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Using carbon nanotubes-gold nanocomposites to quench energy from pinnate titanium dioxide nanorods array for signal-on photoelectrochemical aptasensing

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ABSTRACT

On the basis of the absorption and emission spectra overlap, an enhanced resonance energy transfer caused by excition-plasmon resonance between carbon nanotubes-gold nanoparticles (CNTs-Au) and pinnate titanium dioxide nanorods array (P-TiO_2 NA) was obtained. Three-dimensional single crystalline P-TiO_2 were prepared successfully on fluorine-doped tin oxide conducting glass (FTO glass), and its optical absorption properties and photoelectrochemical (PEC) properties were investigated. With the synergy of CNTs-Au as energy acceptor, it resulted in the enhancement of energy transfer between excited P-TiO_2 NA and CNTs-Au. Upon the novel sandwichlike structure formed via DNA hybridization, the exciton produced in P-TiO_2 NA was annihilated and a damped photocurrent was obtained. With the use of carcinoembryonic antigen (CEA) as a model which bonded to its specific aptamer and destroyed the sandwichlike structure, the energy transfer efficiency was lowered, leading to PEC response augment. Thus a signal-on PEC aptasensor was constructed. Under the optimal conditions, the PEC aptasensor for CEA determination exhibited a linear range from 0.001 to 2.5 ng mL^{-1} with a detection limit of 0.39 pg mL^{-1} and was satisfactory for clinical sample detection. Furthermore, the proposed aptasensor shows satisfying performance, such as easy preparation, rapid detection and so on. Moreover, since different aptamer can specifically bind to different target molecules, the designed strategy has an expansive application for the construction of versatile PEC platforms.

1. Introduction

Resonance energy transfer (RET) is a powerful technique that is caused by the energy transfer between donor and acceptor at the nanometer-scale (Ruland et al., 2011; Lunz et al., 2011). This unique feature of RET enables real-time monitoring the interactions between donor/acceptor and external stimuli (Lai et al., 2013; Freeman et al., 2011). Indeed, this phenomenon has been applied to biosensing contacting with various determination techniques, including fluorescence (Bigall et al., 2012; Hou et al., 2014), surface plasma resonance (SPR) (Hu et al., 2010), and electrochemiluminescence (ECL) (Shan et al., 2010). However, so much effort was commonly put into steering the conduction band (CB) electrons to the electrode or solution-solubilized electron acceptors to give rise to anodic or cathodic photocurrent, the related work focused on photoelectrochemical (PEC) biosensing based on RET was limited (Tu et al., 2012).

As a newly emerged but dynamically developing analysis technique, PEC determination has attracted substantial attention (Gill et al., 2008). In PEC measurement, light utilized to excite the photoactive species and photocurrent is often employed as the detection signal. It is becoming a more and more attractive and promising analytical technique not only because of the complete separation of excitation source (light) and detection signal (photocurrent) but also the low cost compared with conventional optical analytical techniques. At the same time, PEC avoids high overpotential in electrochemistry or ECL measurements. Therefore this paper chooses the PEC determination on the basis of RET.

PEC properties of P-TiO_2 have been extensively investigated since it is photostable, nontoxic, cost-effective, and abundant (Fujishima et al., 1972; Gratzel et al., 2001). At the same time, TiO_2 materials of three-dimensional hierarchical architectures provide a close contact between the donor and acceptor particles that ensure immediate absorption of the emitted light and reduce transmission loss.

Recently, carbon nanotubes (CNTs) has been found to be a promising component on the development of RET biosensors

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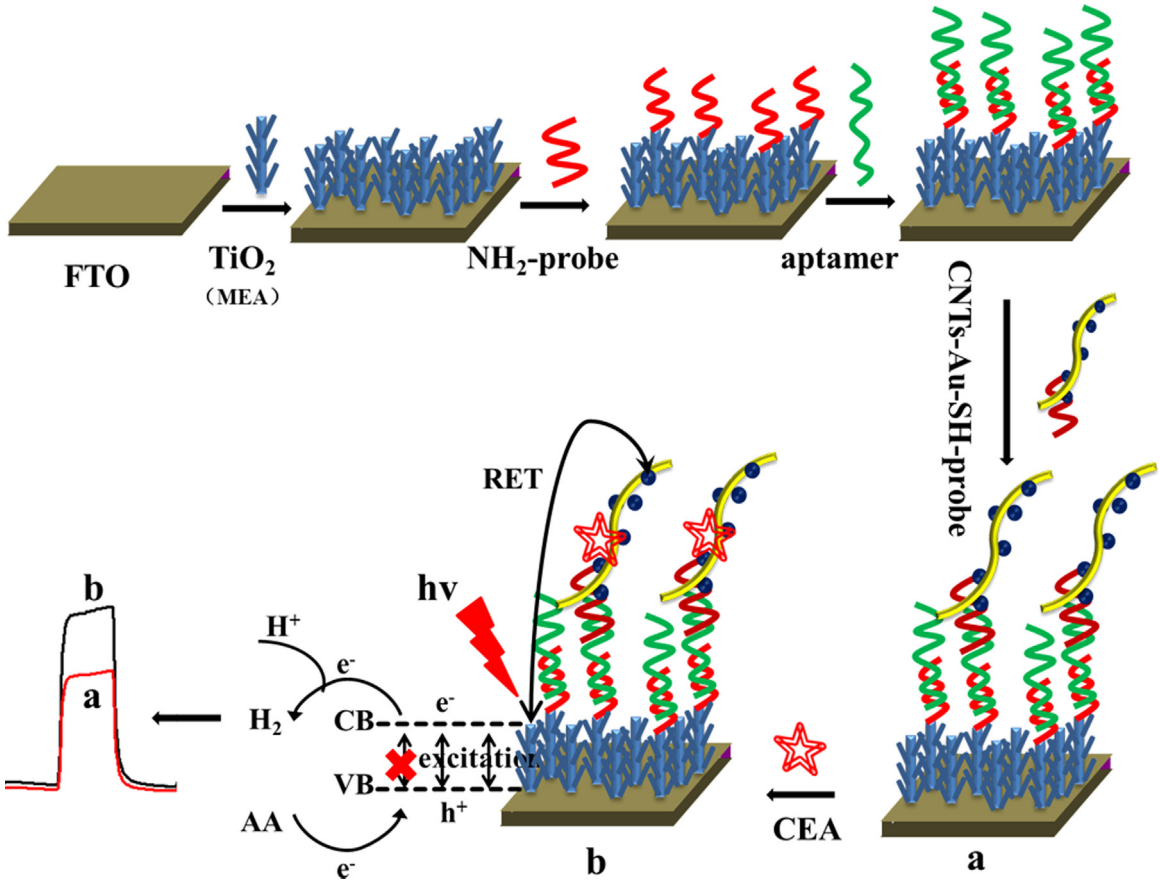

