



N-methylpyrrolidone exfoliated graphene as sensitive electrochemical sensing platform for 10-Hydroxycamptothecine

Xiaoxia Ye^a, Xiaofeng Yang^{a,*}, Piaopiao Wei^b, Kangbing Wu^b

^a School of Pharmaceutical Sciences, Wenzhou Medical University, Wenzhou 325035, China

^b School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Keywords:

10-Hydroxycamptothecine
Electrochemical determination
Graphene
Solvent exfoliation

ABSTRACT

10-Hydroxycamptothecine (10-HCPT), a natural alkaloid, is widely used in clinical practice because of its significant anti-cancer activity and small toxic side effects. In this work, graphene nanosheets (GNs) were prepared by ultrasonic exfoliation of graphite using *N*-methylpyrrolidone (NMP) as the solvent. The prepared GNs were characterized using transmission electron microscopy and scanning electron microscopy, and then used to construct a novel sensing platform for 10-HCPT. The electrochemical behaviors of 10-HCPT on the glassy carbon electrode (GCE) and GNs modified GCE (GNs/GCE) were studied. Compared with bare GCE, the prepared GNs/GCE increased the oxidation signal of 10-HCPT significantly, owing to larger active area of GNs/GCE and thus higher accumulation efficiency of 10-HCPT. Utilizing the signal amplification strategy of GNs, a highly-sensitive electrochemical method was established for the detection of 10-HCPT. The linear range was from 10.0 to 250.0 $\mu\text{g L}^{-1}$, and the detection limit was 3.21 $\mu\text{g L}^{-1}$ (8.81 nM). It was used to detect 10-HCPT in urine samples, and satisfactory results were obtained.

1. Introduction

10-Hydroxycamptothecine (10-HCPT), a natural alkaloid mainly existed in fruits of *Camptotheca acuminata* Decne (*C. acuminata*) [1], has strong anti-tumor activities against gastric carcinoma, hepatoma, bladder carcinoma and lung cancer [2–5]. Besides its significant anti-cancer activity, 10-HCPT has less toxic side effects in both experimental animals and human clinical evaluations [6,7]. Furthermore, it can also inhibit many noncancer cells by affecting their biological functions and mainly used clinically for the treatment of gastrointestinal, jejunal, rectal tumors and leucocythemia [8]. For example, it has been used to cure liver carcinoma, urinary bladder carcinoma, and colorectal cancer, etc. in China [9]. In order to evaluate or control its quality and medicinal preparation, the establishment of a rapid and sensitive method for the determination of 10-HCPT is of great significance in the physiological function and clinical applications.

Several methods have been developed for the detection of 10-HCPT, such as high performance liquid chromatography (HPLC) [10,11], liquid chromatography-mass spectrometry (LC-MS) [12] and capillary electrophoresis with amperometric detection (CE/AD) [13]. These techniques require complex pre-treatment steps, highly trained operators and time-consuming detection processes. From the molecular structure that shown in Fig. 1, it is found that 10-HCPT is

electrochemical active because of its phenolic hydroxy group, and its electrochemical behaviors on glassy carbon electrode (GCE) have been reported [14]. However, the studies regarding electrochemical determination of 10-HCPT are very rare.

Graphenes have attracted much attention due to its excellent physical and chemical properties [15–17], and various methods have been developed to produce this remarkable material, including chemical oxidation [18], chemical vapor deposition [19], organic synthesis [20], mechanical exfoliation [21], liquid-phase exfoliation [22] and electrochemical intercalation [23]. Among these methods, liquid-phase exfoliation is one of the most convenient and up-scalable approach for the production of high-quality graphene sheets [24]. Moreover, many factors that may influence the yield or quality of NMP-exfoliated graphene have also been investigated such as different additives [25,26], centrifugal speed [27] and ultrasonic conditions [28,29]. Until now, graphenes including liquid-phase exfoliated graphenes have been widely used in electrochemical sensing owing to large surface area, high catalytic activity and strong accumulation ability. For example, the graphene-modified electrodes have been reported to have remarkable signal enhancement effects toward a large variety of species such as small biological molecules [30,31], food colorants [32–34], environmental estrogens [35,36] and phenolic substances [37,38].

The aim of this work is to construct a novel sensing platform for

* Corresponding author.

E-mail address: yang_xiaofeng@163.com (X. Yang).

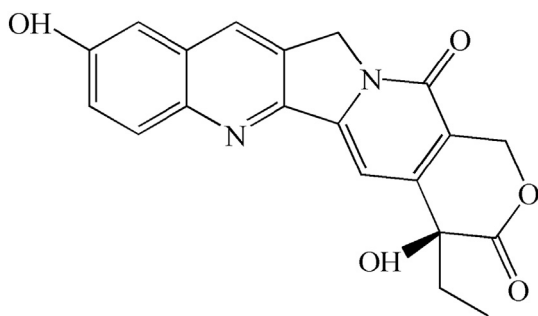


Fig. 1. The chemical structure of 10-HCPT.

trace levels of 10-HCPT utilizing the excellent properties of liquid-phase exfoliated graphene. Using *N*-methylpyrrolidone (NMP) as the liquid exfoliation solvent, graphene nanosheets (GNs) were easily prepared by ultrasonic exfoliation of graphite powders, which was confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). After that, the obtained GNs were used to modify the surface of glassy carbon electrode (GCE), and it was found that the prepared GNs/GCE exhibited remarkable enhancement effects toward the oxidation of 10-HCPT. Compared with the oxidation signals on bare GCE, it was almost improved by 250-fold on the surface of GNs/GCE, resulting in much higher detection sensitivity. The effects of pH values, amount of modification, accumulation time and accumulation potential were studied. As a result, an electrochemical method at 8.81 nM level was successfully developed for the determination of 10-HCPT, and successfully used in urine sample measurements.

