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Photoelectrocatalytic enzymeless detection of glucose at reduced graphene oxide/CdS nanocomposite decorated with finny ball CoOx nanostructures

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ABSTRACT

In this study, the photoelectrocatalytic oxidation of glucose on reduced graphene oxide/cadmium sulfide composite (rGO/CdS) decorated with finny ball nanostructures (FBN_S) of cobalt oxide (CoOx) was reported. Potential cycling was used for growth of CoOx FBN_S on the surface of rGO/CdS nanocomposite. The morphology and electrochemical properties of ternary rGO/CdS/CoOx hybrid is characterized by scanning electron microscopy, cyclic voltammetry, amperometry and electrochemical impedance spectroscopy techniques. The glassy carbon electrode (GCE) modified with proposed nanocomposite, showed excellent electrocatalytic activity toward glucose oxidation and under visible light irradiation, the photoelectrocatalytic current response of the proposed system significantly enhanced. The application of GCE/rGO/CdS/CoOx as an electrochemical sensor for glucose measurement was investigated. The detection limit and sensitivity of the fabricated sensor toward glucose detection were 0.87 and 0.40 μM, 0.1204 and 0.2242 μA/μM in dark and under visible light irradiation, respectively, at linear range up to 1000 μM. Furthermore, the proposed sensor showed good stability, fast response time and excellent anti-interference ability toward various easily oxidized compounds such as ascorbic acid, dopamine, uric acid and carbohydrate such as lactose and fructose. Finally, the proposed sensor is successfully applied to the detection of glucose in human serum as a real sample. The modified electrode, can be used for develop of photoelectrochemical enzyme free glucose sensor, bioanode and related biodevices.

1. Introduction

Glucose plays an important role in different fields such as biotechnology, clinical diagnostics, food and pharmaceutical industries [1]. Furthermore, substantial evidence has demonstrated that the glucose concentration increases in blood serum of diabetic patients [2]. On the other hand, the presence of glucose in urine can reflect serious kidney diseases [3]. So, the development of efficient glucose sensors or biosensors with high sensitivity, excellent selectivity and fast response has gained special focus in analytical chemistry. Electrochemical glucose sensor has aroused enormous interest because of its remarkable features such as high sensitivity and selectivity, simple instrumentation, and easy operation. During last decade, the various nanomaterials have been widely used in development of non-enzymatic or enzymatic glucose sensors or biosensors. However, because enzymes are expensive and their activity is significantly affected by many factors (such as temperature, pH, ionic strength, etc.), the nonenzymatic glucose sensor has become a hot research topic in recent years. So, development of enzyme-free methods for detection of glucose by using new nanomaterials or nanocomposites with improved sensitivity still remains a challenge.

Cobalt oxide nanomaterials have been widely used recently in many research areas such as energy storage systems, electrochromic thin films, magnetoresistive devices and non-homogeneous electrocatalysts due to their biocompatibility, good conductivity, high electrocatalytic activity and low cost and toxicity [4–7]. Different cobalt oxide morphologies such as nanoparticles, nanofibers, nanowires, etc. were synthesized by various methods such as hydrothermal, chemical bath deposition, electrochemical deposition and spray pyrolysis [8–14]. Among different methods that have been used for synthesis of cobalt oxide nanostructures, electrodeposition method has been proved as an extremely versatile and simple method, due to ambient condition for synthesis, controllable morphology, good adhesion of nanostructures on the electrode surface and using of simple chemicals.

Graphene as an atomic-layer-thick two-dimensional material is a good supporting substrate for active species because of its good conductivity, high chemical stability and large surface area (2600 $m^2\ g^{-1}$), low cost, easy adsorption of catalyst nanoparticles, which can be used to construct a modified electrode with highly efficient electrocatalytic activity [15–20]. So, graphene provides a good support material for

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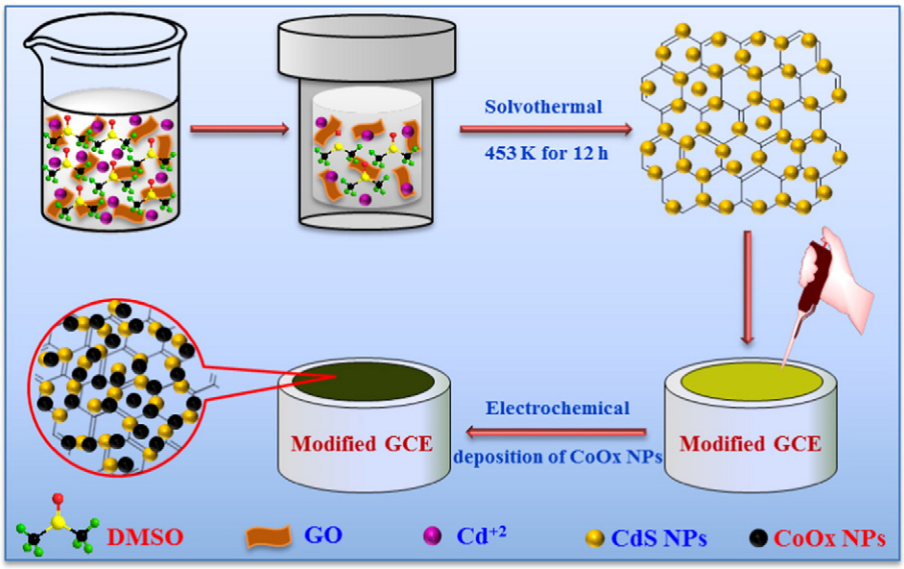

