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Dopamine fluorescent sensors based on polypyrrole/graphene quantum dots core/shell hybrids

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ABSTRACT

A facilely prepared fluorescent sensor was developed for dopamine (DA) detection with high sensitivity and selectivity based on polypyrrole/graphene quantum dots (PPy/GQDs) core/shell hybrids. The composites exhibit strong fluorescence emission, which is dramatically enhanced as high as three times than pristine GQDs. The prepared sensor allows a highly sensitive determination of DA by fluorescent intensity decreasing with the addition of DA and presents a good linearity in range of 5–8000 nM with the detection limit of 10 pM ($S/N=3$). Furthermore, the application of the proposed approach have been demonstrated in real samples and showed promise in diagnostic purposes.

1. Introduction

Dopamine (DA), a kind of neurotransmitter and hormone of the phenethylamine and catecholamine families, plays a critical role in the human body and brain (Qu et al., 2013). The dysfunctions of dopamine systems may lead to several nervous system diseases such as Parkinson's disease and schizophrenia (Wu et al., 2012). Thus, a sensitive and precise detection of DA is of great importance in the clinical diagnosis of neurological diseases. Substantial efforts have been taken to quantify the DA, including enzymatic methods (Fritzen-Garcia et al., 2013), electrochemistry (Yu et al., 2012; Biji and Patnaik, 2012; Qian et al., 2014), capillary electrophoresis (Bouri et al., 2012), high performance liquid chromatography (Syslova et al., 2011) and ultraviolet–visible spectrophotometry (J.J. Feng et al., 2013; X.M. Feng et al., 2013; Xu and Yoon, 2011). However, most of these techniques do not meet the increasing requirements for developing simpler, more reliable and more cost-efficient DA sensors (Yang and Li, 2014; Yildirim and Bayindir, 2014). Therefore, further development of high sensitivity and selectivity sensors for DA is desired. Compared with the described approaches, fluorescence spectroscopy for DA analysis, as a simple, efficient and sensitive method, is attracting great interest.

During the past decades, the semiconductor quantum dots (SQDs), a type of photoluminescent nanomaterials, have drawn extensive attention due to their good performance in cell imaging and sensing (Bruchez et al., 1998). However, the SQDs have suffered from intrinsic limitations such as heavy metals potential toxicity and environmental hazards (Valizadeh et al., 2012; Cao et al., 2007). Therefore, looking for eco-friendly alternatives has been becoming highly desirable and urgent. Recently, graphene quantum dots (GQDs), as a new-style quantum dot system, offer strong potential for promising candidates to replace traditional SQDs. GQDs are consisted of a single layer or few-layer of carbon atoms in a closely packed honeycomb structure (Jiang et al., 2013). Because of the quantum confinement and edge effects, they possess some distinct properties, such as high biocompatibility, chemical inertness, good water-solubility, stable photoluminescence and high electrical conductivity (Zhou et al., 2014; Dong et al., 2013), which suggest great potential as a new platform in photovoltaic devices and imaging fields (Li et al., 2013; Ran et al., 2013). However, the GQDs prepared for chemical sensing are few reported, probably due to the difficulty in seeking GQDs that can both selectively identify a target and give sensitive signal response (Dong et al., 2012b).

Nowadays, polypyrrole (PPy) is a booming and increscent investigated class of conjugated materials because of its excellent electronic, optical and thermal properties (Jeon et al., 2011). Also this material has been found promising application in many different fields including supercapacitors, functional electrodes and sensors (Yang et al., 2012; Chen et al., 2013; Qian et al.,

