Journal of Electroanalytical Chemistry 804 (2017) 16–22

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical detection dopamine by Ester-calix[*n*]arenes/graphene nanosheets modified electrodes

Gang Zheng, Chao Shen, Long Huan, Rongfang Zhao, Ming Chen*, Guowang Diao*

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, PR China

ARTICLE INFO

Keywords:
Ester-calix[*n*]arenes
Graphene nanocomposites
Self-assembly
Modified electrodes
Dopamine

ABSTRACT

In this study, graphene nanosheets (GN) were modified by three ester-calix[n]arenes (ECnA, n = 4, 6, 8) using a simple self-assembly strategy. Three obtained ECnA/GN nanocomposites were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscope and electrochemical impedance spectroscopy, which confirmed that the various amount of ECnA molecules had been effectively loaded onto the surface of GN. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements showed that the ECnA/GN modified electrodes exhibited high supramolecular recognition and enrichment capability and consequently displayed high electrochemical response toward dopamine (DA). At low concentration of guest molecule, the ECnA/GN modified electrodes show the better enrichment performances. Especially, EC8A/GN modified electrode exhibited an excellent electrochemical performance for DA with high current densities of 4.46 mA $\text{mmol}^{-1}\,\text{L}\,\text{cm}^{-2}$, broad linear range (0.5 to 400 μM) and low detection limit (0.2 μM) at a signal-to-noise ratio of 3.

1. Introduction

Molecular recognition of host-guest chemistry has drawn enormous research enthusiasm in nowadays. The recognition performance of organic macrocyclic molecules are extensively employed by electrochemical sensors [1–8]. Calixarenes with cavity-shaped cyclic phenol molecules, regarded as the third host molecules after crown ethers and cyclodextrins, can generate various host-guest inclusions with different inorganic, organic, and biological guest molecules, which show high molecular selectivity and the engaging supramolecular recognition ability [9–12]. Specifically, the selective association of target molecules to the hydrophobic cavity of calixarene has been used to develop different sensors and separation matrices based on the strong recognition and enrichment function of calixarenes [13–15].

In recent years, graphene nanosheets, as a two-dimensional material (2D), have attracted considerable attention on the horizon of material science owing to remarkable and unique properties, such as excellent mechanical properties, extremely high specific surface area, fascinating electronic transfer at room temperature [16–19]. These outstanding properties support graphene as an ideal building blocks in nanocomposites and also holding great promise for potential applications in many scientific fields such as catalysis [20–22], sensors [8,23–27], energy storages [28–30], electronics, and photonics [23]. However, GN is hydrophobic and easily forms agglomerates irreversibly through strong π-π stacking interaction in aqueous solution or organic solution, which extremely restricts its application in many field [21,23,25,31].

The functionalization of GN or reduced graphene oxide (rGO) has been considered to be important for improving their dispersity in aqueous solution or organic solution. Up to now, various types of molecules have been used to disperse GN or rGO to avoid aggregation in water or organic solution [32–34]. Some water-solubility calixarenes are employed to disperse rGO, such as calix [4,6,8] arenesulfonates and amphiphilic amino resorcinarene [13,14]. However, GN decorated by the water insoluble calixarenes has not been reported. The dispersity of GN by calixarenes in organic solution will be improved. Meanwhile, GN retains the excellent conductivity and the electronic transfer performance. In addition, when calixarenes are introduced to GN surface to form nanocomposites, they might simultaneously possess the large surface area and good conductivity of GN and high supramolecular recognition and enrichment capability of calixarenes through combining their individual properties. Therefore, the integration of GN and calixarenes will expand potential applications in various fields such as sensors, electrocatalysis and biological probe, and thus arouse extensive research interest.

In this paper, ester-calix[*n*]arenes (ECnA, n = 4, 6, 8) were used to disperse GN in organic solvent (Fig. 1). Though π-π interaction, ECnA molecules successfully self-assemble on the surface of GN to obtain the ECnA/GN hybrid nanosheets which are characterized by Fourier

---

* Corresponding authors.
E-mail addresses: chenming@yzu.edu.cn (M. Chen), gwdiao@yzu.edu.cn (G. Diao).

http://dx.doi.org/10.1016/j.jelechem.2017.09.037
Received 16 August 2017; Received in revised form 13 September 2017; Accepted 17 September 2017

