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Efficient one-pot synthesis of molecularly imprinted silica nanospheres embedded carbon dots for fluorescent dopamine optosensing

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ABSTRACT

A new type of eco-friendly molecularly imprinted polymer (MIP) was synthesized through an efficient one-pot room-temperature sol–gel polymerization and applied as a molecular recognition element to construct dopamine (DA) fluorescence (FL) optosensor. Highly luminescent carbon dots (CDs) were firstly synthesized via a one-step reaction in organosilane, and their surface were anchored with MIP matrix (CDs@MIP). The resulting composite of a synergetic combination of CDs with MIP showed high photostability and template selectivity. Moreover, the composite allowed a highly sensitive determination of DA via FL intensity decreasing when removal of the original templates. The new MIP-based DA sensing protocol was applied to detect DA concentration in aqueous solution, the relative FL intensity of CDs@MIP decreased linearly with the increasing DA in the concentration range of 25–500 nM with a detection limit (3σ) of 1.7 nM. Furthermore, the proposed method was successfully intended for the determination of trace DA in human urine samples without the interference of other molecules and ions.

1. Introduction

The molecularly imprinted polymer (MIP) technique, a synthetically efficient method towards polymers with molecular recognition properties, has been demonstrated as one of the most promising techniques in sensor field because of its simplicity, reliability, capability of miniaturization, and low cost method of fabrication (Chen et al., 2011; Haupt and Mosbach, 2000). Multifarious methods have been explored to prepare MIP, such as bulk polymerization (Ye et al., 1998), multi-step swelling polymerization (Haginaka et al., 1999), suspension polymerization (Mayes and Mosbach, 1996), and precipitation polymerization (Tamayo et al., 2003), etc. By comparison, the sol–gel polymerization (Makote and Collinson, 1998) exhibits three distinct advantages that: (i) the ease fabrication with thin films and/or bulk gels; (ii) the eco-friendly reaction solvent (water or ethanol), which is quite different from the general solvent (chloroform, acetonitrile or toluene) that used in the above mentioned polymerization methods; (iii) the mild polymerization conditions that allow specific reagents to be readily introduced within the highly cross-linked, porous host structure without the problems of thermal or chemical decomposition.

Dopamine (DA) is an important neurotransmitter in mammalian central nervous systems, detection and quantification of DA are important in diagnoses, monitoring, prevention and treatments of several neurological disorders, e.g., Schizophrenia, Huntington's disease, and Parkinson's disease (Ali et al., 2007). Different analytical methods have been reported for DA determination, such as fluorometry (Huang et al., 2012), visible spectrophotometry (Abbaspour et al., 2009), chromatography combined with mass spectrometry (LC/MS) (Ji et al., 2008), and electrochemical techniques (Shang et al., 2009). Their detection limits are 0.14 μM, 3.0 μM, 33 pM, and 5 nM, respectively. Although LC/MC method can reach very low detection limit, the determination requires sample pretreatment, lengthy analysis times, and high costs. In addition, there are a number of problems with electrochemical methods due to the nature of the oxidative electrode reaction of DA. The concentration of DA in the extracellular fluid of the central nervous system is 0.01 ~ 1 μM compared to 100–500 μM for ascorbic acid (AA, undergo oxidation within the same potential window as DA). Therefore, fluorescence technique is a good choice to combine with MIP technique, which converts the binding events on MIP to physically detectable signals. The combination can achieve both good sensitivity and excellent selectivity.

Photoluminescent carbon dots (CDs) constitute a fascinating class of recently discovered nanocarbons owing to their attractive attributes, including tunable photoluminescence (PL) properties, eco-friendliness, low cytotoxicity and excellent biocompatibility (Baker and Baker, 2010). CDs form attractive application as labels for bioimaging (Cao et al., 2007; Yang et al., 2009), but they are rarely involved in the sensor field at present (Gonçalves et al., 2010). The main obstacles are encompassed by immobilization of

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CDs in a suitable matrix that remains all CDs' PL properties, permeates to the analytes, and avoids the leaching of CDs.

It should be pointed out that II–IV semiconductor quantum dots (QDs) coated with molecularly imprinted silica film through the sol–gel polymerization approach have been previously reported (Li et al., 2010; Liu et al., 2010; Wang et al., 2009a, b). The fabricated optical sensors could selectively and cooperatively bind to the template molecules. Nevertheless, in order to improve the interaction between QDs and molecularly imprinted silica matrix, QDs have to be capped with organosilane before the sol–gel hydrolysis and condensation imprinted polymerization reaction. It means that the polymer preparation process needs at least two steps.

