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π-π nanoassembly of water-soluble metalloporphyrin of ZnTCPP on RGO/AuNPs/CS nanocomposites for photoelectrochemical sensing of hydroquinone

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ABSTRACT

The RGO/AuNPs/CS/ZnTCPP nanocomposites were successfully prepared with reduced graphene oxide (RGO) loaded with Au nanoparticles (AuNPs) existed in chitosan (CS) and water-soluble zinc meso-tetra (4-carboxylphenyl) porphyrin (ZnTCPP) by π-π nanoassembly method and were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), ^{1}H NMR spectra and UV–vis absorption spectroscopy. The most important advantage of the RGO/AuNPs/CS/ZnTCPP nanocomposites was environmentally friendly. Indium tin oxide (ITO) electrode surface was modified with the RGO/AuNPs/CS/ZnTCPP nanocomposites exhibited a good photocurrent response at −0.2 V under whitelight of Xenon lamp illumination. The photocurrent response could be greatly increased by adding hydroquinone (HQ) to the solution. Electrons of ZnTCPP were excited from HOMO to LUMO by irradiating light. The photoexcited electrons injected into the RGO, and then transferred to AuNPs further to the ITO. Addition of HQ resulted in the enhanced photocurrent signal by acting as a sacrificial electron donor; Thereby scavenged the photogenerated holes of the excited ZnTCPP and oxidized to benzoquinone (BQ). Based on the above interaction, detection of HQ was developed by a novel photoelectrochemical (PEC) sensor (S/N = 3) with a linear range from 5 to 300 nmol/L (r = 0.997) and detection limit of 0.5 nmol/L. Proposed biosensor is simple, rapid and this was successfully applied for the quantification HQ in the real sample matrices.

1. Introduction

Porphyrin compounds exhibit attractive optical properties, high absorption coefficient and ultrafast electron injection ability [1–5]. Metalloporphyrins such as copper meso-tetra (4-carboxylphenyl) porphyrin (CuTCPP) and zinc meso-tetra (4-carboxylphenyl) porphyrin (ZnTCPP) are good alternatives for photosensitivity due to good photochemical and photoelectrochemical properties. The best feature of CuTCPP and ZnTCPP is their environmental friendliness and water-solubility. Hence, it is worth paying attention to their photochemical and photoelectrochemical applications.

Graphite oxide (GO) [6] easily takes part in electrochemical reactions by receiving electrons. The GO can be reduced by chemical reaction with reducing agents such as hydrogen sulphide [7], hydrazine [8–12] and sodium borohydride [13], which are either toxic or hazardous. So it is necessary to use an environment-friendly and effective method such as flash reduction [14], vitamin C [15–17],aluminum powder [18],reducing sugar [19,20] and L-cysteine [21] as the environment-friendly reductant to reduce GO for the preparation of RGO. Therefore, we have chosen one of the environment-friendly reducing sugars i.e. CS to reduce GO.

HQ is toxic organic compound, which can be formed when two para hydrogen of benzene is substituted by hydroxyl. HQ is mainly used for anthraquinone dyes, azo dyes, pigment, rubber antioxidant, stabilizers and antioxidants. HQ is often found in industrial wastewaters. HQ accumulation in the body will lead to serious damage of the health, such as headache, dizziness, tinnitus, pale and other symptoms. The oxidation-reduction of HQ and BQ is found in many biological molecules, it

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plays an important role in proton transfer and electron transfer in the body's respiratory chain. There are a lot of analytical methods for the detection of HQ such as high-performance liquid chromatography (HPLC) [22], gas chromatography/mass spectrometry (GC/MS) and chromatography [23,24], flow injection chemiluminescence (FI-CL) strategy [25], photoluminescence (PL) [26], fluorescent spectrometry [27,28] and electrochemical methods [29–35]. Compared with the above mentioned methods, a newly developed photoelectrochemical (PEC) [36–40] detection of biomolecules attracted the attention of the interesting approach in developing analytical method. PEC methods showed an efficient photocurrent response under the light illumination as a detection signal [41–43] and have following advantages: remarkable sensitivity, inherent miniaturization, easy integration and portability. The general principal of PEC methods developed can be generalized as follows: First, the photosensitive materials are irradiated to generate charge carriers, then the added biomolecule [44,45] as an analyte capture the holes by donating electrons, further the biomolecule at relatively lower oxidation potential will undergo oxidation. Herein we report an efficient and environmentally friendly organic optoelectronic functional nanocomposites were constructed with RGO loaded with AuNPs existed in CS and water-soluble ZnTCPP by π-π nanoassembly method. The nanocomposites of RGO/AuNPs/CS/ZnTCPP coated on ITO surface, showed an efficient photocurrent response under Xenon lamp illumination at −0.2 V attributed to the good conductivity of AuNPs, the excellent optical properties of ZnTCPP, the fast electron transfer capability of RGO and the synergistic effect of RGO/AuNPs/CS/ZnTCPP nanocomposites. The photocurrent response was greatly increased after adding HQ to the solution served as a basis for developing the PEC method for HQ quantification. This material provided a novel and facile PEC interface for the detection of HQ in practical samples. Therefore, the PEC sensor also provided the basis for the detection of HQ in the biological samples.