Scheme 1. Schematic representation of the fabrication of the PEC aptasensor.

(Zhang et al., 2011; Yuan et al., 2015). Besides, Au nanoparticles (AuNPs), with a high extinction coefficient and broad absorption spectrum in visible light that overlapped with the emission spectra of usual energy donors, played an important role in energy transfer systems (Oh et al., 2005; Huang et al., 2013). Therefore, the AuNPs and CNTs synthesized according to the previous report (Guo and Sun, 2012) might improve the energy transfer efficiency. The CNTs-Au nanocomposites were favorable for their applications in bioassays.

In this work, a universal signal-on PEC platform based on RET between P-TiO_2 NA and CNTs-Au nanocomposites was developed (Scheme 1). At first, an electrode modified with P-TiO_2 NA, then monoethanolamine (MEA) blocking and DNA hybridization, the carcinoembryonic antigen (CEA) aptamer and CNTs-Au-SH-probe assembled on the electrode in sequence. CEA bonded to its aptamer and destroyed the sandwichlike structure accompanied with declined quenching efficiency of the exciton produced in P-TiO_2 NA (Lin et al., 2012), resulting in the interruption of energy transfer between excited P-TiO_2 NA and CNTs-Au nanocomposites and the augment of PEC signal. On the basis of the RET and using the aptamer as a recognition module (Nelson et al., 2010; Li et al., 2008), a signal-on PEC aptasensor for CEA detection was proposed.

2. Experimental section

2.1. Reagents

Titanium butoxide ($Ti(OC_4H_9)_4$) was purchased from Sigma Aldrich. Hydrochloric acid (HCl, 36–38% by weight) was supplied by Merck India. Multiwalled carbon nanotubes (CNTs, CVD method, purity $\geq$98%, diameter 60–100 nm, and length 1–2 μm) were purchased from Nanoport Co. Ltd. (Shenzhen, China). Hydrogen tertrachloroaurate (III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$) and Ascorbic acid (AA) were bought from Shanghai Chemical Reagent Company (Shanghai, China). Monoethanolamine (MEA) and glutaraldehyde (GA, 25% aqueous solution) were purchased from Alfa Aesar China Ltd. Ethylene glycol (EG) and 3-aminopropyl triethoxysilane (APTES) were gotten from Tianjin Guangcheng chemical reagent Co. Ltd. (Tianjin, China). Carcinoembryonic antigen (CEA) standard solutions were bought from Shanghai Linc-Bio Science Co. LTD (Shanghai, China). tris(2-carboxyethyl)phosphine (TCEP) and bovine serum albumin (BSA) were purchased from Alfa Aesar China Ltd. The washing solution was tris(hydroxymethyl)-aminomethane-hydrochloric acid (Tris–HCl) buffered saline (10 mmol L^{-1}, pH 7.4, C_{NaCl}=0.1 mol L^{-1}). The oligonucleotides were purchased from Sangon Biological Engineering Technology & Company Ltd. (Shanghai, China) and purified using high-performance-liquid chromatography. Their sequences were CEA aptamer, 5′-ATACCAGCTTATTCAATT-3′; NH_2-probe, 5′-NH_2-AAAAAATTGAATA-3′; and SH-probe, 5′-AGCTGGTATAAAA-SH-3′. The clinical serum samples were provided by Shandong Tumor Hospital. Ultrapure water obtained from a Millipore water purification system ($\geq$18 MΩ cm, Milli-Q, Millipore) was used in all assays. All other reagents were of analytical grade and used as received.

2.2. Apparatus

The PEC measurements were carried out on a MPI-E multifunctional electrochemical and chemiluminescence analytical system (Shanghai Remex Analytical Instrument Ltd. Co.) biased at 800 V. Ultraviolet-visible (UV–vis) absorption spectra were recorded on a UV-2550 spectrophotometer (Shimadzu, Japan). The fluorescent properties were tested on a RF-5301 pc spectrofluorophotometer