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Resonance energy transfer from CdTe quantum dots to gold nanorods using MWCNTs/rGO nanoribbons as efficient signal amplifier for fabricating visible-light-driven "on-off-on" photoelectrochemical acetamiprid aptasensor

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ABSTRACT

To develop novel resonance energy transfer (RET) system can provide opportunities for the goal of sensitive and inexpensive detection of aptamer-related targets such as DNA and microRNA, protein, and small-molecule. In this work, a novel RET system from CdTe quantum dots (QDs) to Au nanorods (Au NRs) was fabricated, by employing MWCNTs/reduced graphene oxide nanoribbons (MWCNTs/rGONRs) as the photoelectrochemical (PEC) signal amplifier and ideal support for QDs anchored. The photocurrent signal of CdTe QDs was amplified for ~3.3-fold due to the sensitization effect of MWCNTs/rGONRs, and the proposed CdTe-MWCNTs/rGONRs exhibited the typical fluorescence emission at 713 nm, which showed good spectral overlap with the UV–vis absorption spectrum of Au NRs. Furthermore, a visible-light-driven "on-off-on" PEC sensing strategy for sensitive and selective determination of acetamiprid was designed. Under optimal conditions, the resulting PEC aptasensor was found to be linearly proportional to the logarithm of target acetamiprid concentration in the range from 0.5 pM to 10 μM with a detection limit of 0.2 pM. Moreover, the proposed sensor displayed high selectivity and good reproducibility, and has been successfully applied in the direct detection of acetamiprid in real food samples. This method could resist environmental interfering agents and be extended for sensitive and reliable detection of a wide range of analytes in complex samples.

1. Introduction

As a powerful technique for probing real-time changes in the distance between energy donors and acceptors, resonance energy transfer (RET) is ideal for the sensitive detection of molecular binding events in response to interactions with a particular target molecule such as DNA, protein and etc [1–3]. Recently, various types of DNA sensors or aptasensors have been fabricated on the basis of RET involving fluorescence RET [4], chemiluminescence RET [5], bioluminescence RET [6] and electrochemiluminescence RET [7–9]. As we all know, the key to promoting the detection sensitivity of the RET-based sensor is to improve the efficiency of RET between energy donor and acceptors, which is highly dependent on the spectral overlap between the donor's emission and the acceptor's absorption [10,11]. Thus, to select suitable donor/acceptor pairs shows great importance in the fabrication of RET-based sensors, which is also the core of the RET technique. The RET between semiconductor nanocrystals (such as CdS, CdSe and CdTe, donor) and Au nanoparticles (NPs, acceptor) have been reported as an efficiency strategy for biological applications [12–14], due to the broad absorption spectrum of Au NPs in the visible-light region that overlapped with the emission spectra of usual energy donors [15]. Interestingly, recent work pointed out that Au nanorods (Au NRs) should be a better energy acceptor candidate compared with widely used Au NPs, because their scattering and absorption bands can be tuned by adjusting the aspect ratio of the nanorods and their high extinction coefficient [16,17]. Inspired by these, Xu's group designed an electrochemiluminescence-RET system for sensitively

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and selectively detection of DNA based on the energy transfer from CdS:Eu nancrystals and Au NRs [18], which opened an new way for using Au NRs as the novel energy acceptor for RET technique.

Most recently, the marriage of the newly emerged photoelectrochemical (PEC) process to RET strategy created real opportunities to advance PEC-based bioanalysis, which provided an elegant route for probing various biological interactions in PEC bioassays [13,19]. In the classic RET case, the donor must have a wide range of emission tunability for the better controlment of the spectral overlap with the absorption spectra of a particular acceptor [20]. CdTe quantum dots (QDs), due to their distinct advantages including narrow and symmetric emission with tunable colors and reasonable stability, have attracted much attention in the field of RET sensing to meet the particular demand [21]. For example, based on RET between CdTe QDs and RGO-AuNPs nanocomposites, Dai's group reported a signal-on PEC aptasensor for carcinoembryonic antigen detection [13]; Lei's group has constructed an electrochemiluminescence RET system from CdTe nanocrystals to Au nanoclusters for selective detection of microRNA [22]. These studies indicated that CdTe QDs with the advantage of emission tunability, could be used as an ideal energy donor for RET, which provided potential opportunities for the fabrication of the novel RET system in the field of aptasensing.

Acetamiprid is a kind of neonicotinoid class with relatively low chronic mammalian toxicity, but it still could generate potential health risk of human beings when exposed to the primary route of the polluted food, water and environments [23,24]. Therefore, it is highly desirable to develop a simple, highly sensitive and selective method for quantification of acetamiprid residues in food and environment to keep people from potential health risk. In the present work, a novel RET system using CdTe QDs as donor and Au NRs as acceptor was fabricated, and MWCNTs/reduced graphene oxide nanoribbons (MWCNTs/rGONRs) was employed as the support for QDs anchored and efficient signal amplifier for enhancing the PEC signal of QDs. Furthermore, an "on-off-on" PEC aptasensor for acetamiprid detection was constructed. The sandwich structure was formed by two hybridization reactions between a DNA sequence (DNA1) immobilized on CdTe–MWCNTs/rGONRs modified electrode and aptamer, and then the aptamer and Au NRs modified with another DNA sequence (DNA2) that was complementary to another end of the aptamer, as shown in Scheme 1. In the presence of target acetamiprid, the binding of acetamiprid with aptamer led to the disassembly of the aptamer, and thus the low loading of the energy acceptor Au NRs at the electrode surface, which achieved the target-induced structure switching and thus increased the PEC signal. The increase of PEC signal depended on the concentration of target acetamiprid. This "on-off-on" strategy has been successfully applied in the direct detection of acetamiprid in real food samples and possessed its potential application in quality and safety of agricultural products.

