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Water-soluble pillar[6]arene functionalized nitrogen-doped carbon quantum dots with excellent supramolecular recognition capability and superior electrochemical sensing performance towards TNT

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ABSTRACT

By combining the merits of water-soluble pillar[6]arenes (WP6s) and nitrogen-doped carbon quantum dots (N-CQDs), a sensitive electrochemical sensing platform was constructed by using the WP6-N-CQD nanocomposites as an electrode material for the detection of trinitrotoluene (TNT). N-CQDs were prepared via microwave route by using urea and citric acid as raw materials. Two kinds of macrocyclic hosts, β-CD and WP6, were incorporated on to the N-CQDs via hydrogen bonding and $\pi-\pi$ interactions, respectively. The FTIR, TGA, and XPS characterizitions demonstrated that the β-CD-N-CQD and WP6-N-CQD composites were successfully prepared. The WP6-N-CQD-modified glass carbon electrode (GCE) indicated an enhanced electrochemical signal than the β-CD-N-CQDs/GCE in the reduction of 2,4,6-trinitrotoluene (TNT), which was attributed to the higher supramolecular recognition capability of the WP6 host than that of β-CD towards TNT. The linear ranges of 0.001 μM–1.0 μM and 1.0 μM–20.0 μM were obtained by using this electrochemical sensing platform. The detection limit was 0.95 nM (S/N = 3). The developed electrochemical sensing technique was successfully applied for the detection of TNT in lake water samples. Therefore, WP6-N-CQD nanocomposites are promising for the construction of high performance electrochemical sensors for the detection of explosives.

1. Introduction

Over the last decade, the utilization of artificial receptors, especially macrocyclic hosts, has garnered considerable attention in the field of optical/electrochemical sensing because of their high selectivity and sensitivity for the reliable, rapid and simple detection of different kinds of analytes [1]. Host-guest interactions have been widely used to construct nanoscale devices in electrochemical sensing or biosensing [2]. Recently, many researchers have attempted to develop macrocycle nanocomposites (*e.g.*, cyclodextrin, calixarenes, pillararene) and carbon nanomaterials (*e.g.*, graphene, carbon nanodots, CNT) for diversified applications, for instance, electrochemical/bio sensing, fluorescence sensing, cell/bio imaging, drug/gene transportation, and so on. For example, Guo et al. [3] demonstrated that cyclodextrin (CD)-graphene composites exhibited outstanding supramolecular recognition capabilities and enhanced electrochemical responses towards electroactive molecules than pure graphene. Zhu et al. [4] reported that β-CD-CNTs nanohybrids revealed higher electrochemical signals and excellent sensing performances than pure CNTs. Moreover, it has been proved that calix[6]arene-modified graphene can be employed as a 'turn on' receptor for fluorescence sensing L-carnitine in cells [5]. In addition, higher electrochemical responses were obtained on the calix[4,6,8]arene modified reduced graphene oxide (RGO) composites than pure RGO [6]. Yang et al. [7] also indicated that disulfide bridged β-CD-functionalized CNTs exhibited higher supramolecular recognition capabilities and higher electrochemical responses than that of natural β-CD-CNT composites towards three phenols.

As a new developing family of macrocycles, pillar[n]arenes, mainly pillar[5,6]arenes which were first reported by Ogoshi et al. [8]. Pillar[n]arenes are composed of hydroquinone units linked by methylene ($-CH_2-$) bridges at their *para*-positions. They have a hydrophobic cavity sandwiched between two functionalizable rims and have shown excellent binding abilities towards various types of guests with high selectivities due to their rigid symmetrical pillar architectures and hydrophobic electron-donating cavities [9–15].

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Besides, pillar[n]arenes also have several outstanding advantages such as easier synthesis, easier derivatization, and higher solubility in aqueous solutions as compared to other traditional macrocycles [16–18]. They have been described as "fascinating cyclophanes with a bright future" [19]. The synthesis, derivatization, host-guest chemistry, and self-assembly of pillar[n]arenes have been widely explored [20–24]. However, the electrochemical/optical sensing applications of pillar[n]arenes are rarely reported [25].

On the other hand, carbon quantum dots (CQDs), which have emerged as a new family of carbon nanomaterials, have attracted considerable attention recently because of their distinct benefits, such as green synthesis, excellent solubility, easy functionalization, chemical inertness, stable photoluminescence, high electrochemical activity, and excellent biocompability [26–35]. As a green substitute for toxic transition metal quantum dots, CQDs have promising applications in many areas such as fluorescence/electrochemical sensing, electrocatalysis, bioimaging, drug delivery, etc. It has been repoted that N-doping can improve the electrocatalytic activity of carbon materials. For instance, N-doped carbon quantum dots [36], N-doped graphene quantum dots [37], and N-doped reduced graphene oxide [38] have exhibited excellent electrocatalytic activity. Thus, N-CQDs were employed in the present study. If N-CQDs are functionalized with water-soluble pillar[n]arenes, new materials with the fascinating electrocatalytic property of N-CQDs and excellent supramolecular recognition and enrichment capability of pillar[n]arenes will likely be obtained. Therefore, the integration of N-CQDs and pillar[n]arenes could have numerous potential applications in electrochemical sensing.

