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Electrodeposition one-step preparation of silver nanoparticles/carbon dots/reduced graphene oxide ternary dendritic nanocomposites for sensitive detection of doxorubicin

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ABSTRACT

In this article, ternary nanocomposites consisting of silver nanoparticles (AgNPs), carbon dots (CDs) and reduced graphene oxide (rGO) were newly synthesized *via* a one-step electrodeposition method. Upon cyclic voltammetry (CV) scanning, ternary nanocomposites with dendritic structure were facilely generated and electrodeposited on glass carbon electrode (GCE), without involving toxic solvents and reducing agents. The nanocomposites were characterized by means of scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) techniques. Characterization results revealed that the nanocomposites showed dendritic structures and dispersible narrow-sized nanoparticles were deposited on the matrix of rGO, mainly attributed to the use of $Ag(NH_3)_2OH$ instead of $Ag(NO_3)_2$ as the precursor. The nanocomposites deposited on GCE had superior electrocatalytic activities for doxorubicin (DOX) reduction. The electrocatalytic activities were strongly affected by $Ag(NH_3)_2OH$ concentration. The best electrocatalytic activities could be obtained when the volume ratio of CDs-GO (3:1, v/v) to $Ag(NH_3)_2OH$ was fixed to 1:1. The peak current intensities of AgNPs-CDs-rGO/GCE sensing system linearly increased upon the increase of coexisting DOX concentration in the range from 1.0×10^{-8} to 2.5×10^{-6} M ($R^2 = 0.9956$), together with a limit of detection as low as 2 nM.

1. Introduction

Doxorubicin (DOX), as one of important anthracycline antibiotics, has been extensively applied in the treatment of several categories of cancers, such as tissue and osteogenic sarcoma, soft breast and thyroid, lymphoblastic leukemia, and so forth [1,2]. As established, the use of DOX at a high dose is closely associated with the therapy of cardiomyopathies and myelo-suppression [3]. Most serious effects of DOX on human body can result in life-threatening heart damage [4]. Owing to above characteristics of DOX, it is meaningful to develop a simple and efficient analytical method for DOX detection. Especially, the detection of DOX in biomedical samples is significant, which potentially serves as a reliable indicator for the monitoring of human body health factors, diagnose and therapy of several relative cancers [5].

So far, many conventional analytical technologies have been developed in succession and used for qualitative or quantitative DOX detection, including high performance liquid chromatography [6–17], liquid chromatography and capillary electrophoresis [18,19], UV–vis absorption spectrum [20], fluorescence emission spectrum [21–23], electrochemical analysis [24–28], etc. Conventional instrument analytical technologies for the determination of DOX generally have some limitations, such as complicated preconcentration, time-consuming operation and low sensitivity. By contrast, electrochemical analysis methods especially electrochemical sensors have unique advantages and received tremendous attention, which are mainly due to the superior electroactivity of quinone and hydroxiquinone groups of DOX. The most obvious advantages of electrochemical sensors include simplicity, low cost and high sensitivity, and the electrochemical sensor of DOX has been reported in previous researches [29–40].

In the process of electrochemical sensing, the electron transfer rate becomes very slow when unmodified electrodes are used for DOX sensing. On this account, some modified electrodes have been exploited towards the electrochemical sensing of DOX. For instance, recently nano-TiO_2/Nafion composite film modified

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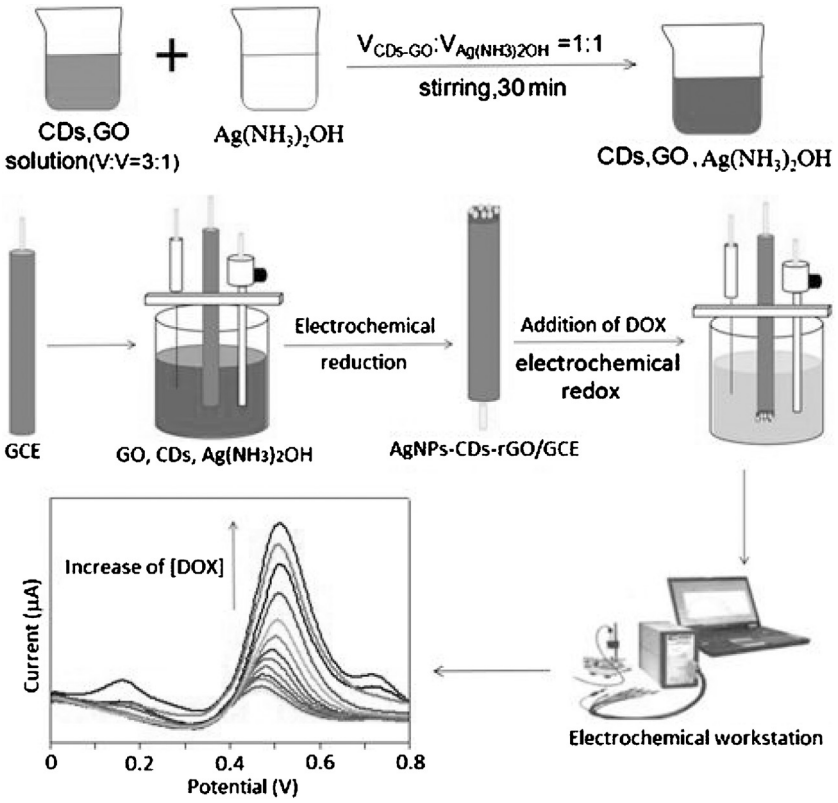