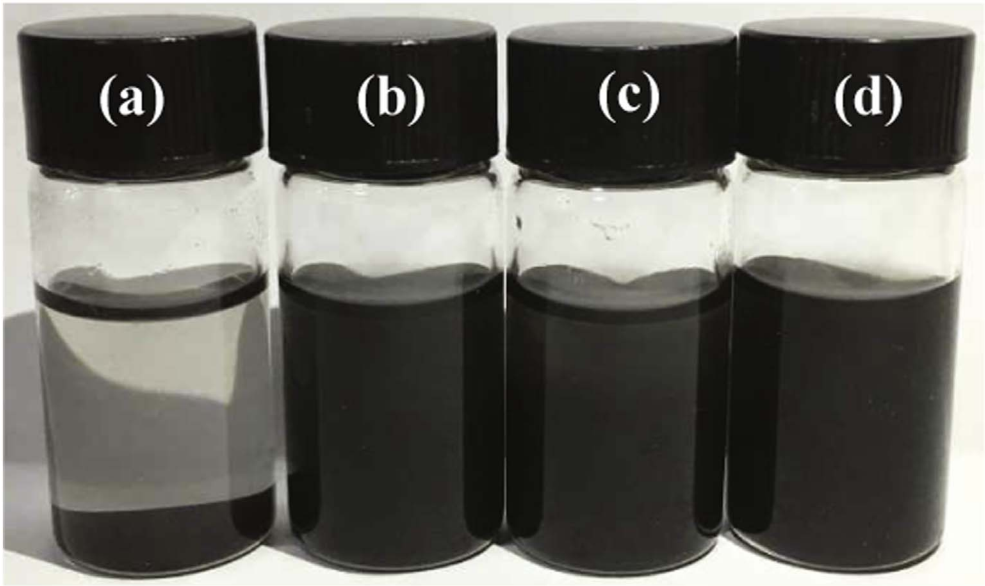


Fig. 1. Photos of (a) GN, (b) EC4A/GN, (c) EC6A/GN and (d) EC8A/GN in DMF.

transform infrared spectra (FTIR), thermal gravimetric analysis (TGA), scanning electron microscope (SEM), and electrochemical impedance spectroscopy (EIS). To evaluate the performance detection of ECnA/GN modified electrodes, dopamine (DA) is chosen as the guest molecule. The electrochemical inspection by cyclic voltammetry measurement (CV) and differential pulse voltammetry (DPV) shows the ECnA/GN modified electrodes display enrichment performance and exhibit high electrochemical response to DA molecule.

2. Experimental section

2.1. Synthesis of ECnA/GN nanocomposites

The ester-calix[*n*]arenes (ECnA, n = 4, 6, 8) were synthesized according to the literature [35–37]. Then, graphene nanosheets (GN) (10 mg) and ECnA (20 mg) were dispersed in 20 mL dimethyl formamide (DMF) by bath-sonicating, and then three mixtures were allowed to stir for 12 h at room temperature. The stable black dispersion was obtained and then was filtered, and then washed with DMF three times to obtain ECnA/GN that can be readily dispersed in dichloromethane (1.0 mg mL^{-1}) by ultrasonication again.

2.2. Preparation of ECnA/GN modified electrodes

The GCE was polished with 50 nm Al_2O_3 powders and then was cleaned with deionized water and sonicated in ethanol and water (each for 1 min). Then, the electrode was dried in air. A volume of 10 μL of the ECnA/GN (the concentration of each carbon materials was 1.0 mg mL^{-1}) was dropped onto a GCE and the electrodes were dried in air for more than 12 h. Finally, the modified electrodes were activated by several successive scans with a scan rate of 100 mV s^{-1} in 0.1 M PBS (pH 6.8).

2.3. Apparatus

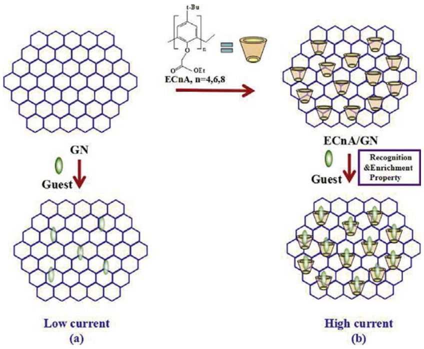
FT-IR spectra for the various samples were recorded on a Bruker Tensor 27. Field-emission scanning electron microscopy (FESEM) was carried out with Zeiss_Supra55 (Germany). Carefully weighed quantities of the different samples were subjected to TGA on a STA409PC (NETZSCH) TGA instrument at a heating rate of 10 °C min^{-1} under vacuum from 30 to 800 °C. EIS was measured with an Autolab/PG30 electrochemical analyzer system (ECO Chemie B. V. Netherlands) and were performed in a 0.1 M KNO_3 solution containing 5 mM $K_3[Fe(CN)_6]$ + 5 mM $K_4[Fe(CN)_6]$ (1:1) at ambient temperature. The interfacial charge-transfer resistances for different modified surface were determined by EIS in the frequency range from 0.1 Hz to 1 MHz with a perturbation signal of 5 mV. All electrochemical experiments were carried out with a CHI660c electrochemical workstation (Chenghua, China) with a three-electrode cell including a GCE (diameter: 3 mm) as the working electrodes, a Pt wire electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials reported in this paper were against SCE.

Cyclic voltammograms (CV) experiments were performed with a CHI660c electrochemical workstation (Chenghua, Shanghai). Electrochemical impedance spectroscopic (EIS) experiments were performed with an Autolab Electrochemical Analyzer (Ecochemie, Netherlands). All electrochemical measurements including CV, EIS and differential pulse voltammetry (DPV) were performed at 25 °C using a three-electrode system that consists of a KCl saturated calomel reference electrode (SCE), a platinum counter electrode, and the working electrode (gold electrode and modified electrodes).

3. Results and discussion

3.1. Characterization of ECnA/GN nanocomposites

Scheme 1 shows the procedure for preparing ECnA/GN hybrid nanosheets, and then sensing the guest molecules by an electrochemical strategy. The dispersion of GN was mixed with ECnA in DMF under ultrasonic condition (Scheme 1a). Then the suspensions were filtered to



Scheme 1. Schematic diagram of the procedure for preparing ECnA/GN and GN, and sensing the guest molecules by an electrochemical method.