



N-hydroxysuccinimide-mediated photoelectrooxidation of aliphatic alcohols based on cadmium telluride nanoparticles decorated graphene nanosheets



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ABSTRACT

A simple nonenzymatic electrochemical protocol is proposed for the oxidation of aliphatic alcohols using formed N-hydroxysuccinimide (NHS) radical cation on the graphene nanosheets/L-cysteine/cadmium telluride quantum dot (QD) nanocomposite (GNs/Cys/CdTe) modified glassy carbon (GC) electrode. At first, graphene oxide (GO) is chemically synthesized from graphite after which Cys is covalently functionalized to GO through formation of amide bonds between carboxylic acid groups of GO and amine groups of Cys. The resulting GNs/Cys is used as a capping agent to synthesize CdTe QD nanoparticles. After the characterization of the as-made nanocomposite which confirmed the successful attachment of CdTe nanoparticles to the GNs, the ability of the GNs/Cys/CdTe modified GC electrode toward the nonenzymatic ethanol electrooxidation is examined in the presence of NHS as an effective mediating system. Our results revealed that the proposed system possess a good activity to NHS electrooxidation and subsequently, ethanol oxidation. Moreover, the GNs/Cys/CdTe modified electrode displayed a significant photoelectrocatalytic activity toward the ethanol oxidation upon illumination by visible light. The photoactive GNs/Cys/CdTe nanohybrid presented here showing favorable photoelectrochemical features for nonenzymatic aliphatic alcohols oxidation may hold great promise to the development of electrochemical sensors and biofuel cells.

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1. Introduction

Nowadays, the interesting chemical and physical properties of graphene are wellknown for scientists in many fields of science. Graphene has been the major focus of recent research to exploit an sp^2 hybrid carbon network in applications such as capacitors, cell images, sensors, devices, drug delivery, and solar cell [1–6]. In addition, graphene is an ideal material for electrochemistry [7–11] because of its very large 2-D electrical conductivity (550 S cm^{-1}) [6], large surface area ($2630\text{ m}^2\text{ g}^{-1}$) [1] and a large number of electrochemically favorable edge carbons per mass of graphene which facilitate electron transfer between molecules to an electrode substrate with a low overpotential. It has most of the advantageous properties of carbon nanotubes (such as homogeneous distribution of electrochemically active sites on a nanometer scale) without carrying the most challenging element of carbon nanotube materials – that is, residual metallic impurities

[7]. Moreover, graphene bears advantages in terms of its easy preparation from inexpensive graphite [12].

The chemical functionalization of graphene and graphene oxide is an interesting method to make engineering on their band gap and other physicochemical properties for using graphene nanosheets in different applications. From various characterization data, it is found that graphene oxide has abundant structural defects, mainly hydroxyl ($-\text{OH}$) and epoxy ($-\text{O}-$) groups on the basal plane and carboxylic acid groups ($-\text{COOH}$) at the edge sites which are advantageous to attach to other functional groups for electrochemical applications [7,13,14]. It is also evident that electrical conductivity of graphene oxide due to converting some sp^2 carbon atoms to sp^3 or absorbing H_2O molecules by oxygen containing functionalities in the sheet structures is substantially lower than graphene [15–17]. Therefore, the physical and chemical properties of graphene oxide can be improved by removing oxygen groups from graphene oxide by means of chemical reduction with reducing agents [15,18], electrochemical reduction [19] and thermal mediated reduction [20], or adding other chemical functionalities to graphene oxide [15,21,22].

Besides the applications of graphene oxide (GO) and reduced graphene oxide (r-GO), integration of nanoparticles (NPs) and graphene into nanocomposites has recently become a hot topic

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of research due to their new and/or enhanced functionalities that cannot be achieved by either component alone, and therefore holds great promise for a wide variety of applications in catalysis, optoelectronic materials, surface enhanced Raman Scattering, biomedical fields, and so on [23–28]. Among them are nanocomposites of quantum dots (QDs) and graphene oxide (GO) (QDs/GO) which show significantly improved properties in electrocatalysis, supercapacitors, high performance lithium ion batteries, solar cells, etc. [29–31]. QDs are semiconductor nanoparticles that due to their unique photo-physical and electronic properties, offer some advantages in many aspects, such as high emission quantum yield, good chemical and photostability, and size-controlled luminescence properties, which give rise to their potential use in a variety of fields including light conversion, preparation of sensors and biosensors, biological imaging and clinical diagnosis [32,33]. Thus far, although a number of researchers have proposed methods for the preparation of QDs/GO finding applications in various optical fields [29–31] as much as we know, the electrochemical sensing applications of these nanocomposites are rarely reported.

The oxidation of aliphatic alcohols such as methanol and ethanol is particularly important in biological analysis and fuel cell applications, because they can be derived from biological materials. Thus, direct electrooxidation of these compounds on platinum nanoparticles or other transition metals as catalysts has been widely considered in recent years [34–37]. However, most of these techniques are costly, besides, the electrooxidation processes need to be performed in highly basic or acidic media.

