Electrochimica Acta 187 (2016) 433–441

Contents lists available at ScienceDirect

Electrochimica Acta

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

A sensitive electrochemiluminescence folic acid sensor based on a 3D graphene/CdSeTe/Ru(bpy)$_3^{2+}$-doped silica nanocomposite modified electrode

Xiaoyu Li, Xuecai Tan*, Jun Yan, Qi Hu, Jiawen Wu, Hui Zhang, Xiao Chen

School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Guangxi Key Laboratory of Chemistry and Engineering of Forest Products, Key Laboratory of Guangxi Colleges and Universities for Food Safety and Pharmaceutical Analytical Chemistry, Nanning 530008, China

ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form 17 October 2015
Accepted 15 November 2015
Available online 1 December 2015

Keywords:
electrochemiluminescence sensor
3D grapheme
CdSeTe quantum dots
Ru(bpy)$_3^{2+}$-doped silica nanoparticle
folic acid

ABSTRACT

A rapid, facile, sensitive electrochemiluminescence sensor was fabricated based on a 3D graphene/CdSeTe/Ru(bpy)$_3^{2+}$-doped silica nanocomposite modified electrode for the detection of folic acid (FA). 3D graphene which has the ability to enhance the intensity of electrochemiluminescence (ECL) was synthesized by a one-pot hydrothermal method. Then CdSeTe served as amplification elements were successively labeled on the layer of 3D graphene. In addition, per Ru(bpy)$_3^{2+}$-doped silica nanoparticle encapsulated a great deal of Ru(bpy)$_3^{2+}$, the ECL intensity has been further greatly enhanced. Importantly, the ECL signal on the 3D graphene/CdSeTe/Ru(bpy)$_3^{2+}$-doped silica nanocomposite modified electrode was amplified by FA. The optimum detecting conditions were established by single-factor analysis and response surface multivariate optimization methodologies. Under the optimum conditions, the ECL intensity was well-proportional to logarithmic FA concentration range from 1.0×10^{-11} M to 1.0×10^{-6} M with the detect limit as low as 3.6×10^{-12} M. In application to detect FA in drugs, the recoveries range from 95.0% to 97.5%, which indicates this sensor having potential application in folic acid analysis in real samples.

1. Introduction

Electrochemiluminescence (ECL) is chemiluminescence triggered by electrochemical reaction, which expresses speedy, excellent sensitivity, wide linear range, low detection limit and good controllability [1]. Because of the advantages of ECL, it has been widely used in food and drug safety, environmental monitoring, and bioanalysis. Tris (2,2'-bipyridyl) ruthenium(II) (Ru(bpy)$_3^{2+}$), a stable and efficient chemiluminescent reagent, has caused widespread attention because of it high ECL efficiency, good electrochemical stability and wide linear range. In consideration of the consumption and waste of Ru(bpy)$_3^{2+}$ in the solution-phase ECL, considerable efforts have been made to immobilized Ru(bpy)$_3^{2+}$ on the electrode surface to construct a cost-effective, sensitive and regenerable sensor [2]. Doping SiO_2 nanoparticles (NPs) has become a popular method for obtaining cost-saving, brilliant, stable, biocompatible solid-state ECL sensor. Because Ru(bpy)$_3^{2+}$-doped silica nanoparticles (RuSiNPs) not only immobilize Ru(bpy)$_3^{2+}$ firmly because of the strong electrostatic interaction between Ru(bpy)$_3^{2+}$ and silica matrix, but also reserve the original electrochemical and luminescent properties of Ru(bpy)$_3^{2+}$ [3–5].