2. Experimental

2.1. Materials

Tellurium powder, $CdCl_2{\cdot}2.5H_2O$, $NaBH_4$, Ethylenediaminetetraacetic acid disodium salt (EDTA), and Tris(hydroxymethyl)aminomethane (Tris) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). 3-Mercaptopropionic acid, 1-Ethyl-3-(3-(dimethylamino)-propyl) carbodiimide (EDC), *N*-hydrox-ysuccinimide (NHS), tris(2-carboxyethyl)phosphine (TCEP), chloroauric acid ($HAuCl_4{\cdot}4H_2O$), acetamiprid, carbaryl, methyl parathion, ethoprophos and chlorphrifos were obtained from Sigma-Aldrich. The CdTe-MWCNTs/rGONRs nanocomposite was prepared according to our previous literature [25]. 1 mM stock solution of acetamiprid was dissolving in methanol, and the standard solutions were prepared by diluting the store solution to desired concentration with water. Phosphate buffered solution (PBS, 0.10 M) of various pH values were prepared by mixing stock standard solutions of NaH_2PO_4 and Na_2HPO_4, and adjusted the pH with 0.10 M NaOH or H_3PO_4 solution. The oligonucleotides were purchased from Sangon Biotech Co., Ltd. (Shanghai, China) and purified using high-performance–liquid chromatography. The corresponding sequences are as following: acetamiprid aptamer: 5′-TGT AAT TTG TCT GCA GCG GTT CTT GAT CGC TGA CAC CAT ATT-ATG AAG A-3′; NH_2-probe (DNA1): 5′-AGA CAA ATT ACA-NH_2-3′; SH-probe (DNA2): 5′-HS-TCT TCA TAA TAT-3′. Double-distilled water was used in all experiments. All the reagents were used as purchased without further purification. Double-distilled water was used throughout the study.

2.2. Apparatus

Transmission electron microscopy (TEM) image was taken with a JEOL 2100 transmission electron microscopy (JEOL, Japan) operated at 200 kV. The UV–vis absorption spectra were measured by an UV-2450 spectrophotometer (Shimadzu, Japan) and fluorescence spectrum were recorded on a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan). All experiments were carried out at room temperature using a conventional three-electrode system with a modified ITO electrode (1×1 cm) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel as the reference electrode. All the PEC measurements were performed with a 250 W Xe lamp (Beijing Trusttech Co. Ltd.) as the visible-light source (passing through a 400 nm UV-cut filter) at the intensity of 100 mW cm^{-2}. The electrochemical impedance spectroscopy (EIS) was performed with a ZENNIUM electrochemical workstation (Zahner Instruments, Germany) in 0.10 M KCl solution containing 5.0 mM $Fe(CN)_6^{3-/4-}$.

2.3. Preparation of Au NRs

The Au NRs were prepared by the previously-reported seed-mediated growth method [18,26]. Firstly, the seed solution was prepared by quickly adding 0.6 mL of a freshly prepared ice-cold 0.01 M $NaBH_4$ solution into an aqueous mixture consisting of 0.105 mL of 1% $HAuCl_4$ and 10 mL of 0.10 M CTAB, followed by vigorously stirring for 2 min. The resultant seed solution was kept at 30 °C for at least 2 h. To synthesize the Au NRs, 0.415 mL of 1% $HAuCl_4$ and 0.20 mL of 0.10 M $AgNO_3$ were added to 20 mL 0.10 M CTAB, following by gentle stirring of the mixing solution. Then, 0.16 mL of 0.10 M ascorbic acid was added, and the obtained growth solution changed from dark yellow to colorless. Afterward, 48 μL of the pre-prepared seed solution was rapidly injected. The resultant solution was gently mixed for 10 s and left undisturbed 20 h in a 30 °C water bath to initiate growth to yield Au NRs. Finally, the Au NRs solution was centrifuged twice at 10,000 rpm for 10 min to remove excess CTAB and re-dispersed in pure water.

2.4. Bioconjugation of DNA2 to Au NRs

DNA2 was conjugated on the surface of Au NRs through the strong affinity of Au-S bonding [27]. Firstly, 15 μL of 10 mM TCEP was added into 30 μL of 50 μM SH-probe and incubated for 30 min at room temperature in order to reduce the disulfide bonds [19]. Then, the required amount of Au NRs was added to the above solution. After incubating for 16 h at room temperature, the solution was mixed with 0.25 mL of 10% NaCl. Next, the Au NRs/DNA2 was centrifuged twice at 6000 rmp for 20 s to remove excess DNA2, the precipitate was redispersed in 0.1 M PBS of pH 7.0 containing 0.1 M