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# A novel label-free photoelectrochemical sensor based on N,S-GQDs and CdS co-sensitized hierarchical $Zn_2SnO_4$ cube for detection of cardiac troponin I

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ABSTRACT

A novel label-free photoelectrochemical (PEC) sensor based on graphene quantum dots doped with nitrogen and sulfur (N,S-GQDs) and CdS co-sensitized hierarchical $Zn_2SnO_4$ cube was fabricated to detect cardiac troponin I (cTnI). The unique hierarchical $Zn_2SnO_4$ cube was synthesized successfully by the solvothermal method, which has a large specific surface to load functional materials. N,S-GQDs nanoparticles were assembled to the surface of cubic $Zn_2SnO_4$ coated ITO electrode, which efficiently accelerated the electronic transition and improved photo-to-current conversion efficiency. Then, CdS nanoparticles further were modified by in-situ growth method to form $Zn_2SnO_4$/N,S-GQDs/CdS composite with prominent photocurrent, which was 30 times that of the $Zn_2SnO_4$ cube alone. In this work, the specific immune recognition between cTnI antigens and cTnI antibodies (anti-cTnI) reduced the intensity of the photoelectric signal. And the intensity decreased linearly with the logarithm of cTnI concentration range from 0.001 ng/mL to 50 ng/mL with a detection limit of 0.3 pg/mL. With high sensitivity, excellent selectivity, good stability and reproducibility, the fabricated PEC sensor showed promising applications in the sensor, clinical diagnosis of myocardial infarction and PEC analysis.

## 1. Introduction

Recently, photoelectrochemical (PEC) analysis, a dynamically promising technique, has gained more and more attention (Fan et al., 2017a, 2017b; Liu et al., 2016; Wang et al., 2009b; Yang et al., 2004). PEC sensor has become one of the most potential detection tools in the fields of life sciences, environmental science, agricultural science and food safety detection (Fan et al., 2016; Wu et al., 2007; Xia et al., 2015; Yang et al., 2006), owe to its distinct advantages, such as rapid test, desirable sensitivity, low background signal, low cost, simple devices and so on (Freeman et al., 2013; Li et al., 2016; Wang et al., 2009a; Zhu et al., 2000).

As an important semiconductor material with excellent properties, zinc stannate ($Zn_2SnO_4$), has been extensively applied in solar cells, gas sensors, photocatalysts and lithium ions battery (Lin et al., 2009; Rong et al., 2006; Tan et al., 2007). Currently, various $Zn_2SnO_4$ nanostructures have been synthesized such as irregular particle morphology, nanorods, nanowires and well-defined polyhedra (Bai and Zhou, 2014; Lana-Villarreal et al., 2007; Zhao et al., 2007). The cubic $Zn_2SnO_4$ has unique properties, including high specific surface area, low density and better penetration (Yang et al., 2010). However, $Zn_2SnO_4$ was difficult to be efficiently excited in visible-light due to its wide band-gap (Zhao et al., 2016). Therefore, it was necessary to enhance the visible-light activity of $Zn_2SnO_4$ particles. In this study, a new kind of hierarchical $Zn_2SnO_4$ cube was prepared successfully, then N,S-GQDs and CdS with narrow-band gaps were employed to co-sensitize $Zn_2SnO_4$, which accelerated the electronic transition and enhanced the photoelectric properties of $Zn_2SnO_4$.

Graphene quantum dots (GQDs) was a sort of single or few-layer graphenes and have satisfying conductivity, adjustable band gap and unique photoelectric properties (Xia et al., 2017). Thus, they have been used in many fields such as photocatalysis (Roushani et al., 2015), ion detection (Cai et al., 2014), biological imaging (Tan et al., 2015) and electrochemical biosensor (Zhang et al., 2015). The major disadvantage of GQDs based PEC sensor was that the sensitivity and selectivity were limited due to the nonspecificity of GQDs. However, many researches recently have shown that the photoelectric properties of GQDs could be effectively regulated by doping heteroatoms (Cai et al., 2017a, 2017b; Kundu et al., 2017). In particular, doping N and S could effectively modulate their band gap and electronic density to enhance the

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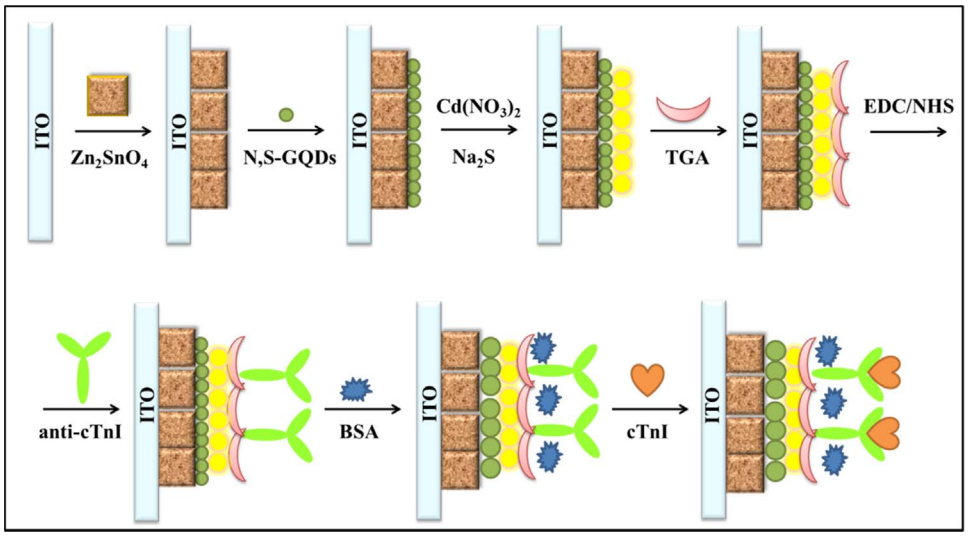


**Fig. 1.** The construction process of photoelectrochemical sensors.

absorption of visible light. Hence, the graphene quantum dots doped with nitrogen and sulfur (N,S-GQDs) were devoted to sensitize $Zn_2SnO_4$, which could efficiently accelerate the electronic transition and improve photo-to-current conversion efficiency. Meanwhile, as an excellent nanomaterial, CdS has narrow band-gap (2.4 eV) and excellent absorption to visible light (Liu et al., 2016). Therefore, CdS nanoparticles were assembled by in-situ growth method to form $Zn_2SnO_4$/N,S-GQDs/CdS composite, which could further enhance the photoelectric signal in visible light.