In this work, we introduce a process with which CDs can be encapsulated with silica imprinted film through a one-pot sol–gel reaction. Furthermore, the PL properties of CDs are maintained since silica is a transparent and inert material (Yang and Gao, 2005). The silica imprinted film here can not only avoid CDs leaching from the matrix, but also show excellent permeability to the template molecules. In the experiments, multi-aminosilane was used as a coordinating solvent to synthesize highly luminescent CDs functionalized with methyldimethoxy silane groups (Wang et al., 2011). And silica molecular imprinted nanospheres could be fabricated in a simple and efficient way from CDs, template molecules (DA), functional monomer (3-aminopropyltriethoxysilane, APTES), and cross-linker (tetraethoxysilane, TEOS) by means of the hydrolysis and condensation reaction in the presence of aqueous ammonia solution as the catalysis (Li et al., 2010). Therefore, a new type of eco-friendly MIP-based DA fluorescence optosensor has been developed by anchoring the MIP matrix on the surface of CDs via an efficient one-pot room-temperature sol–gel molecular imprinting process.

2. Experimental section

2.1. Reagents and materials

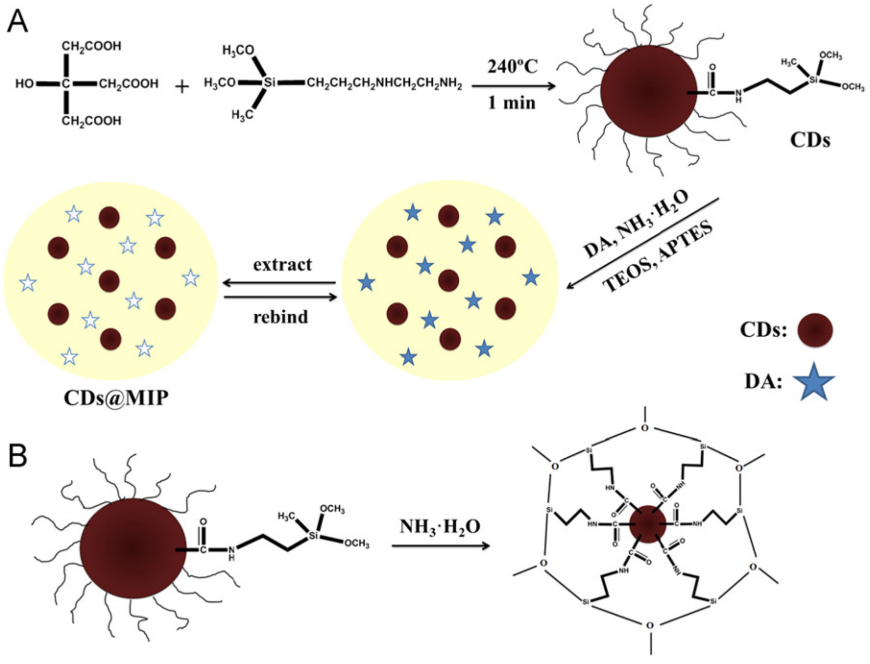
N-(β-aminoethyl)-γ-aminopropyl methyldimethoxy silane (AEAPMS), TEOS, APTES, citric acid anhydrous were purchased from Alfa Aesar. Dopamine hydrochloride (DA) and epinephrine (EP) were obtained from Sigma. Ascorbic acid (AA) was purchased from Fluka. Ammonia solution (25% in water), petroleum ether, and ethanol were obtained from Beijing Chemicals, China. All aqueous solution were prepared with ultrapure water (> 18 MΩ cm) obtained from a Milli-*Q* Plus system (Millipore).

2.2. Instruments and measurements

Fluorescence spectra were recorded using an F-4600 Hitachi spectrometer. UV–vis spectra were measured on a U-3900 Hitachi spectrometer. Transmission electron microscopy (TEM) images were obtained using a Hitachi-600 transmission electron microscope operating at 100 kV. High-resolution TEM (HRTEM) image was recorded with a Philips TF-F20 transmission electron microscope operating at 200 kV. Because the AEAPMS-passivated CDs tend to hydrolyze and self-condense to a gel catalyzed by heat and/or trace water from air during the drying process, the HRTEM sample was prepared on a copper grid by dropping 10 μL of the CDs ethanol solution onto the mesh and drying it in room-temperature. All Fourier transform infrared (FTIR) spectroscopic measurements were performed on a Bruker Vertex 70 spectrometer. Dynamic light scattering (DLS) was recorded on a Malvern Nano-ZS instrument.

2.3. CDs synthesis

CDs were synthesized from citric acid anhydrous following a method reported by Wang et al. (2011). 10 mL AEAPMS were placed into a 100 mL three-necked flask, and degassed with nitrogen for about 10 min. Then, the system was heated to 240 °C, 0.5 g citric acid anhydrous was quickly added to the flask with vigorous stirring. The mixture was then kept at the temperature for 1 min. After natural cooling to room-temperature, the final products were purified by precipitation with petroleum ether three times. The synthesized CDs were dispersed in a certain amount of ethanol for the next experiments.



Scheme 1. Illustration of the preparation of CDs@MIP.