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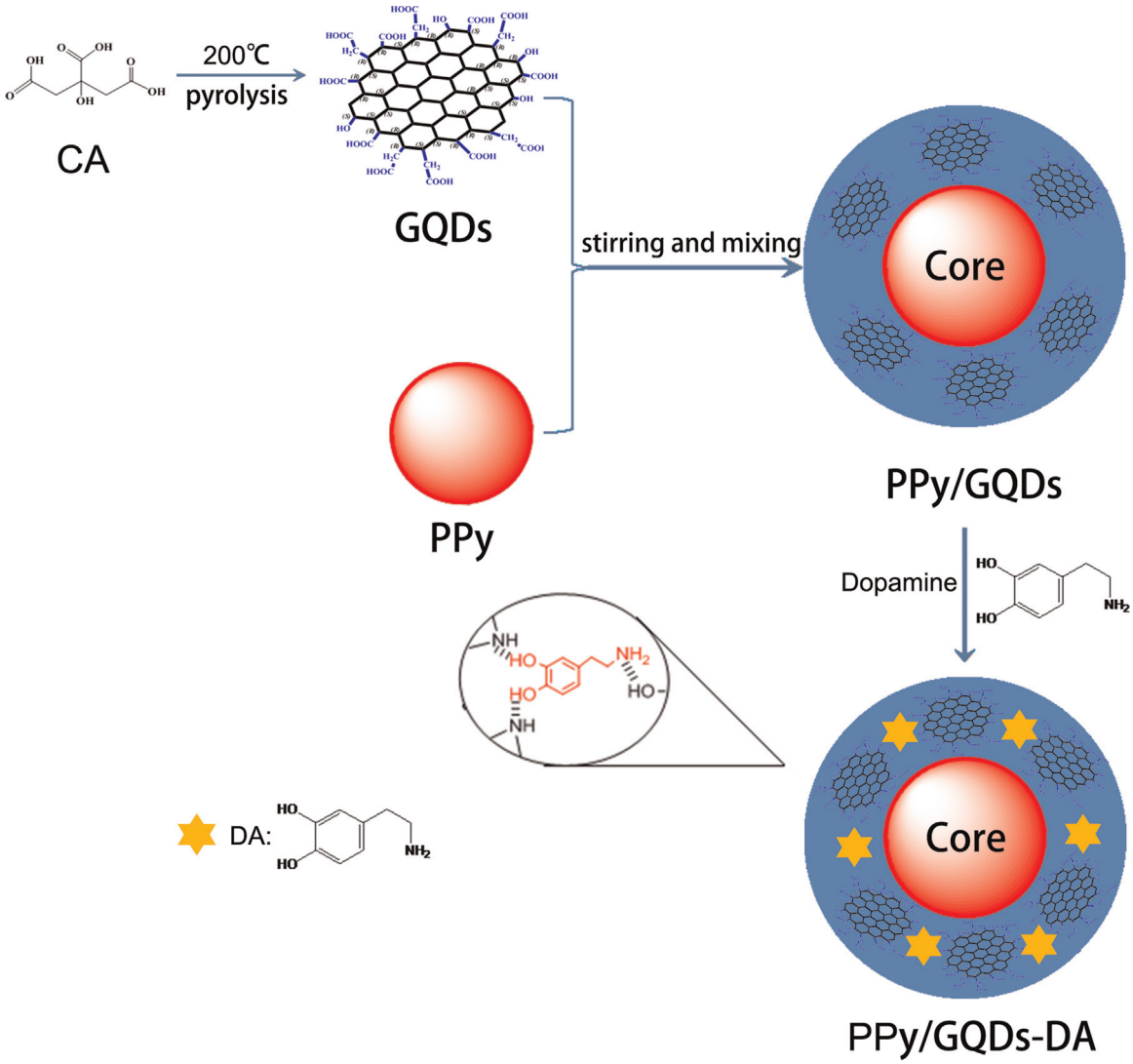

Fig. 1. Illustration of the preparation of PPy/GQDs.

2013b, 2013a; Chatterjee et al., 2013). In this study, we report a facile fabrication of PPy/GQDs core/shell composites by synthesizing GQDs in the presence of PPy microspheres (Fig. 1). The existence of amine groups on the PPy backbone may lead to enhancement of fluorescence intensity of GQDs by surface passivation (Dong et al., 2012a; Shen et al., 2012). Moreover, abundant oxygen-containing groups at the surface of PPy microspheres enable to adsorb the DA molecules effectively onto the surface of composites by interaction with amine and hydroxyl functional groups in DA through hydrogen bonds (Qian et al., 2014), thus multiply recognizing DA with high sensitivity and specificity.

2. Materials and methods

2.1. Reagents and materials

Hydrogen peroxide (H_2O_2, 30% AR) and pyrrole (AR) were purchased from Sinopharm Chemical Reagent Co. (China). NaOH (AR) and $FeCl_2$ (AR) were obtained from Shanghai Chemical Reagent Co. (China). Citric acid (AR) was purchased from Nanjing Chemical Reagent Co. Ltd. (China). Deionized water was applied for all polymerization and reaction processes. Ascorbic acid (AA), DA, uric acid (UA), norepinephrine (NE) and 3,4-dihydroxyphenylacetic acid (DOPAC) were purchased from Aladdin Chemical Reagent Co. (China). 5-Hydroxyindole acetic acid (5-HIAA) was obtained from Sigma-Aldrich Co. Human serum and urine were provided by the local hospital and stored at 4 °C.

2.2. Instruments and measurements

Fluorescence measurements were carried out on an LS SS Perkin Elmer spectrometer. UV–vis spectra were measured on a Lambda 35 Perkin Elmer spectrometer. Transmission electron microscopy (TEM) images were obtained by a JEM 2100 high-resolution TEM. Zeta potential was recorded on a Malvern Nano-Z Instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 VersaProbe. All Fourier transform infrared (FTIR) spectroscopic measurements were performed on a Nicolet NEXUS870 spectrometer.

2.3. Synthesis of the PPy microspheres

In a typical preparation procedure, PPy was initiated with the addition of 5 mL H_2O_2 to the pyrrole/$FeCl_2$/H_2O (1 mL/0.1 g/94 mL) mixture and lasted for 6 h. After that, centrifugation was used for concentrating the products, which had been washed with water several times to remove reaction byproducts and unused