In our work, a novel label-free PEC sensor based on N,S-GQDs and CdS co-sensitized hierarchical $Zn_2SnO_4$ cube was constructed to detect cardiac troponin I (cTnI). Throughout the ages, heart attacks and cardiovascular diseases have been harmful to the health of human. As one of the subunits of cardiac troponin complexes, cTnI was biochemical markers of myocardial damage (Zhou et al., 2014). At present, cTnI has been increasingly applied in the diagnosis of diseases such as myocardial infarction and stenocardia, owing to its myocardial specificity and excellent sensitivity (Guo et al., 2005; Jo et al., 2017). Hence, cTnI was employed as the testing target to appraise the label-free photoelectrochemical sensor.

## 2. Experimental

### 2.1. Materials and reagents

The cTnI and cTnI antibodies (anti-cTnI) were supplied by Shanghai Linc-Bio Science Co., Ltd. $ZnCl_2$ was obtained from Tianjin Commie Chemical Reagent Co., Ltd. $SnCl_4{\cdot}5H_2O$ and pyrrole were obtained from Shanghai Macklin Biochemical Co., Ltd. Citric acid was obtained from Tianjin Damao Chemical Reagent Factory. Thiourea and $Cd(NO_3)_2$ were obtained from Guoyao Chemical Reagent Co., Ltd. $Na_2S$ and ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, China. Ultrapure water (Milli-Q, Millipore) used in all experiments was deionized to 18.25 MΩ cm. The other materials were provided in Electronic Supporting information (ESI†).

### 2.2. Apparatus

The PEC tests were obtained using a CHI760E electrochemical workstation, which was purchased from Chenhua Instrument Shanghai Co., Ltd, China. Meanwhile, a 100 W LED lamp of white light was used for an irradiation source. The wavelength range of LED lamp (Fig. S1) and other details were shown in ESI†.

### 2.3. Synthesis of hierarchical $Zn_2SnO_4$ cubes

The preparation of $Zn_2SnO_4$ cubes were as follows. Firstly, a certain amount of polypyrrole/N-vacancy graphitic carbon nitride (PPy/g-$C_3N_4$-VN) (the synthesis was shown in EIS†) were added into a mixed solution containing 20 mL ultrapure water and ethanol (1:1) with ultrasound for 0.5 h. Secondly, 1.25 mmol $ZnCl_2$ and 0.625 mmol $SnCl_4{\cdot}5H_2O$ were dissolved in the above solution. Then, the NaOH aqueous solution (5.0 mL, 1.0 mol/L) was added. The obtained solution was transferred into a Teflon-lined autoclave (50 mL) after stirring for 15 min, and then heated at 200 °C for 24 h. Separated using centrifugation and then cleaned three times with ultrapure water, the precipitates were acquired after drying.

### 2.4. Preparation of N, S-GQDs

The N, S-GQDs were synthesized according to previous report (Qu et al., 2013). 2.5 mmol of citric acid and 10.0 mmol of thiourea were added into ultrapure water (12 mL). The above solution was poured into autoclave (50 mL) after stirring for 5 min, and then heated at 160 °C for 8 h. After adding a certain amount of ethanol, the precipitates were separated from the solution with centrifugation (9000 rpm) and then washed three times.

### 2.5. Fabrication of PEC sensor

Before assembled of sensor, ITO slices were cut into 2.5 × 0.8 $cm^2$ pieces with ultrasonic for 30 min in acetone, ethanol and ultrapure water, separately. Under the nitrogen stream, the ITO substrates were dried for the preparation of sensor. Construction procedure of the novel PEC sensor was demonstrated in Fig. 1. Firstly, 4 mg/mL of $Zn_2SnO_4$ aqueous solution was disposed with ultrasonic for 0.5 h. Then, the 10 μL of $Zn_2SnO_4$ suspension was coated onto a ITO electrode. After drying in air, 1 mg/mL N,S-GQDs solution (4 μL) was dropped on the above electrode, followed by drying in air for 0.5 h. After rinsing, 4 μL of Cd $(NO_3)_2$ and $Na_2S$ solution were dropped successively on the $Zn_2SnO_4$/N,S-GQDs electrodes for 0.5 h by in-situ growth method and then washed with ultrapure water. Subsequently, 4 μL of 0.1 mol/L TGA was dropped onto the $Zn_2SnO_4$/N,S-GQDs/CdS electrode for 0.5 h and then washed with ultrapure water. Then, 4 μL of EDC/NHS (0.01 mol/L / 0.002 mol/L) solution was dropped on the $Zn_2SnO_4$/N,S-GQDs/CdS/TGA electrode for 0.5 h to activate -COOH of TGA. After removing the redundant EDC/NHS by washing, 5 μL anti-cTnI was dropped onto the $Zn_2SnO_4$/N,S-GQDs/CdS/TGA/(EDC/NHS) electrode to incubate for 0.5 h and then rinsed to remove the loosely bounded anti-cTnI. After