However, because of the intrinsic characteristics of RuSiNPs, this immobilize way might cause the lack of conductivity, nanoparticales were added to improve the electroconductibility and sensitivty of the sensor. Graphene, a massless Dirac fermion system with high electron mobility, holds great promise for constructing electrochemical materials due to its high surface area, rapid conductive rate and excellent environment stability [6–8]. Considering to practical applications in devices, it is necessary to require assembly of two dimensional (2D) graphene sheets into three dimensional(3D) morphology [9,10]. 3D graphene is 2D graphene in the distinct 3D plicated structure with large surface area. On the one hand, the excellent intrinsic properties have been reserved, but on the other the 3D structure has more wrinkles and ripples, which provide easier access of analyte and electrolyte, more active sites for the decoration of other materials [11–14]. The numerous advantages such as high conductivity, great mechanical strength and large specific surface made 3D grahene a great promise for environment, energy, sensing and bioanalysis [15]. What is more, it is well known that the combination of quantum dots (QDs) with carbonaceous materials can significantly improve ECL property and biocompatibility. QDs which have size tunable

* Corresponding author. Tel.: +86 771 3267015.
E-mail address: gxunxctan@126.com (X. Tan).

http://dx.doi.org/10.1016/j.electacta.2015.11.082
0013-4686/

physical properties, low cost and good luminescent properties, has been widely used to fabricate sensors for detecting immunoglobulin [16], cholesterol [17], antibodies [18] and so on. Among a lot of QDs, the high quantum efficiency of CdSeTe made it ideal luminophore, and the combination of CdSeTe with other nanomaterials can also improve luminescence performance [19,20]. Therefore, the 3D graphene and the CdSeTe were desiged integrated to further improve the sensitivity of the sensor.

Folic acid (FA), N-[4-[[(2-amino-1, 4-dihydro-4-oxo-6-pteridiny) methyl] amino] benzoyl]-l-glutamic acid, is a well-known water-soluble part of vitamin B-complex which found in vegetables, fresh fruit, yolk and liver. It is essential for the growing and differentiation of cells [21]. What is more, FA is a routine medicine for pregnant women and a treatment for preventing megaloblastic anemia [22]. FA deficiency may cause mental devolution, neural tube defects, congenital anomalies of spine and brain, foetal development defects and heart attack. Therefore, various methods such as fluorimetry [23], spectrophotometry [24], liquid chromatography [25–27], flow injection chemiluminometry [28], chemiluminescence analysis [29–31] and electroanalytical techniques [32–34] have been applied to FA analysis. However, the abovementioned techniques have certain disadvantages such as being time-consuming, laborious, tedious and requiring expensive and large facilities. Therefore, it is significant to develop a simple, efficient and highly sensitive method for the analysis of FA.

Herein, this study aims at the construction of an accurate, simple and effective ECL sensor for the determination of FA in practical samples. Combining the high $Ru(bpy)_3^{2+}$ loading capacity of $Ru(bpy)_3^{2+}$-doped silica nanoparticles, effectively luminescent properties of QDs and excellent electro transfer ability of 3D graphene which makes it a highly sensitive solid-state ECL sensor for FA detection. This sensor has been used for FA detection in the actual drugs with satisfactory results.

2. Experimental

2.1. Chemicals and materials

Tris (2,2'-bipyridyl) dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2{\cdot}6H_2O$) and nafion (5wt%) were purchased from Sigma-Ardrich (Madrid, Spain). Tetraethyl orthosilicate (TEOS) and hexyl Alchol were purchased from Damas-beta (Shanghai, China). Triton X-100 (TX-100) was supplied by Biosharp (Hefei, China). Folic acid, cadmium chloride hydrate ($CdCl_2{\cdot}2.5\ H_2O$), and sodium borohydride (NaBH4) were all purchased from Kelong Chemical Reagent Company (Chengdu, China). Selenium powder (Se) was obtained from Kemiou Chemical Reagent Co.,Ltd (Tianjin, China). Tellurium power (Te) and 3-Mercaptopropionic acid (MPA) were purchased from Xiya Chemical Reagent Company (Chengdu, China). Grapite powder was offered by Beilian chemical company (Tianjin, China). Double distilled water (DDW, 18.2 $M\Omega\,cm^{-1}$) used throughout all experiments were further purified by the Millipore system. All supplementary chemicals are analytical grade and without extra purification.