Scheme 1. Schematic flowchart for synthesis of rGO/CdS NPs/CoOx FBNs.

decoration of many nanostructures such as quantum dots [21–23] and metal oxides [24]. Quantum dots (QDs) with unique properties and astonishing characteristics such as high fluorescence yield, photostability, photoelectrochemical activity and luminescence features [25,26] have been widely used in fields of biosensing, in-vivo imaging, labeling, and nanoelectronics [27,28]. Among the various semiconductors, cadmium sulfide (CdS) with a band gap of 2.52 eV at room temperature, has attracted considerable interest in photocatalysis [29–36], photoelectrochemical process [37,38], light emitting diodes [39], water splitting [40], solar cells [41–43], photosynthesis [44] and photo-fuel-cells, (PFCs) [45]. Based on its band gap value, CdS nanomaterials can absorb blue and green wavelengths [33,46]. Through coupling CdS quantum dots with graphene, an excellent synergetic combination can be achieved by retarding the electron-hole recombination process and thus, the photocurrent can be dramatically enhanced; so, under visible light irradiation which leads to the generation of hole-electron pairs, electrons can transfer to graphene and holes are able to oxidize organic compounds such as ethanol and glucose. Furthermore, we anticipated that the construction of ternary nanocomposites containing of rGO/CdS decorated with electrocatalysts should have shown

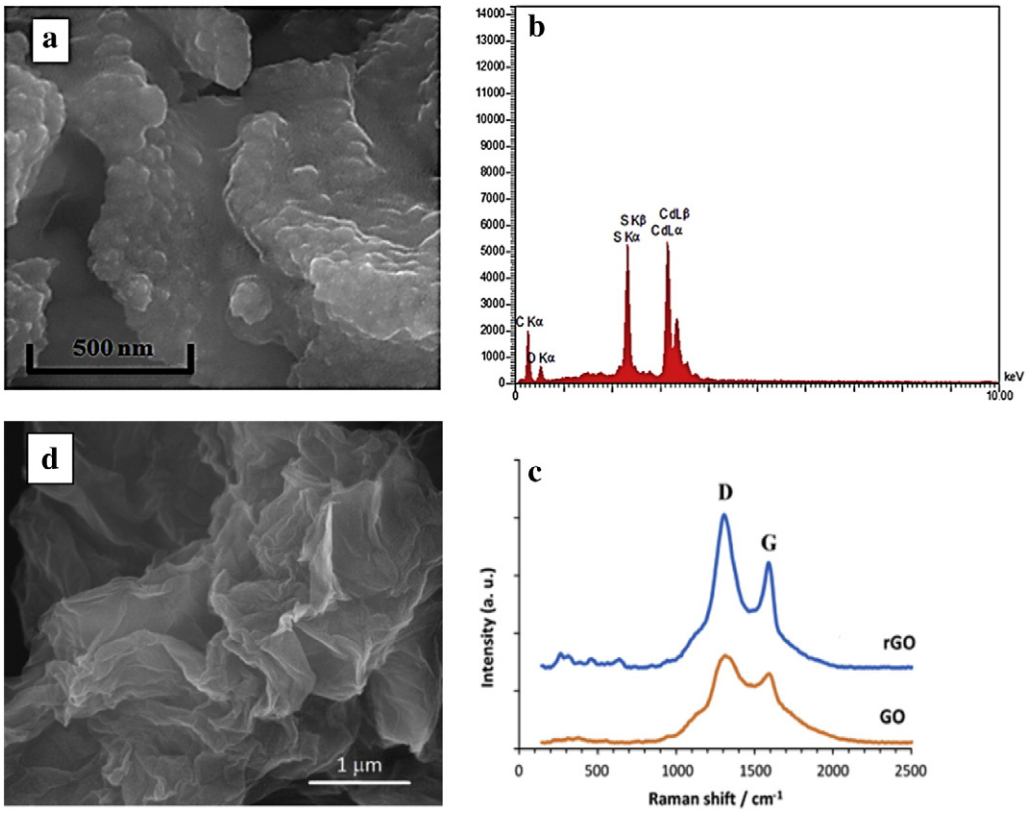

Fig. 1. (a)SEM image of rGO/CdS nanocomposite and rGO (d), (b) EDX of the rGO/CdS nanocomposite, and (c) Raman spectra of GO and -rGO.