Sensors and Actuators B 254 (2018) 159–165

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Quenching effect of exciton energy transfer from CdS:Mn to Au nanoparticles: A highly efficient photoelectrochemical strategy for microRNA-21 detection

Bing Wang[a,b], Yu-Xiang Dong[a,b], Yu-Ling Wang[a,b], Jun-Tao Cao[a,b,*], Shu-Hui Ma[c], Yan-Ming Liu[a,b,*]

[a] College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China
[b] Institute for Conservation and Utilization of Agro-bioresources in Dabie Mountains, Xinyang Normal University, Xinyang 464000, China
[c] Xinyang Central Hospital, Xinyang 464000, China

ARTICLE INFO

Article history:
Received 22 May 2017
Received in revised form 4 July 2017
Accepted 12 July 2017
Available online 14 July 2017

Keywords:
Energy transfer
CdS:Mn
AuNPs
Photoelectrochemical biosensor
microRNA-21

ABSTRACT

A novel and simple photoelectrochemical (PEC) biosensing method for microRNA-21 (miRNA-21) detection is reported based on energy transfer (ET) between CdS:Mn doped structure (CdS:Mn) and Au nanoparticles (AuNPs). In this protocol, TiO_2-CdS:Mn hybrid structure was used as a sensing platform for hairpin DNA immobilization. In the absence of miRNA-21, the immobilized DNA was in the hairpin form. In this state, the photocurrent of the electrode was greatly depressed, due to the effective ET effect produced by short interparticle distance between CdS:Mn and AuNPs. In the presence of miRNA-21, the hairpin DNA hybridized with miRNA-21 and changed into a more rigid, rodlike double helix, which forced the AuNPs away from the electrode surface, leading to obvious recover of photocurrent because of the vanished damping effect. Integrating the fine PEC performance of TiO_2-CdS:Mn hybrid structure with the significant ET effect between CdS:Mn and AuNPs, the sensitive detection of miRNA-21 was realized in a linear range of 1.0 fM to 10.0 pM with a low detection limit of 0.5 fM. This method might be aussichtsreich for the detection of miRNAs and other biomarkers.

1. Introduction

Photoelectrochemical (PEC), emerged as a newly promising method for the detection of biomarkers, with features such as high sensitivity, low price, simple equipment, and easy miniaturization [1–5]. Moreover, it owns potentially high sensitivity because of the totally separated and different energy forms of the excitation source and detection signal, resulting in the reduced background signals. Hence, PEC holds great promise for the applications in bioassay [6–10]. Since the demand for sensitive detection of biomarkers, it is vital to seek effective and sensitive method to evidently enlarge photoelectric transformation efficiency of the sensor. For this purpose, integrating of the large band gap semiconductors with narrow band gap semiconductive materials to fabricate sensitized structure has provided an effective approach to increase PEC signal [11–13]. Highly ordered TiO_2 nanotube arrays (NTs) as an excellent substrate material, with inherent features such as chemical and physical stability, high surface area, photoelectric activity, biocompatibility etc. [14], have been widely used to construct PEC sensing platform [15–18]. However, TiO_2 can only absorb the UV-light (<387 nm) due to the wide energy band gap (~3.2 eV), causing the insufficient employment of optical energy. The band gap of CdS (~2.4 eV) could match with the suitable absorption range of medium wavelength light (<520 nm). Mn^{2+} is usually drew into CdS to bring CdS:Mn doping structure (CdS:Mn) to significantly inhibit the electron-hole recombination, because the doped Mn^{2+} ion could create a new band gap in the midst of CdS [19–22]. Consequently, coupling TiO_2 with narrow band gap semiconductors to form sensitized structure should be a very useful avenue to promote the electron transfer, depresses electron-hole recombination and improve the photoelectric conversion efficiency.

Gold nanoparticles (AuNPs) with beneficial physical properties have been extensively studied and utilized in bioassay [23–25]. In a PEC system, due to certain spectral overlap, the luminescence resulted from the photoexcitation of the CdS QDs would induce the surface plasmon resonance of the proximal AuNPs, and in turn adjust the exciton states in the CdS QDs through the energy transfer

* Corresponding authors at: College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China.
E-mail addresses: jtcao11@163.com (J.-T. Cao), liuym9518@sina.com (Y.-M. Liu).

http://dx.doi.org/10.1016/j.snb.2017.07.078
0925-4005/

(ET) effect, causing the obvious photocurrent reduction [26–28]. So, is there a similar ET effect between CdS:Mn and AuNPs?

Herein, we developed a PEC biosensing platform for highly sensitive detection of microRNA-21 (miRNA-21) based on the structure of CdS:Mn sensitized TiO_2 NTs (TiO_2-CdS:Mn) and AuNPs. There is a novel ET between CdS:Mn and AuNPs produced signal quenching effect for PEC detection. The detailed fabrication process of the biosensor was investigated. The prepared biosensor was successfully applied for the determination of miRNA-21 in real samples.