Scheme 1. Schematic illustration of the preparation and application of AgNPs-CDs-rGO/GCE sensing system.

electrodes [41], and β-cyclodextrin-graphene hybrid nanosheets modified GCE [42] have been developed. The use of modified electrodes was expected to realize the improvement of electron transfer rate and sensitivity in the sensing process of DOX. In order to further improve electron transfer rate and sensitivity for electrochemical sensing applications, the selection of carbon nanomaterials or noble metal nanoparticles (NPs) seems very necessary. When electrode interface was modified with different substances containing carbon nanomaterials (graphene oxide, multi-walled carbon nanotube or carbon dots) or noble metal NPs (gold or silver NPs), larger active surface area and superior electron transfer efficiency on the modified electrode interface could be obtained rationally. In earlier reports, carbon nanomaterials modified electrodes such as the composite film (containing magnetic graphene oxide (GO) grafted with chlorosulfonic acid, Fe_3O_4-GO-SO_3H) modified electrode [43], graphene quantum dots modified electrode [44], and oxidized multi-walled carbon nanotube (MWCNT) modified electrode [45] were constructed to improve the electrochemical sensing efficiency of DOX.

In previous reports, the electrochemical sensing of DOX has been developed based on modified electrodes. As summarized in Supporting Information (Table S1), the interface of electrodes was generally modified with different substances containing single species of carbon nanomaterials or noble NPs. However, when the substances that were used to modify electrode interface involved the combination of carbon nanomaterials and noble NPs, the synergist effect from different species of electroactive nanomaterials could be achieved reasonably [45–51]. Potentially, combination of electroactive nanomaterials on electrode interface could lead to the improvement of conductivity, the increase of surface areas and active sites, and so dramatically accelerate electron transfer rate. When substances containing multiple electroactive nanomaterials were used to modify electrode interface to construct sensing system, multiple-amplifying electrochemical signal response would be obtained and suitable for highly sensitive detection of analytes.

Herein, ternary nanocomposites consisting of silver nanoparticles (AgNPs), carbon dots (CDs) and reduced graphene oxide (rGO) were firstly prepared *via* a one-step electrodeposition method. Through cyclic voltammetry (CV) scanning, ternary nanocomposites with dendritic structure were facilely produced and electrodeposited on glass carbon electrode (GCE), without the use of toxic solvents and reducing agents. Since the nanocomposites-modified GCE sensing system contained multiple electroactive nanomaterials, its multiple-amplifying electrochemical signal responses on electroactive targets (*e.g.* DOX) would be generated. Hence, the sensing system could be further developed for highly sensitive determination of targets. According to the unique characteristics of this as-synthesized one-step electrodeposition method for preparation of novel dendritic ternary nanocomposites (*e.g.*, simplicity, low cost, non-toxicity and high efficiency), this as-synthesized method would be promising. In this work, the ternary nanocomposites were deposited on GCE to construct sensing system, which possessed superior electrocatalytic activities for DOX reduction. Highly sensitive electrochemical signal responses to DOX could be detected. Owing to the almost linear relationship between the peak current intensities and coexisting DOX concentration [DOX], this as-synthesized AgNPs-CDs-rGO/GCE sensing system had a significant potential for highly sensitive detection of DOX (Scheme 1).

2. Experimental section

2.1. Chemicals and reagents

DOX was purchased from Shanghai Sangon Biotech Co. Ltd. China. $AgNO_3$ (99.7%), ammonia solution (25 wt%), H_2SO_4 (98%), HNO_3 (98%) and other chemicals with the analytical grade were