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Enhanced non-enzymatic glucose biosensor of ZnO nanowires via decorated Pt nanoparticles and illuminated with UV/green light emitting diodes

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ABSTRACT

ZnO nanowires were synthesized hydrothermally on a glass substrate, and then decorated with Pt nanoparticles to fabricate the working electrode for a non-enzymatic glucose biosensor. The Pt nanoparticles, acting as a catalyst, enhanced the biosensor's glucose sensitivity 10-fold in comparison with the initial ZnO nanowires electrode. Under the UV and green LEDs, the respective wavelengths of which were 367 nm and 539 nm, the sensing current of the Pt-nanoparticle-decorated ZnO nanowires biosensors increased ~4 times. These biosensors under UV and green illumination feature superior sensitivity (UV: 928.1 $\mu A\,cm^{-2}\,mM^{-1}$, green: 123.0 $\mu A\,cm^{-2}\,mM^{-1}$) than those reported in previous non-enzymatic glucose sensing studies. The performance of these non-enzymatic glucose-sensing biosensors was enhanced by reducing the Schottky barrier and localizing the surface plasmonic resonance effect under such illumination.

1. Introduction

The glucose biosensor is one of the most common and extensively investigated sensing technologies, and has been applied in clinical analysis, biological detection, environmental monitoring, medical science and food processing industry [1–3]. Such wide-ranging application and study have resulted in glucose sensors currently having a more than 85% market-share of the biomedical-sensing industry [4]. One of the main factors motivating this focus on glucose sensing is diabetes mellitus, which is the fastest-growing global public-health concern.

It is well-known that the normal concentration range of blood glucose is 110 ± 25 mg/dl (around 4.7 mM–7.5 mM), and that some diabetics may have much higher values (>20 mM) [4]. To measure blood glucose levels, most glucose biosensors require the use of enzymes to improve sensitivity and selectivity [5–7]. Among these enzymes, glucose oxidase (GOD) has attracted much research attention due to its high sensing performance and linear detection range [5–7]. High isoelectric point (IEP) materials act as positively charged templates for the immobilization of low IEP molecules, such as enzymes, DNA and proteins. One such high-IEP material is ZnO (IEP ~9.5), which is suitable for immobilizing GOD (IEP ~4.3) [7]. Be that as it may, the immobilized-enzyme activity of glucose sensors has drawbacks, namely, the reproducibility and long-time stability are inadequate. Moreover, GOD is susceptible to various effects stemming from the experimental conditions, such as temperature, humidity, pH, ionic detergents and toxic chemicals. Consequently, a highly-sensitive and selective non-enzymatic glucose biosensor that can be manufactured cost-effectively is required.

ZnO 1-D nanostructures (NSs) have been widely used and applied in various fields, such as solar cells [8], gas sensors [9], humidity sensors [10], photodetectors [11], light-emitting diodes [12], piezoelectric nanogenerators [13], field-effect transistors [14], field emitters [15] and biosensors [5–7]. One such structure is ZnO nanowires (NWs), which have a large surface-to-volume ratio that is critical for the electrode template for a non-enzymatic glucose biosensor [16]. In recent years, noble metals (Au, Pt, Pd) [17–19], transition metals (Ni, Cu, Ag, Co) [20–23] and binary composite