TNT, or 2,4,6-trinitrotoluene, is a well-known explosive that is widely used in military and nonmilitary applications [36,37]. The detection of TNT remains an important area of research both for preventative measures as well as decontamination of affected sites [39]. In addition, TNT is toxic and mutagenic, and is known to contaminate soil and groundwater, increasing the need for sensitive and rapid detection methods. Recently, electrochemical sensing techniques have been widely used for the detection of TNT due to their inherent selectivity, ease of use, low cost, short analysis time, and low limit of detection [40]. Various electrode materials such as sliver NPs-graphene [41], ionic liquid-graphene [42], and Pt/Pd nanocube-graphene nanoribbons [43], as well as several metal oxide-based electrodes [44,45] have been employed for TNT detection. Nevertheless, there remains a need for electrode materials with unique properties that provide enhanced sensitivity and selectivity.

To the best of our knowledge, by combining the merits of water-soluble pillar[6]arene (WP6) and nitrogen-doped carbon quantum dots (N-CQDs), a sensitive and selective electrochemical sensing platform based on WP6-N-CQDs composites modified electrode is reported here for the electrochemical reduction and determination of TNT for the first time. N-CQDs were prepared *via* microwave synthesis using citric acid and urea as raw materials. Two kinds of macrocycles, β-CD and WP6, were incorporated on to the N-CQDs *via* hydrogen bonding and π-π interactions, respectively. Due to the higher supramolecular recognition capability of WP6 than β-CD towards TNT, a higher electrochemical response was obtained at the WP6-N-CQD-modified electrode as compared to that of β-CD-N-CQDs towards TNT. The proposed electrochemical sensing platform is provided in Scheme 1.

2. Materials and methods

2.1. Chemicals

WP6 (Scheme S1) was synthesized according to a previously published procedure [46]. β-CD was obtained from Aladdin Chemical Reagent Lo., Ltd. (Shanghai, China). TNT, nitrobenzene (NB), 4-nitrotoluene (4-NT), 2-nitrotoluene (2-NT), 2,6-dinitrotoluene (2,6-DNT), and 2,4-dinitrotoluene (2,4-DNT) were purchased from Shanghai Adamas Reagent Co., Ltd. (Shanghai, China). All aqueous solutions were prepared with deionized water (DW, 18 MΩ cm).

2.2. Synthesis of N-CQDs

N-CQDs were prepared according to a previously published method with minor modifications [29]. Briefly, 3 g urea and 3 g citric acid were dissolved in 10 mL DW. Then, the above mixed solution was heated in an 800 W microwave oven for 4 min, throughout this process, the mixed solution changed from a colorless liquid to a brown solid, suggesting the formation of N-CQDs. An aqueous solution of the N-CQDs was centrifuged (3000 rpm, 10 min) to remove the aggregated particles. The resulting brown supernatant was lyophilized to obtain the N-CQD powder.

2.3. Preparation of β-CD-N-CQDs and WP6-N-CQD composites

Fifty milliliter of 1.0 mg mL^{-1} WP6 aqueous solution was prepared. One hundred milligram of N-CQDs was added into the above WP6 solution and sonicated at room temperature for 4 h. Then, the resulting mixed suspension was centrifuged at 18,000 rpm and washed using DW for three times to remove free WP6. Finally, the WP6-N-CQD composites were received by lyophilization. The β-CD-N-CQDs were obtained using a similar process except that the WP6 was replaced by β-CD.

2.4. Construction of nanocomposite-modified electrodes

A glass carbon electrode (GCE, 3 mm in diameter) was polished with 0.05 μm Al_2O_3 powder and sonicated in DW to remove the physically adsorbed Al_2O_3 and dried at room temperature under air. The WP6-N-CQDs were dissolved in DW at 1.0 mg mL^{-1} with the aid of ultrasonic agitation for 30 min, resulting in a homogeneous suspension. Using the same procedure, 1.0 mg mL^{-1} homogeneous suspensions of β-CD-N-CQDs and N-CQDs were also prepared. The WP6-N-CQD-modified GC electrode was assembled by casting 5 μL of 1.0 mg mL^{-1} WP6-N-CQD suspension onto the GC electrode. The prepared working electrode was dried at room temperature and termed WP6-N-CQDs/GCE. The β-CD-N-CQDs/GC and N-CQDs/GC electrodes were also constructed by using the similar procedure.

3. Results and discussions

3.1. Characterization of β-CD-N-CQD and WP6-N-CQD composites

The morphology of the N-CQDs was determined using transmission electron microscope (TEM). As shown in Fig. 1A, the N-CQDs were monodispersed with an average size of approximately 1.6 ± 0.3 nm (Fig. 1A, inset), which was determined using the size distribution by measuring approximately 100 carbon dots. The TEM images of the β-CD-N-CQDs and WP6-N-CQDs were also obtained (Fig. S1). It can ben seen that the TEM images of the β-CD-N-CQDs and WP6-N-CQDs show some differences compared with the pure N-CQDs (Fig. 1A) and the size (approximately 2.0 nm) is a little bigger than that of N-CQDs (1.6 ± 0.3 nm). The Raman spectrum of the N-CQDs (Fig. 1B) showed a peak at approximately 1360 cm^{-1} caused by the D (sp^3-hybridized) band, which is associated with the vibrations of carbon atoms with dangling bonds in the termination plane of disordered graphite. And another band at 1598 cm^{-1} is the G (sp^2-hybridized) band, which is ascribed to the E_{2g} mode of graphite and is related to the vibrations of sp^2-hybridized carbon atoms in a two-dimensional hexagonal lattice