2.2. Apparatus

The ECL singles were obtained by using a MPI-B model electrochemliuminescence analyzer (Xi'an Remax Electronic Science & Technology Co., Ltd., China) with the voltage of 800 V provided by the photomultipliertube (PMT). The CHI 660E electrochemical workstation (Chenhua Apparatus Co., Ltd., China) was employed for electrochemical studies. All the experiments were carried out with a three-electrode system including a glassy carbon electrode (GCE, 3 mm diameter) as a working electrode, a platinum pole electrode as an auxiliary and an Ag/AgCl electrode as a reference. UV-visible spectrum was obtained by a UV–visible spectrophotometer (Ls55, Perkin Elmer Instruments, America) and fluorescence spectrum by a fluorescence spectrophotometer (Agilent Cary 60, Agilent Technology, America). Field emission scanning electron microscope (SEM) (SUPPRA 55 sapphire, German Carl ZESS, German) and transmission electron microscope (TEM) (Tecnai G20, FEI, America) were applied for observing the exterior and interior morphologies of synthetic materials.

2.3. Procedures

2.3.1. Synthesis of 3D graphene

First, graphene oxide (GO) was synthesized according to the modified Hummers' method [35]. In brief, graphite powder (3.0 g), concentrated sulfuric acid (70 ml) and sodium nitrate (1.5 g) were mixed under stirring and the mixture was cooled using an ice bath. Then $KMnO_4$ (9.0 g) was slowly added to the reaction vessel and the temperature was maintained below 20 °C. Next, the reaction system was transferred to a water bath at 35–40 °C for about 0.5 h to form a thick paste. After that, water(140 ml) was added and reaction temperature was increased to 98 °C, at which point the reaction mixture was stirred for about 40 min. Successively, more water (70 ml) was added to terminate reaction. Then, H_2O_2 was slowly added to the mixture until the color of solution from brown to yellow. The yellow GO dispersion was filtered and washed by 1:10 HCl aqueous solution and water repeatedly to remove the remaining impurities. Finally, 3D graphene can be easily prepared by heating homogeneous GO aqueous dispersion (2 mg/ml) sealed in a Teflon-lined autoclave at 180 °C for 12 h [36]. In order to improve the dispersion stability of 3D graphene, appropriate Nafion solution (5 wt%) was added in the 3D graphene aqueous solution.

2.3.2. Synthesis of CdSeTe

The synthetic procedure of CdSeTe was based on the reported method [37]. $CdCl_2$ aqueous solution (5 mM, 50 ml) was mixed with MPA (37 μL), and regulated the pH to 12.2 by NaOH solution (0.1 M), then bubbled with highly pure N_2 for 30 min. NaHTe and NaHSe was freshly prepared by adding Te and Se powder to $NaHB_4$ aqueous solution separately. Then premixed solution of NaHTe and NaHSe added into the $CdCl_2$ solution with the molar ratio of Cd/Te/Se was 25/1/0.2. The mixture was stirred under ice bath with N_2 protection. After stirring for 1 h, the bright orange CdSeTe solution was acquired.

2.3.3. Synthesis of $Ru(bpy)_3^{2+}$-doped silica nanoparticles

$Ru(bpy)_3^{2+}$-doped silica nanoparticles were synthesized by the microemulsion method according to the previous report with appropriate modifications [38]. Generally speaking, TX-100 (1.77 mL), cyclohexane (7.5 mL), 1-hexanol (1.8 mL), water (340 μL) and $Ru(bpy)_3^{2+}$ aqueous solution (0.1 M, 80 μL) were mixed. In the presence of TEOS (100 μL), the reaction was initiated by adding $NH_3{\cdot}H_2O$ and completed after stirring 24 h. The generated precipitate was isolated with acetone, followed by centrifuging and washing with ethanol and water for several times. Finally, 8 mg $Ru(bpy)_3^{2+}$-doped silica nanoparticles were dispersed in 1 mL ethanol and mixed with Nafion (0.4 wt%) in the volume ratio of 1:1. After that, the mixture RuSiNPs stored in 4 °C refrigerator for further experiments.

2.3.4. Preparation of the modified electrode

The modified electrodes were fabricated by the following steps (Scheme 1). Firstly, the GCE was polished with 0.3, 0.05 mm alumina powder sequentially to obtain a mirror like surface. And then it was washed with distilled water and successively sonicated in distilled water, ethanol, respectively, then dried at room