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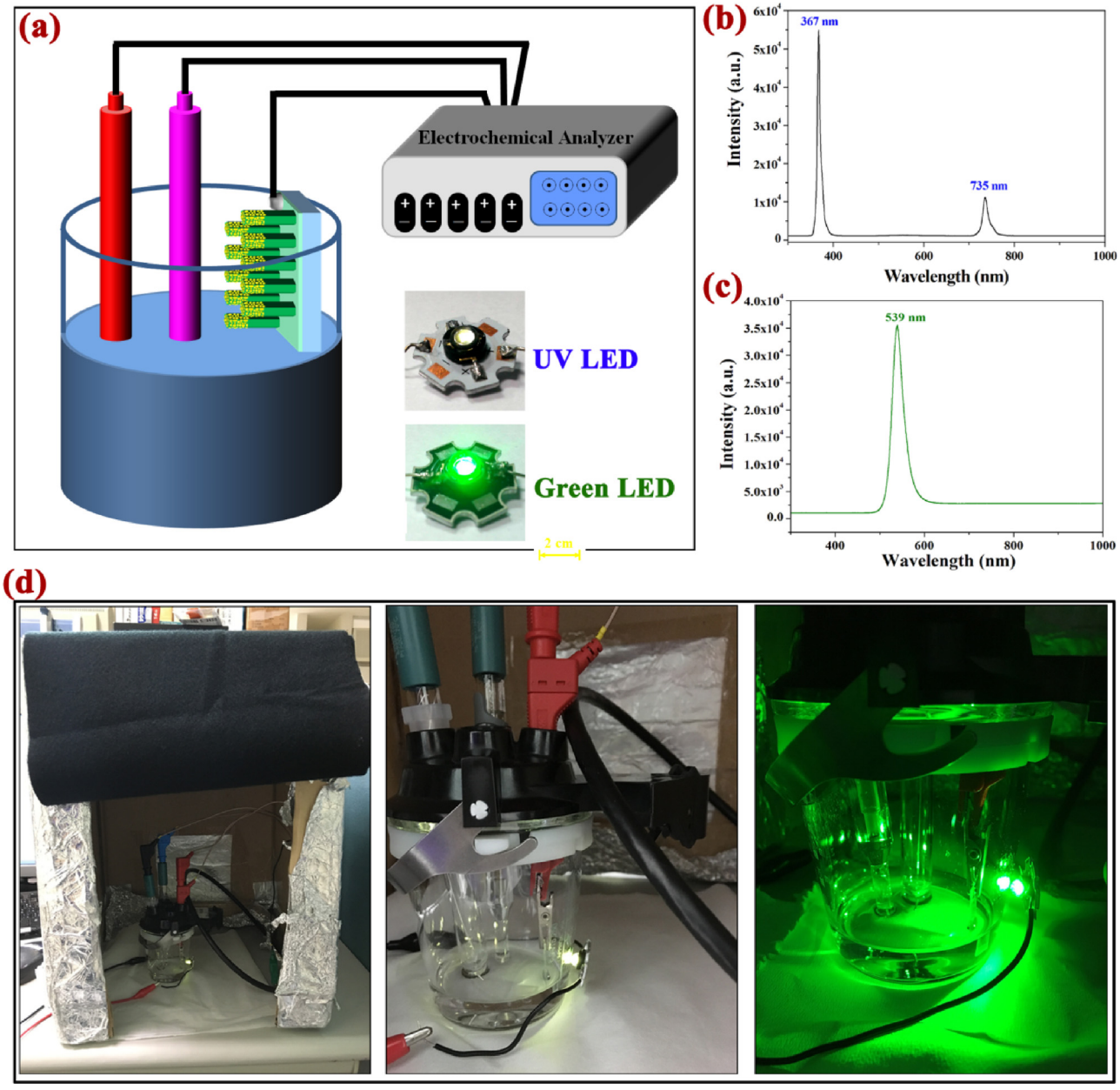

Fig. 1. (a) Schematic illustration of the non-enzymatic glucose sensing measurement system. EL curve of (b) UV and (c) green LED. (d) The photographs of the setup used for glucose sensing under LED illumination.

alloy metals (Pt-Au, Pt-Pb, Ni-Cu) [24–26] have been applied as catalysts for non-enzymatic glucose sensing. However, uric acid or ascorbic acid is mixed with the measured electroactive components, which affects the performance of the non-enzymatic glucose sensor. Further, the surface of noble metals easily absorbs intermediates and chloride poisoning, while transition metals lack electrode poisoning of carbohydrate oxidation, resulting in decreased sensing sensitivity. Nevertheless, noble metals currently exhibit superior sensing performance and measurement reproducibility compared with transition metals. Accordingly, noble metal nanoparticles (NPs) have attracted much attention recently since they can absorb visible light, thereby producing the surface plasmon resonance (SPR) phenomenon. This study investigated the non-enzymatic glucose sensing properties of ZnO NWs and Pt-NP-decorated ZnO NWs. These glucose biosensors were fabricated on glass substrates, the glucose sensing characteristics of which were enhanced by UV and green LED illumination. Details of the Pt-NP-decorated ZnO NWs growth and the properties of the fabricated non-enzymatic glucose biosensors and their sensing characteristics are discussed.

2. Experimental

Supplementary Fig. S1 schematically depicts the fabrication processing steps of the proposed Pt/ZnO NW/glass electrode. This experiment used a light-transmitting and chemically stable glass substrate (Corning® EAGLE XG). The glass substrate was first rinsed 2 or 3 times with acetone/deionized water (DI); then, a ZnO seed layer (thickness = 100 nm) was deposited on the glass substrate by radio frequency (RF) magnetron sputtering. ZnO NWs were subsequently synthesized on the ZnO seed layer by the hydrothermal method. This process involved placing the sample substrates in a 0.06 M hexamethylenetetramine ($C_6H_{12}N_4$) and 0.06 M zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) solution, and then heating at 95 °C