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Microwave-assisted preparation of N-doped carbon dots as a biosensor for electrochemical dopamine detection

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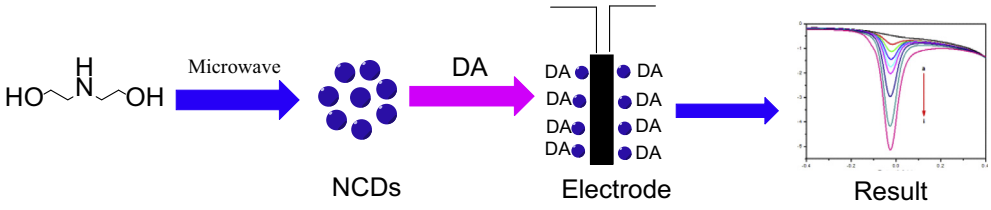
GRAPHICAL ABSTRACT



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ABSTRACT

A new N-doped carbon dots (NCDs) could be prepared by using the microwave-assisted technique within 10 min without the need for any solvent or catalyst. The NCDs exhibited a highly sensitive electrochemical response toward dopamine (DA) in Phosphate Buffered Saline (PBS) (pH = 6.5). The detection limit of DA was calculated by differential pulse voltammetry (DPV) as low as 1.2×10^{-9} mol/L with a linear dynamic range of 5.0×10^{-8} to 8.0×10^{-6} mol/L. These results suggested that this new NCDs could be effectively used for the direct and rapid detection of trace levels of DA in human serum and urine samples.

1. Introduction

The neurotransmitter dopamine (DA) plays an important role in the central nervous system of biological organisms [1], but abnormal levels of DA in the brain can often lead to Parkinson's disease, Alzheimer's disease, or schizophrenia [2–6]. Therefore, the development of highly selective and sensitive analytical methods on the direct and rapid determination of trace dopamine is of great significance. So far, various analytical methods, such as liquid chromatography, chemiluminescence, capillary electrophoresis, fluorescence techniques [7–11] have been used for dopamine determination. However, most of these techniques are limited by time consuming, high cost, complicated equipment requirements, lack of sensitivity and selectivity. Recently, electrochemical techniques have received considerable interest for the real-time detection of DA at low concentration condition due to their simple, high sensitivity and rapid response. It is well known that bare electrodes for detection of DA is ineffective [12], therefore there is an urgent need for developing novel sensors, which can offer high sensitivity and selectivity for the direct detection of DA at low concentration in the presence of interfering compounds.

As a new member of the carbon family, carbon quantum dots (CQDs) can exhibit excellent optical and electro-optical properties due to their quantum confinement and edge effect [13], which could be considered as a promising material in replacement of traditional semiconductor quantum dots and organic dyes in various applications, including sensors, bioimaging, photovoltaics, and energy-conversion devices [14–19] due to low toxicity, good photo-stability, excellent biocompatibility, high chemical stability [20–23]. So far, many efforts have been devoted to developing methods for the preparation of CQDs including laser ablation

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[24], electrochemical synthesis [25], chemical oxidation [26], microwave synthesis [27], and solvothermal methods [28]. Among these methods, microwave-assisted irradiation technique can effectively offer both rapid and uniform heating of the reaction medium, which can shorten the reaction time and greatly improve the product yield and purity [29–33]. Therefore, microwave-assisted irradiation technique can be regarded as a simple, direct and efficient approach for the preparation of CQDs [34–36].

In this study, we described a novel and large-scale strategy for the high-yield synthesis of NCDs based on the microwave irradiation technique without any solvent or catalyst by using the starting product diethanolamine (DEA). Herein, DEA can serve as both a carbon source and a nitrogen source. Furthermore, the resulting NCDs possess a large number of hydroxyl and amino groups on the surface of NCDs which can attract the electroactive compound dopamine (DA) and act as a novel electrochemical sensor for the direct detection of trace levels of DA in human serum and urine samples with a high sensitivity and excellent selectivity.

2. Materials and methods

2.1. Reagents and chemicals

Both dopamine and ascorbic acid in 99% purity were purchased from Sigma–Aldrich Chemical Company. Ethanol, ethyl acetate (EA), tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and diethanolamine (DEA) were commercially available and directly used without further purification. Phosphate Oxygen-free nitrogen was bubbled through the cell prior to each experiment. All experiments were carried out at room temperature.