2. Experimental section

2.1. Reagents

All chemicals were of analytical grade and used as received. Graphite powder, sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), NMP and dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). 10-HCPT was purchased from Aladdin. 1.0 mg mL^{-1} stock solution of 10-HCPT was prepared with DMF, and stored at 4°C in the dark. Ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was obtained from a Milli-Q water purification system and used throughout.

2.2. Instruments

Electrochemical measurements were performed on a CHI 820D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode is a GCE with diameter of 3 mm, the reference electrode is a saturated calomel electrode (SCE), and the counter electrode is a platinum wire. SEM characterization was performed with a Quanta 200 microscope (FEI Company, Netherlands), and TEM images were measured using a Tecnai G220 microscope (FEI Company, Netherlands).

2.3. Preparation of GNs/GCE

GNs were prepared via ultrasonic exfoliation of graphite powder in NMP. In a typical procedure, 600 mg graphite powder and 600 mg sodium citrate were added into 30 mL NMP. The resulting mixture was sonicated in a KQ-100B ultrasonicator (100 W) for 2 h. After 20-min centrifugation at a centrifugal speed of 4000 rpm, the supernatant was collected as GNs suspension. A GCE was firstly polished with 0.05 mm alumina slurry, and ultrasonically washed using ultrapure water. After that, 6.0 μL of the resulting GNs suspension was added onto the cleaned GCE surface, and the solvent was evaporated under an infrared lamp. The resulting modified GCE was denoted as GNs/GCE.

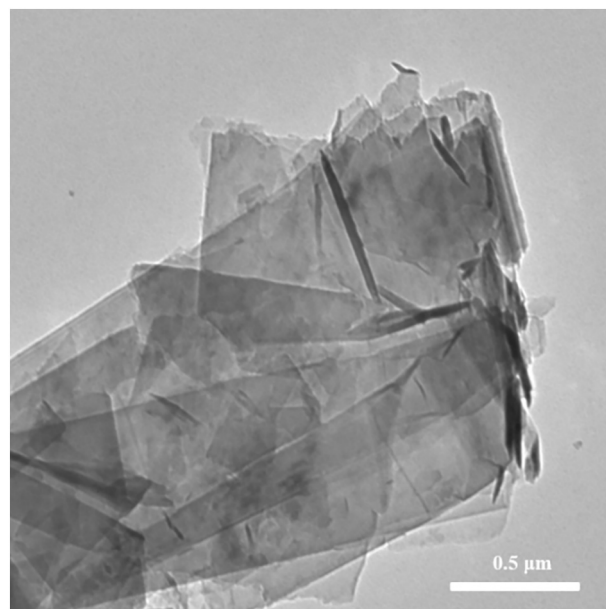


Fig. 2. TEM image of the prepared GNs.

2.4. Analytical procedure

0.1 M acetate buffer solution with pH of 4.0 was used as the supporting electrolyte for the detection of 10-HCPT. After 5-min accumulation at 0.4 V, the differential pulse voltammograms were recorded from 0.4 to 1.0 V, and the oxidation peak currents at 0.78 V was measured for 10-HCPT. The pulse amplitude was 50 mV, the pulse width was 40 ms, and the scan rate was 40 mV s^{-1} .

3. Results and discussion

3.1. Characterization of GNs

The structure of the prepared graphene was characterized by TEM, and the results were displayed in Fig. 2A number of transparent and thin nanosheets were clearly observed, suggesting that large-scaled graphite powder was successfully exfoliated into sheet-structured graphene. In addition, graphene nanosheets appear to be stacked on top of each other, in some cases the sheet edges tend to scroll and fold slightly.

The surface morphology of unmodified GCE and GNs/GCE were observed using SEM. The surface of bare GCE was very smooth (Fig. 3A), and numerous nanosheets were observed after modification of the prepared GNs (Fig. 3B). From the comparison, it is very clear that the modification of GNs obviously increase the surface roughness of GCE, providing larger response area and more active sites.

The electrochemical active area of GCE and GNs/GCE were studied using the probe of $\text{K}_3\text{Fe}(\text{CN})_6$. As seen in Fig. 4, a pair of redox peaks was observed on the surface of GCE (Fig. 4A) and GNs/GCE (Fig. 4B). As increasing the scan rate (ν) from 10 to 250 mV s^{-1} , the peak potentials kept unchanged, while the peak currents increased linearly with the square root of scan rate. Based on the $i_{\text{pa}} - \nu^{1/2}$ plots in Fig. 4C and D, the values of electrode area (A) were calculated to be 0.071 cm^2 and 0.083 cm^2 for GCE and GNs/GCE according to Randles-Sevcik equation. Clearly, the modification of GNs enhances the real electrode area of GCE, likely due to the increased surface roughness.

3.2. Enhancement effects of GNs/GCE

The electrochemical behavior of 10-HCPT in 0.1 M pH 4.0 acetate buffer solution on GCE and GNs/GCE were compared using differential pulse voltammetry (DPV), and the results were shown in Fig. 5. In the

Download English Version:

<https://daneshyari.com/en/article/6661785>

Download Persian Version:

<https://daneshyari.com/article/6661785>

[Daneshyari.com](https://daneshyari.com)