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Carbon nitride nanosheets sensitized quantum dots as photocathode for photoelectrochemical biosensing

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ABSTRACT

A highly efficient photocathode, based on graphite-like carbon nitride nanosheets (CNNS) sensitized CdTe quantum dots (QDs), was constructed for photoelectrochemical (PEC) biosensing. Using dissolved oxygen as an electron acceptor, the hybrid photocathode showed a sensitive photocurrent response at −0.2 V bias potential under 405 nm illumination. The CdTe/CNNS hybrid photocathode demonstrates about 100% increase of photocurrent compared to CdTe QDs modified electrode owing to the formation of heterojunction through contact of two semiconductor materials. The improved charge separation efficiency was identified by the extension of electron transit time (τ_d) and electron lifetime (τ_n) in this PEC system. The introduction of Cu^{2+} on the surface of hybrid photocathode could decrease photocurrent via the exciton trapping quenching effect. A sensitive PEC sensor for Cu^{2+} was thus developed with a good linear range from 20 nM to 100 μM and a detection limit of 3.3 nM, and was successfully applied in the detection of Cu^{2+} in human hair samples. The CNNS-sensitized photocathode provides a good alternative for enhancement of the PEC signal transduction and could be widely used in biosensing and clinical diagnosis.

1. Introduction

Photoelectrochemical (PEC) technique, as a novel strategy integrating electrochemistry with photochemistry, has attracted growing attention in various areas such as photovoltaic devices, photocatalysis and bioanalysis [1–3]. The PEC strategy has exhibited a large number of unique advantages such as low bias potential, high sensitivity and low background owing to the separation of excitation signal (light) and detection signal (current) [4]. Various photoelectrochemical biosensors have been designed based on organic materials [5], metal oxide semiconductor [6], quantum dots [7,8], and hybrid materials [9] for the detection of metal ions [10], biomolecules [11], and even cells [12]. For the amplification strategy of PEC, the hybrid materials provide an efficient way to improve the charge separation efficiency due to the synergic effect among their components. In particular, the assembly of dye-sensitized semiconductor is a kind of strategy to amplify PEC signal [13]. Meanwhile, the incorporation of noble metal nanoparticles has been discovered for enhancing the photoconversion efficiency of TiO_2 via surface plasmon resonance [14,15]. Here, in order to further improve the photoelectrochemical conversion efficiency, the carbon nitride nanosheets are introduced to sensitize quantum dots as a photocathode for enhancing the PEC activity.

As a medium band gap and metal-free indirect semiconductor material, graphite-like carbon nitride (g-C_3N_4) simply prepared by polymerization of melamine possesses well electrical and optical properties, and excellent stability [16]. Conventionally, the bulk and mesoporous g-C_3N_4 have been applied in the areas of photoluminescence detection, photocatalysis, photodegradation and photovoltaic device [17–22]. Recently, the exfoliated g-C_3N_4 nanosheets (CNNS) with a band gap of 2.7 eV was found to be chemically reactive and exhibit excellently photocatalytic activity [23–26]. More interestingly, combining CNNS substrates with supported metal nanoparticles could result in controlled access to metal−semiconductor heterojunction and enhanced electron transfer between photoexcited semiconductor and gold nanoparticles [27]. Therefore, it is rational to design a PEC sensing platform by using CNNS as supporter to contact with QDs, in which the injection of electrons might mediate from QDs into CNNS conduction band (CB) by heterojunction, and improve the photoinduced charge separation, thus leading to the enhanced photocurrent for PEC biosensing.

Using copper ions (Cu^{2+}) as a model analyte, the PEC behavior and application potential of this CNNS/CdTe hybrid photocathode was evaluated through the quenching effect of Cu^{2+} on the photocurrent. Copper is an essential trace element for humans, which acts as key element for activities in some important proteins. However, excess Cu^{2+} ions become harmful to humans' body [28]. Therefore, it's necessary to develop reliable and sensitive detection strategy of Cu^{2+}. In this work, a hybrid photocathode was constructed based on CNNS sensitized CdTe QDs as PEC materials via stepwise modified method (Scheme 1). The heterojunction between CNNS and CdTe was formed through stacking and contacting of two semiconductor layers, in

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which the Femi energy of CdTe and CNNS adjust to suit each other, and reach the equilibrium, thus resulting in the high efficiency of charge separation. The CdTe/CNNS hybrid photocathode demonstrates about 100% increase of photocurrent compared to CdTe QDs modified electrode. The introduction of Cu^{2+} onto hybrid photocathode generated exciton-traps, which inhibited the generation of photocurrent [29]. The quenching photocurrent of CdTe/CNNS photocathode is utilized for the sensitive and selective detection of Cu^{2+} with a 4-order linear range and a detection limit low to nanomole, and has been successfully applied in detection of Cu^{2+} in human hair samples, showing the potential applications in practice.