2.2. Apparatus

The particle size distributions of the NCDs were observed using transmission electron microscopy (TEM). The IR spectrum of NCDs was measured by a Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrophotometer with a resolution of 4 cm^{-1} and scan times of 64. IR sample was prepared by applying the NCDs ethanol solution on the surface of a KBr wafer and then dried under an infrared lamp. Ultraviolet–Visible (UV–Vis) absorption spectrum was measured with a Varian Cary 50 spectrophotometer at 1 cm of the light path length. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5000 Versa probe electron spectrometer from ULVAC-PHI. All electrochemical measurements were carried out with a CHI660E (Shanghai CH Instrument Company, China). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a conventional three-electrode system with glassy carbon electrode (GCE) as the working electrode (WE), a platinum counter electrode (CE) and an Ag/AgCl (sat. KCl) reference electrode (RE). Microwave reactor (Yu Hua Instrument, China, 1 kW, 2.45 GHz).

2.3. Microwave-assisted preparation of NCDs

Typical preparation of NCDs were described as follows: 5 mL DEA was put into a 25 mL quartz ampoule, and then the ampoule was placed inside the microwave reactor and irradiated for 10 min (1 kW, 2.45 GHz). After cooling to room temperature, the resulting dark-yellow transparent solution is mixed with ultra pure water and centrifuged at a 10,000 rpm for 10 min, and then further filtered by a 0.22 μm syringe filter to remove the large particles. The obtained NCDs were concentrated by freezing (−80 °C) and drying under vacuum.

3. Results and discussion

3.1. Characterization of NCDs

The solubility of the resulting NCDs were tested in several common solvents which was carried out by dissolving 10 mg of NCDs in 5 mL of water, ethanol, EA, THF, DMF and DMSO (Fig. S1), respectively. In each case, NCDs could form a clear solution in these solvents. As evident from the TEM image of NCDs (Fig. 1a), it could be clearly observed that the NCDs could be highly dispersed in aqueous solution, and their nanoparticle diameters are distributed in the range of 8–25 nm with an average diameter of 16.4 nm (Fig. 1b).

Fig. 2 provides the FT-IR spectrum of the NCDs with some main absorption peaks such as the O—H stretching vibration at 3363 cm^{-1}, C—H stretching vibrations at 2980 and 2870 cm^{-1}, strong C=O stretching vibration at 1643 cm^{-1}, C=C stretching vibrations at 1571 cm^{-1}, the characteristic stretch band of the amine C=N bond at 1470 cm^{-1}, indicating that the surface of NCDs is rich in negatively charged carboxylic acid groups and dopamine molecule can bind to NCDs particles through electrostatic interaction or hydrogen bond. Element analysis data (C 72.65%, N 5.670%, O 20.78%) of NCDs were performed by XPS technique (Fig. S3) which can further confirm this NCDs containing carbon, nitrogen and oxygen elementals as FT-IR spectrum described above. The UV–Vis absorption spectra of NCDs and DEA (Fig. S4) revealed that only the NCDs can exhibit an absorption peak at 285 nm arising from a π–π^* transition of the C=C bond which may be formed by the microwave irradiation process.

3.2. Effect of buffer pH

The effect of pH on the electrochemical response of DA attached to NCDs-modified electrode were examined by DPV within a pH range of 6.0–9.0 (Fig. S5). It is clearly found that the peak current

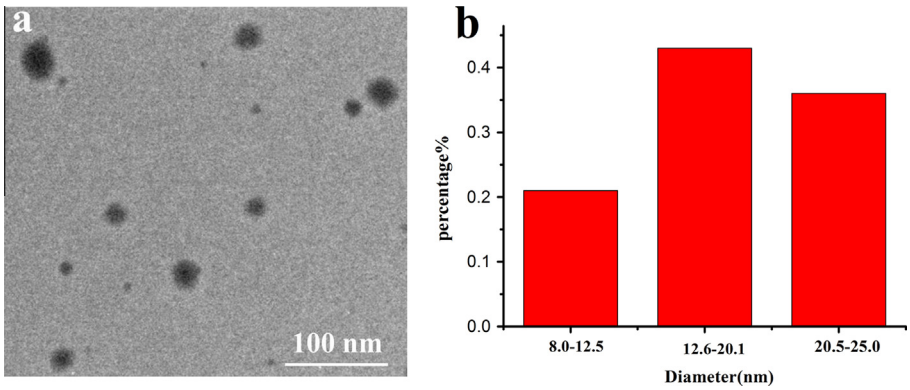

Fig. 1. (a) TEM image of NCDs and (b) particle size distribution of NCDs.