2. Experimental

2.1. Chemicals

Hydrofluoric acid (HF), glacial acetic acid, methanol and ethanol were bought from Tianjin Yongda Chemical Reagent Co., Ltd. (China). Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$), manganese acetate ($Mn(Ac)_2{\cdot}4H_2O$) and sodium sulfide ($Na_2S{\cdot}9H_2O$) were purchased from Shanghai Aladdin Reagent Inc. (China). Sodium borohydride ($NaBH_4$) was from Tianjin BASF Chemical Co., Ltd. (China). $HAuCl_4{\cdot}4H_2O$ was from Shanghai Chemical Reagent Co., (China). AuNPs were prepared by $NaBH_4$ reduction of $HAuCl_4$ in aqueous solution [29]. Ascorbic acid (AA), chitosan powder (CS) and glutaraldyhyde (GLD) (50% aqueous solution) were from Sinopharm Chemical Reagent Co., Ltd. (China). Dipotassium hydrogen phosphate ($K_2HPO_4{\cdot}3H_2O$), monosodium phosphate ($NaH_2PO_4{\cdot}2H_2O$) and muriate of potash (KCl) were from Tianjin Kaitong Chemical Reagent Co., Ltd. (China). All other reagents were of analytical grade and used as received. All aqueous solutions were prepared using ultrapure water (Kangning water treatment solution provider, China). PBS was prepared with $K_2HPO_4{\cdot}3H_2O$, $NaH_2PO_4{\cdot}2H_2O$ and KCl, being employed for washing buffer solution and detecting bottom liquid which contained 0.1 M AA. The oligonucleotides used in this work were from Shanghai Sangon Biotech Co., Ltd. (China) with the following sequences: hairpin DNA, 5′-NH_2-TTT TTT CGC AC TAG CTT ATC AGA TCA ACA TCA GTC TGA TAA GCT A-SH-3′; target miRNA-21, UAG CUU AUC AGA CUG AUG UUG A.

2.2. Apparatus

PEC experiments were carried out using a homemade photoelectrochemical system, containing a CHI660E electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) and a PEAC 200A PEC reaction instrument (Tianjin Aidahengsheng Science-Technology Development Co., Ltd., China) with a three-electrode system: a modified TiO_2 NTs electrode with a geometric area of 0.25 cm^2 as the working electrode, a Pt wire as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. Ultraviolet-visible (UV-vis) absorption spectra and fluorescence spectrum were recorded by an UVmini-1240 UV–vis spectrophotometer and the Hitachi F-7000 spectrofluorophotometer (Shimadzu, Kyoto, Japan), respectively. Scanning electron microscopy (SEM) images were got employing a S-4800 (Hitachi, Tokyo, Japan). Transmission electron microscopy (TEM) images were acquired utilizing a Tecnai G2 F20 TEM system (FEI Co., USA).

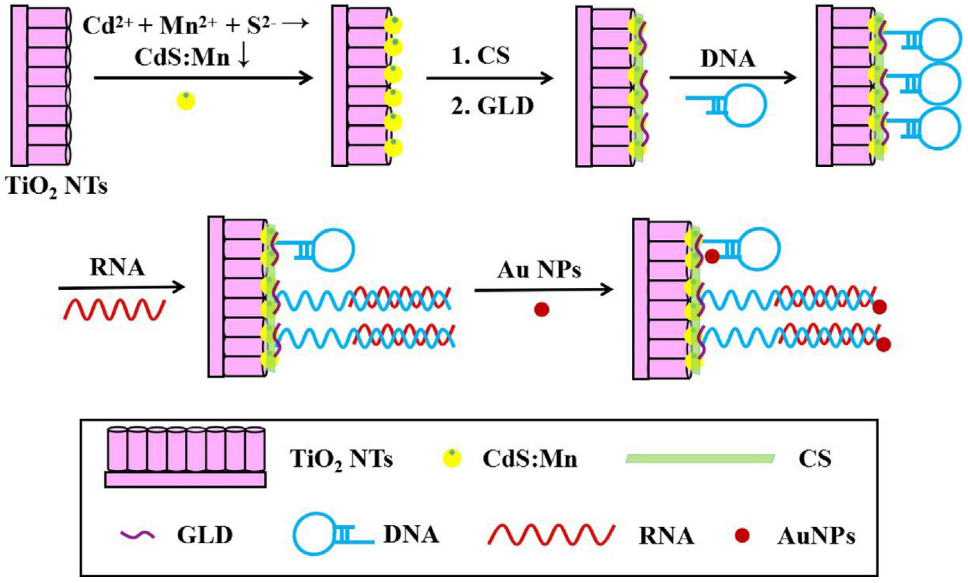
2.3. Fabrication of TiO_2-CdS:Mn electrode

TiO_2 NTs were prepared by the anodic oxidation method according to the literature with minor revision [30]. The modification lies in that the time of anodic oxidation was changed to 50 min.

Next, the TiO_2-CdS:Mn electrode was equipped by the successive ionic layer adsorption and reaction (SILAR) technique with appropriate modifications [31]. Specific for, a prepared TiO_2 NTs was immersed in the methanol solution including 0.1 M $Cd(NO_3)_2$ and 0.08 M $Mn(Ac)_2$ for 2 min, and then dipped into 0.1 M Na_2S ethanol/water mixture (1:1, v/v) for another 2 min, subsequently the film was carefully washed with absolute methanol. This progress was conducted six times, and the TiO_2-CdS:Mn electrode was accomplished.

2.4. Preparation of the biosensor

The detailed procedure was described in Scheme 1. First of all, the TiO_2-CdS:Mn electrode was treated with 20 μL of 2% acetic acid solution containing 0.1 mg/mL CS and dried at 60 °C. Then 20 μL of 2.5% GLD was covered onto the electrode surface and remained for 1 h at room temperature. Next, 20 μL of 0.5 μM hairpin DNA was dropped on the electrode and allowed to incubate at 37 °C for 1 h. For target detection, the electrode was incubated with 20 μL of different concentrations of target miRNA at 37 °C for 1 h. Subsequently the electrode was covered with 20 μL of AuNPs at 4 °C in a humid atmosphere overnight. After each fabrication step, 0.1 M PBS was



Scheme 1. Schematic illustration of the equipment of PEC biosensor for miRNA-21 detection.