrophotometer. Transmission electron microscopy (TEM) images were recorded on a JEM-2100PLUS (JEOL, Japan).

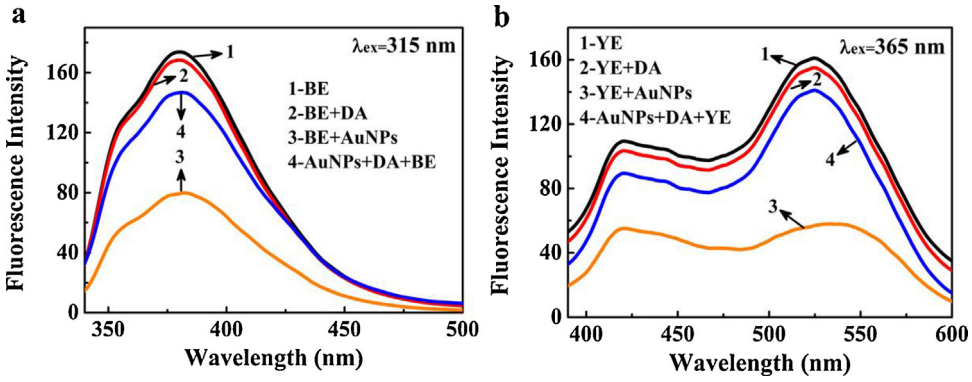

Fig. 2. Fluorescence spectra of BE (a) and YE (b) in absence and presence of DA, AuNPs, and the complex of DA with AuNPs.