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A novel bismuth oxychloride-graphene hybrid nanosheets based non-enzymatic photoelectrochemical glucose sensing platform for high performances

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ABSTRACT

A novel non-enzymatic photoelectrochemical (PEC) glucose sensor was first constructed based on the unique two-dimensional (2D) bismuth oxychloride-graphene nanohybrid sheets (BiOCl-G NHS). We have utilized a facile hydrothermal approach for the preparation of BiOCl-G NHS. Results from cyclic voltammetric and differential pulse voltammetric measurements revealed that the BiOCl-G NHS electrode is capable of generating photocurrent for glucose when its surface is irradiated with a light source (wavelength=365 nm). The photocurrents produced for the presence of glucose at the bias potential of +0.50 V showed a linear dependence on glucose concentration in the range between 0.5 and 10 mM and had a detection limit of 0.22 mM. The PEC detection of glucose at BiOCl-G NHS was not influenced by the presence of other common interfering species. The glucose levels, as determined by the BiOCl-G NHS sensor, agreed well with those obtained by the commercial glucometers. This novel non-enzymatic PEC glucose sensor exhibited good performances, such as a wider concentration range (500 μM-10 mM), high sensitivity (1.878 μM mM^{-1} cm^{-2} (500 μM–2 mM) and 127.2 μM mM^{-1} cm^{-2} (2 mM–10 mM)), good selectivity, reproducibility (RSD=2.4%) and applicability to real sample (human serum).

1. Introduction

Glucose, a six-carbon monosaccharide, is the monomeric form of polysaccharides (or carbohydrates) which belong to one of the four major classes of biomolecules (proteins, nucleic acids, carbohydrate, and lipids). The ability to quantitatively determine the glucose concentration is critically significant in many facets of biological research and medical specialty. This is because glucose is the major source of energy in organisms and an important metabolic intermediate. It is important to note that glucose is one of the most widely tested analyte in clinical diagnostics because its level in blood guides for the diagnosis and treatment of diabetes (Chen et al., 2013). Glucose biosensors have contributed significantly to the clinical monitoring of glucose (Zhu et al., 2014). Among the several techniques established for the determination of glucose, enzyme-based electrochemical biosensors offer good selectivity and sensitivity (Wang, 2008). However, enzyme-based glucose electrochemical sensors have several drawbacks such as complicated enzyme immobilization procedures, instability, restricted operational conditions and poor reproducibility (El Khatib and Hameed, 2011; Wang 2008; Wang et al., 2016). To circumvent these problems, non-enzymatic (enzyme free) glucose biosensors are increasingly developed based on the direct oxidation of glucose (Tarlani et al., 2015; Li et al., 2015a; Gao et al., 2016; Yang et al., 2016; Dong et al., 2012; Tehrani and Ab Ghani, 2012; Gopalan et al., 2016; Wang et al., 2016). Recently, photoelectrochemical (PEC) sensing strategy has attracted much attention because of the capability to detect biomolecules through the photocurrent generated from the oxidation/reduction of the biomolecules (Pardo-Yissar et \al., 2003; Dai et al., 2014; Zhao et al., 2014, 2012a; Li et al., 2015b, Zhao et al., 2015). PEC based sensor provides high sensitivity due to the reduced background signal as the consequence of the involvement of two relatively independent processes; light as the signal generating source and current as the detection output signal (Wenjuan et al., 2013; Li et al., 2012; Wu et al., 2014). PEC detection strategy has therefore been conveniently extended to exploit the photocurrent/photo potential changes brought about by the interactions between the photoactive material and biomolecule using various photoactive materials and strategies (Xiong and Zhao, 2012; Xia et al., 2015; Li et al., 2014a; Komathi et al., 2016).

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Few of the PEC biosensors have been reported for glucose sensing. Reduced graphene oxide/cadmium sulfide (CdS) quantum dots (QDs)/poly-nile blue nanocomposite has been immobilized with glucose dehydrogenase and used for PEC glucose detection (Jafari et al., 2014). In an another report, cadmium selenide (CdSe)/zinc sulphite (ZnS) hybrid QDs were utilized for the PEC sensing of glucose (Schubert et al., 2009). Another enzyme based PEG glucose biosensor was fabricated using glucose oxidase incorporated ZnO nanoparticles. A disposable PEC glucose sensing electrode has been fabricated with ZnS-CdS hybrid QDs and immobilization of glucose dehydrogenase into them (Ertek et al., 2016). Visible light induced PEC glucose sensing platform was developed using near-IR QDs (Wang et al., 2012). These reports on PEC glucose sensors either involve enzyme immobilization in the sensor fabrication or involving oxygen dependency for glucose sensing and hence associated with the problems of the electrochemical biosensors. As compared to enzyme based PEC sensing, non-enzymatic PEC sensing offers higher stability and durability (Wang et al., 2014). To our knowledge, few reports are available on non-enzymatic PEC biosensors for glucose detection based on; core-shell that includes TiC-C nano flower (Zhang et al., 2013), TiO_2-B nanorods (Zhang et al., 2015a), TiO_2 decorated Co_3O_3 a circular nanotube arrays (Gao et al., 2016), CdS decorated graphene(G) (Zhang et al., 2014a) and Cu_2O_2-TiO_2 (Devadoss et al., 2014a) sensing materials. These non-enzymatic PEC glucose sensors exhibited limited glucose concentration detection ranges (<5 mM). Undeniably, photoconversion efficiency plays a crucial role in PEC detection, which in turn depends on the nature of photoactive materials and their nanostructured forms. To expand the PEC biosensing platform and to achieve high performances for non-enzymatic PEC glucose biosensing, herein, we design and demonstrate the first application of the new bismuth oxychloride (BiOCl) – graphene nanohybrid sheets (NHS) for high-performance non-enzymatic PEC glucose biosensor.