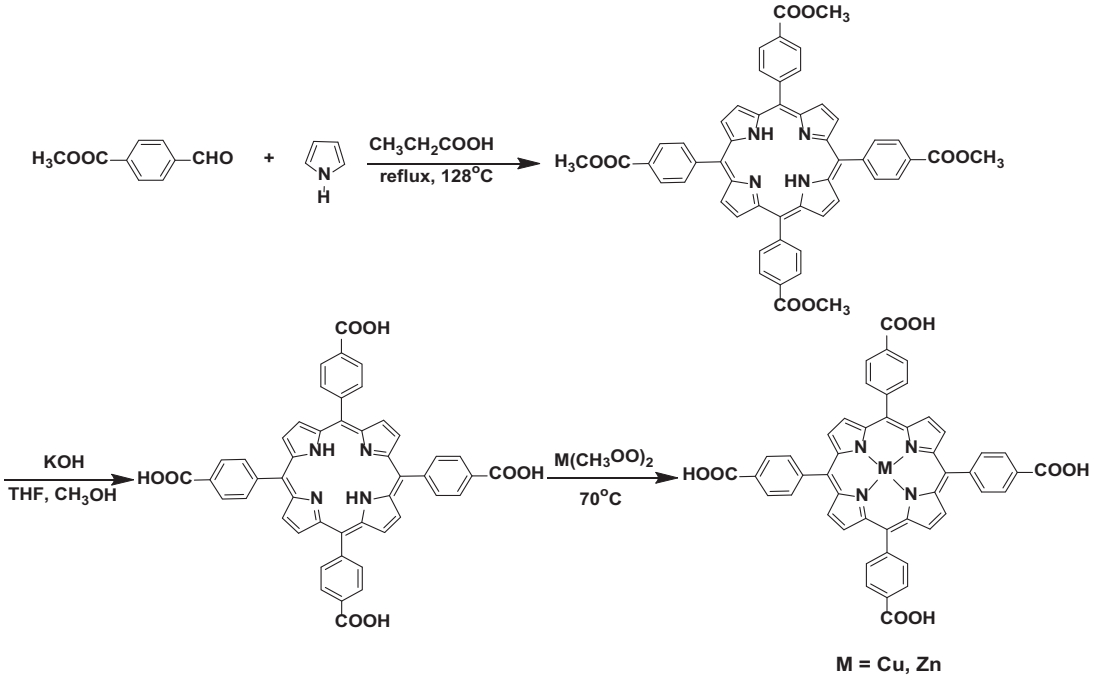
2. Experimental part

2.1. Chemicals and materials

ITO was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, ≥99.0%), disodium hydrogen phosphate (99%) and sodium phosphate monobasic dihydrate (99%) were purchased from Aladdin Industrial Corporation (ShangHai, China). Hydroquinone (HQ, 99%) was purchased from Tianjin Fuchen Reagent Factory. Methyl 4-formylbenzoate (99%) and pyrrole (99%) were purchased from Sahn Chemical Technology Co., Ltd. (ShangHai, China) and Shanghai Macklin Biochemical Co., Ltd. respectively. DuPont nafion solution was purchased from Shanghai Hesen Electric Co., Ltd. Chloroform (≥99.5%), methanol (≥99.5%), petroleum ether and dimethylformamide (DMF, ≥99.5%) were purchased from TianJin Chemical Reagent Factory (Tianjin, China). 0.1 M pH 7.0 phosphate buffer solution (PBS) was always prepared using disodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$) and sodium phosphate monobasic dihydrate ($NaH_2PO_4{\cdot}2H_2O$) with the supporting electrolyte of sodium chloride (NaCl, ≥99.5%). Aqueous solutions were prepared with ultrapure water obtained from Ulupure (Xi'an, 18.25 MΩ·cm, Millipore Corp) and all reagents were of analytical grade.

2.2. Apparatus and instrumentations

Products purification was carried out using flash chromatography with 200–400 mesh silica gel. ^{1}H NMR spectra were recorded on Agilent DD2 400 MHz spectrometers with $CDCl_3$ or DMSO as an internal standard (USA). UV–vis absorption spectra were recorded on a T6 New Century UV Visible Spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). IR spectra were obtained using a Fourier Transform-Infrared spectrophotometer (Digilab FTS 3000, USA). The surface morphology studies were done using scanning electron microscopy (SEM), the TEM images were performed on a JEM-2100 (200 kV) instrument Zeiss Ultra plus (Germany). Electrochemical impedance spectra (EIS) were obtained on a VMP2 Multi-potentiostat (Princeton Applied Research, USA) with the frequencies swept from 10 kHz to 100 mHz. The PEC measurements were done on a home-built PEC system. A 150 W Xe lamp was used as the irradiation source. The detection of photocurrent response was performed on a CHI 900D electrochemical workstation (CH Instruments, Austin, TX). All the electrochemical measurements employed with a three-electrode system at room temperature, the reference electrode is Ag/AgCl, the working



Scheme 1. The reaction steps schematic involved in the synthesis of CuTCPP and ZnTCPP.