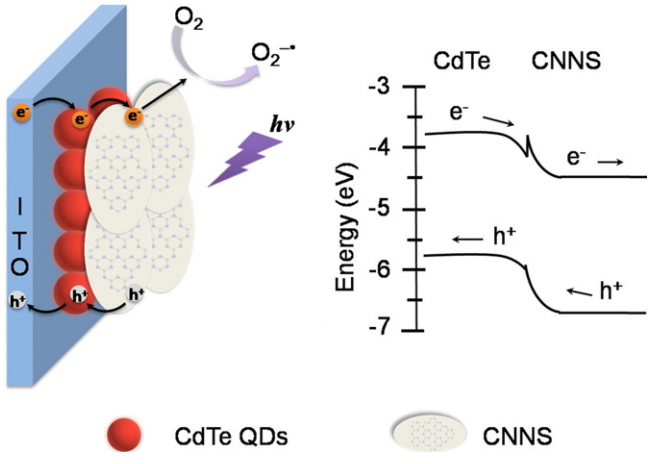
2. Materials and methods

2.1. Materials and reagents

Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) was purchased from Alfa Aesar China Ltd. Tellurium powder and sodium borohydride were purchased from Sinopharm Chemical Reagent Co. Ltd. Cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was purchased from Shanghai Sinpeuo Fine Chemical Co. Ltd. (China). Melamine and 3-mercaptopropionic acid (MPA, ≥99%) were purchased from Sigma–Aldrich (China) and used as supplied. All other chemicals were of analytical grade without further purification. Tris–HCl buffer (10 mM, containing 0.1 M NaCl as supporting electrolyte, pH 7.0) was employed as PEC electrolyte during the photoelectrochemical procedure. Indium tin oxide (ITO) coated glass as the electrode material was purchased from Zhuhai Kaivo Electronic Components Co. Ltd. The ultrapure water (≥18 MΩ, Milli-Q, Millipore) was used throughout the experiment.

2.2. Apparatus

Cyclic voltammetric experiments were performed on a CHI 660D electrochemical workstation (CH Instruments Inc., USA). X-ray photoelectron spectroscopy (XPS) experiments were operated on an ESCALAB 250 spectrometer (Thermo-VG Scientific Co., USA) with an ultrahigh vacuum generator. The UV–Vis absorption spectra were obtained with a UV-3600 UV–Vis–NIR spectrophotometer (Shimadzu Co., Kyoto, Japan). The scanning electron microscopic (SEM) images were obtained by Hitachi S-4800 scanning electron microscope (Japan). The transmission electron micrograph (TEM) was obtained using a JEM-2100 TEM instrument (JEOL, Japan). Photoelectrochemical measurements were detected on a Zahner intensity modulated photo Spectrometer (Zahner Zennium, German) with a LW405 LED light (wavelength at 405 nm) as the light source. All modified processes were performed under 37 °C, and all PEC experiments were carried out at room temperature using a conventional three-electrode system, with a modified ITO electrode, a platinum wire and a saturated calomel electrode as working, counter and reference electrodes, respectively.



Scheme 1. Schematic illustration of the photoelectrochemical mechanism through the formation of heterojunction, and the energy levels of CdTe/CNNS hybrid photocathode.

2.3. Preparation of MPA-CdTe QDs

The synthesis of CdTe QDs was refered to the method reported for thiol-capped CdTe QDs in aqueous phase [30]. First, the Cd precursor solution was prepared by mixing 26 μL of MPA (~6 mM) solution with 50 mL of 2.0 mM $CdCl_2$ solution. After adjusted to pH 9.0 with 1 M NaOH, 0.80 mL of 0.0625 M N_2-saturated NaHTe solution was injected under a N_2 atmosphere and vigorous stirring. The resulting mixture solution was heated to 99–100 °C and refluxed for around 10 h to obtain the MPA-CdTe QDs. Then 900 μL as-prepared QDs solution was mixed with the same amount of isopropanol. The colloidal precipitate was collected by centrifugation (6000 rpm, 5 min) to remove excess reactants, and redispersed with ultrapure water. The CdTe QDs solution was keeped at 4 °C before use.

2.4. Synthesis of C_3N_4 nanosheets

The C_3N_4 nanosheets (CNNS) were synthesized from bulk graphitic-phase carbon nitride (g-C_3N_4) liquid exfoliation route in water according to literature [31]. First, the g-C_3N_4 was synthesized by polymerization of melamine. Then 100 mg bulk g-C_3N_4 powder was added into 100 mL water, and kept ultrasonication for 16 h to dissolve the g-C_3N_4 precipitate. The well-distributed CNNS was centrifuged at 5000 rmp for 20 min to remove the excess bulk g-C_3N_4 and large size of g-C_3N_4 nanoparticles and nanosheets, which offered a pretty uniform size for the construction of PEC sensors. The as-prepared CNNS solution was stored at room temperature.

2.5. Construction and Cu^{2+} detection of PEC sensor

An ITO glass was cut into 4.5 cm × 0.8 cm slices to suit for PEC detection. ITO slices were cleaned by bathing in 0.5 M NaOH and 10% H_2O_2 for 10 min, sequentially. After bathed in acetone for another 30 min, the slices were washed by ultrapure water, and then dried at 37 °C. 10 μL as-prepared CdTe QDs solution was dropped onto the ITO electrode and dried at 37 °C to obtain CdTe QDs modified electrode. Then the CdTe QDs modified electrode was coated by certain concentration CNNS, and dried at 37 °C to construct the CdTe/CNNS photocathode. The hybrid photocathode was used as the working electrode for PEC detection. For Cu^{2+} detection, 10 μL certain concentration Cu^{2+} standard stock solution was dropped onto a working electrode, following dried at room temperature. After constructing the photocathode, the whole assay can be achieved in 15 min.

The time-dependent photocurrent, intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) measurements were performed under light excitation of 405 nm in 10 mM Tris–HCl solution containing 0.1 M NaCl. The intensity of light source was based on specific situation increasing from 10 to 150 W m^{-2}.

The human hair sample was digested with the mixture of 70% (W/W) nitric acid and 60% (W/W) perchloric acid (3:1 V/V). The as-prepared sample solution was diluted and neutralized to pH 6 with 1 M NaOH solution before use. The human hair sample was analyzed in a manner similar to that described above.

3. Results and discussion

3.1. Characterization of CNNS and QDs

The well-distributed CNNS was synthesized by a "green" liquid exfoliation route from bulkg-C_3N_4. The average diameter of CNNS measured from the TEM images is around 100 nm (Fig. 1A). Meanwhile, the UV–