The layered BiOXs (X=Cl, Br, I) have shown excellent photocatalytic performances for a variety of applications and received greater attention by researchers for developing new photocatalytic materials (Guan et al., 2013; Ding et al., 2012; Kim et al., 2014). Among them, BiOCl is considered as one of the most promising material, and its photocatalytic performances are comparable or even superior to that of anatase (Cheng et al., 2014; Jiang et al., 2012; Jing et al., 2016). BiOCl possesses a layered structure consisting of $[Bi_2O_2]^{2+}$ slabs separated by double slabs of chain atoms. The excellent photocatalytic activity of BiOCl is attributed to the effective separation ability for charge carriers as a result of the layered structure and also due to the induced dipole generated within its molecular structure (Zhang et al., 2012). Few strategies have been tried on improving the photocatalytic performances of BiOCl that include control of the nanomorphology of BiOCl (Li et al., 2015c; Ye et al., 2011; Jiang et al., 2013; Gnayem and Sasson, 2013).

Lately, research on nanostructuring of photocatalytic materials has experienced huge growth over the past decade (Chen et al., 2015; Xie, et al., 2016; Kumar et al., 2016). The unique features of two-dimensional nanosheets (NS), such as specific surface area, unexpected optical and electronic properties make them suited for improving the photocatalytic performances (Ida et al., 2014; Zhu et al., 2013). BiOCl NS exhibited high photocatalytic activity, and excellent charge separation capabilities as a result of layered crystal structure and inbuilt electric field vertical to the layer direction (Ye et al., 2011; Zhang et al., 2014b; Li et al., 2014b). Few of heterojunction photocatalytic nanomaterials or nanohybrids (NHs) showed enhanced photosensitivities for PEC biosensors (Devadoss et al., 2014b; Zhao et al., 2015). It has been demonstrated that the unique properties of graphene (G), such as atomic thickness, large sheet area, and excellent bonding properties, provided scope for developing G-included NHS as matrices for improving electron transport characteristics photocatalytic systems (Stankovich et al., 2006). The G included NHS facilitate spatial separation of photocarriers [holes (h^+) and electron (e^-)] and enhanced photocurrent generation. Similarly, G-based NHS, such as TiO_2-G and CdS/G, exhibited enhanced photocatalytic performances (Han et al., 2015; Xiang et al., 2012). It is highly envisioned that the photoactivity of Bi-containing photocatalysts, such as BiOCl, can be enhanced through the formation of heterojunctions with G (Gao et al., 2014; Zhang et al., 2015b).

Herein, we developed the novel and unique BiOCl-G NHS 'for the first time' through judiciously combined the individual advantages of G and BiOCl along with the special characteristic of 2D NS. We have utilized a facile hydrothermal approach for the preparation of BiOCl-G NHS. The preparation of 2D BiOCl-G NHS involved three important stages; i) electrostatic adsorption of bismuth precursor onto carboxylic acid functionalized G (G-COOH), ii) generation of BiOCl nanocrystal as nuclei on the surface of G sheets and iii) growth of BiOCl NS over the G sheets to result in layered stacks of BiOCl and G nanosheets (Scheme 1. A). We further exploited BiOCl-G NHS for the fabrication of a high-performance PEC non-enzymatic glucose sensor. We demonstrated through our results that BiOCl-G NHS sensor exhibited excellent performances such as a wider glucose detection concentration range (0.5–10 mM), high sensitivity, and excellent selectivity for non-enzymatic PEC glucose sensing as compared to the sensor performances of other reported PEC non-enzymatic glucose sensors (Table 1). Besides, we have successfully established the applicability of BiOCl-G NHS for glucose testing in human serum samples.

2. Experimental

2.1. Chemicals

Bismuth(III) nitrate ($Bi(NO_3)_3$), polyvinylpyrrolidone (PVP) (MW $<40{,}000$),, Nafion (5 wt%) and human serum (from human male AB plasma, USA origin, sterile-filtered) were obtained from Sigma-Aldrich, S. Korea. G nanoplatelet sheets were obtained from E Nano TEC (Korea). Sodium chloride, methanol, isopropyl alcohol and phosphate buffer solution (PBS, pH=7) were purchased from DUKSAN, S. Korea.

2.2. Preparation of BiOCl-G NHS

Initially, G sheets were functionalized with carboxylic acid groups to obtain G-COOH (Lee et al., 2015). The preparation of BiOCl-G NHS was carried out as follows: A solution of $Bi(NO_3)_3$ (1 mM) was prepared in 20 mL of deionized water. Then, approximately 0.2 g of PVP and 20 mg of G-COOH were added and stirred to form a homogeneous result. After that, 10 mL of 1 mM NaCl solution was added dropwise to the above mixture and pH of the solution was adjusted to 6.0 by the addition of 1.0 M NaOH. The precursor mixture was then transferred into a Teflon line coated stainless steel autoclave and heated to 180 °C for 4 h. After gradually cooling to room temperature, the black precipitate was collected, rinsed with distilled water and then with absolute ethanol. The obtained precipitate, BiOCl-G NHS was dried at 60 °C for 24 h. For comparability purposes, nanocomposites of pristine G with BiOCl (BiOCl-G NC) and pristine BiOCl were prepared by using pristine G sheets and in the absence of G-COOH, respectively.

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