Herein, we report on a facile method to synthesize GNs/Cys/CdTe nanohybrid using 2-amino-3-mercaptopropanoic acid, L-cysteine as capping agent. L-Cysteine is of utmost interest of scholars due to its multifunctional groups (–SH, –NH₂, and –COO[–]), which can be used for taking amid formation reaction with –NH₂ terminal groups [38], and conjugate to metallic ions or other functional groups [39–42]. Moreover, L-cysteine has been recently reported as an environment-friendly agent for chemical reduction of graphene oxide [43]. At first, we functionalized GO covalently with Cys through amide bond formation between carboxylic acid functionalities at GO edges and amine groups of Cys. After that, the functionalized GNs/Cys was used as a capping agent to synthesize CdTe QDs. After the as-made nanocomposite well-characterized using SEM, TEM, FTIR, fluorescence and UV–vis techniques, the ability of the GNs/Cys/CdTe nanocomposite modified glassy carbon electrode was explored toward the nonenzymatic electrooxidation activity of aliphatic alcohols using N-hydroxysuccinimide (NHS) as an electron transfer mediator. The modified electrode showed an excellent electrocatalytic property toward the NHS cation-radical formation and subsequently, the oxidation of aliphatic alcohols. A significant photoelectrocatalytic activity of the prepared nanocomposite was also observed under visible light irradiation.

2. Materials and methods

2.1. Reagents and equipments

Tellurium powder (>99% purity), cadmium chloride, L-cysteine (Cys), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), N-hydroxysuccinimide (NHS) and graphite powder were purchased from Merck. Transmission electron microscopy (TEM) was performed with a Philips microscope (EM 208, Tokyo, Japan) operating at 100 kV. Scanning electron microscopy (SEM) images were obtained with a Vega-Tescan electron microscope. UV–vis and fluorescence spectra were recorded on a SPECTROD 250-analytikjena spectrophotometer (Germany) and a EL01044753-Varian spectrophotometer (USA), respectively. The FTIR spectra were achieved

by a Vector-22 Bruker spectrophotometer (Switzerland). The electrochemical experiments were performed on an AUTOLAB modular electrochemical system (ECO Chemie, Utrecht, The Netherlands) equipped with a PGSTAT 101 module and driven by GPES software (ECO Chemie) in conjunction with a conventional three-electrode system and a personal computer for data storage and processing. A modified glassy carbon electrode employed as the working electrode and a platinum wire as the counter electrode. All potentials were referred to an Ag/AgCl/KCl (3 M) electrode. PBS solutions (0.1 M) with different pHs were prepared with sodium dihydrogen phosphate (NaH₂PO₄) and disodium hydrogen phosphate (Na₂HPO₄) and used as supporting electrolyte throughout electrochemical studies. All other chemicals not mentioned here were of analytical reagent grade and were used as received. Double distilled water was used throughout.

2.2. Preparation of graphene oxide

The graphene oxide was prepared with modified Hummers and Offeman method [44], as mentioned in the previous work [9]. Briefly, 1 g graphite powder was put into mixture of 3 ml concentrated HNO₃ and 70 ml H₂SO₄ in an ice bath. Then, 3 g KMnO₄ was gradually added. The mixture was stirred for 2 h and then diluted with deionized (DI) water. After that, 5% H₂O₂ was added into the solution until the color of the mixture changed to brilliant yellow, indicating fully oxidized graphite. The as-obtained graphite oxide slurry was re-dispersed in DI water and then exfoliated to generate graphene oxide nanosheets by ultrasonication. Then, the mixture was filtered and washed with diluted HCl solution to remove metal ions. Finally, the product was washed with DI water to remove the acid.

2.3. Preparation of GNs/Cys

The functionalization of graphene oxide with Cys was done such as previously reported method by Yang et al. which has been reported for functionalization of graphene with diaminopropane [45]. Also in this process, graphene oxide may be reduced by L-cysteine according to proposed mechanism by Chen et al. [43]. Briefly, the graphene oxide powder (0.05 g) was dispersed in 12.5 ml dimethyl formamide (DMF) for 2 h and then EDC (0.287 g) and NHS (0.171 g) was added to the mixture at 0–5 °C and it was stirred for 2 h. After that, 0.5 g (4 mmol) of L-cysteine was added and the mixture was stirred for 24 h at room temperature. The modified graphene nanosheets with L-cysteine centrifuged in water and ethanol 5 times and then dried at 35–40 °C (Scheme 1).

2.4. Decoration of GNs with CdTe nanoparticles

The obtained CdTe capped by GNs/Cys was synthesized according to the previously reported procedures with some modifications [46–48]. Briefly, 0.32 g CdCl₂ was dissolved in 20 ml DI water, then obtained GNs/Cys was added to solution and stirred for 20 min under argon bubbling. In the other flask, 0.16 g tellurium powder and 0.4 g sodium borohydride (NaBH₄) was added to 15 ml 0.1 M phosphate buffered solution (pH > 9) under argon atmosphere at 3–5 °C and stirred for 5 min. The obtained purple solution was added to the first flask containing mixture of GNs/Cys–Cd²⁺ and stirred for 30 min at 80–90 °C. The synthesized nanocomposite precipitated by centrifugation and washed with water and ethanol 5 times to remove any unreacted ingredients and then dried in room temperature. The L-cysteine capped CdTe for control experiments was synthesized according to the above mentioned method except that L-cysteine was used instead of GNs/Cys.

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