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Design of electrochemical biosensors with peptide probes as the receptors of targets and the inducers of gold nanoparticles assembly on electrode surface

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ABSTRACT

We reported a general way to design electrochemical biosensors with peptide probes as the receptors of targets and the inducers of gold nanoparticles (AuNPs) assembly on electrode surface. To demonstrate the feasibility of our strategy, human chorionic gonadotropin (hCG) was first determined as a model analyte. Specifically, the hCG-binding peptide triggered the aggregation of AuNPs in solution; by modifying the electrode with the hCG-binding peptide, the peptide-induced AuNPs assembly was achieved on the electrode surface, resulting in the formation of a network of AuNPs and a significant fall of charge transfer resistance. The attachment of hCG onto the electrode surface through the probe-target interaction made the peptide lose its ability to trigger the formation of the AuNPs-based network architecture on electrode surface, thus leading to an increased charge transfer resistance. The electrochemical impedance technique allowed for the determination of hCG with a detection limit 0.6 mIU/mL. Furthermore, the method was used to the selective detection of amyloid-β oligomer (AβO, a reliable molecular biomarker and crucial target for the diagnosis and therapeutic intervention of Alzheimer's disease). Our result indicated that the AuNPs-based colorimetric assay can be developed into a corresponding electrochemical assay with significantly improving sensitivity and selectivity. Taking advantage of the simple principle and the unique physical and chemical properties of AuNPs, our work would be valuable for the design of novel electrochemical biosensors by marrying specific receptors.

1. Introduction

Electrochemical affinity biosensors have been attractive for a broad range of applications in clinical diagnosis, biomedical research, food quality control and environmental monitoring because of their simplicity, rapid response, and compatibility with miniaturization. In particular, electrochemical immunosensors, relying on the specific antigen–antibody interaction, are the most widely used thanks to some of their peculiar features [1]. However, electrochemical immunosensors, usually carried out in an enzyme-linked immunosorbent assay (ELISA)-type pathway, require a labeling procedure to make the transduction possible. Additionally, the utilization of immunosensors might be hindered, especially in the resource-poor setting areas such as undeveloped countries, by their high cost and relatively poor stability. Of the alternatives to antibody-based sensing techniques, aptamer-based methods have become popular over the past decade because of their high specificity and affinity for their targets and good stability in various media, including natural environments and living organisms [2,3]. Recently, peptide aptamers have attracted attention as the valuable recognition elements since they can offer the diverse structural and functional features of proteins for molecular interactions and have numerous advantages over antibodies (e.g. low cost, ease of synthesis and modification, and good chemical/thermal stability) [4–13]. In this work, we attempted to develop a kind of peptide-based electrochemical affinity biosensors with the advantages of convenience, low cost and ease of operation.

For ultrasensitive detection of analytes with electrochemical techniques, a popular approach is driving the enhancement of sensitivity with signal amplification. To date, many efforts to reduce detection limits focus on amplifying the signal using various labels, such as liposomes, enzymes and nanomaterials [14–20]. Among of them, nanomaterials feature unique physicochemical properties that can be of great utility in pushing the enhancement of detection

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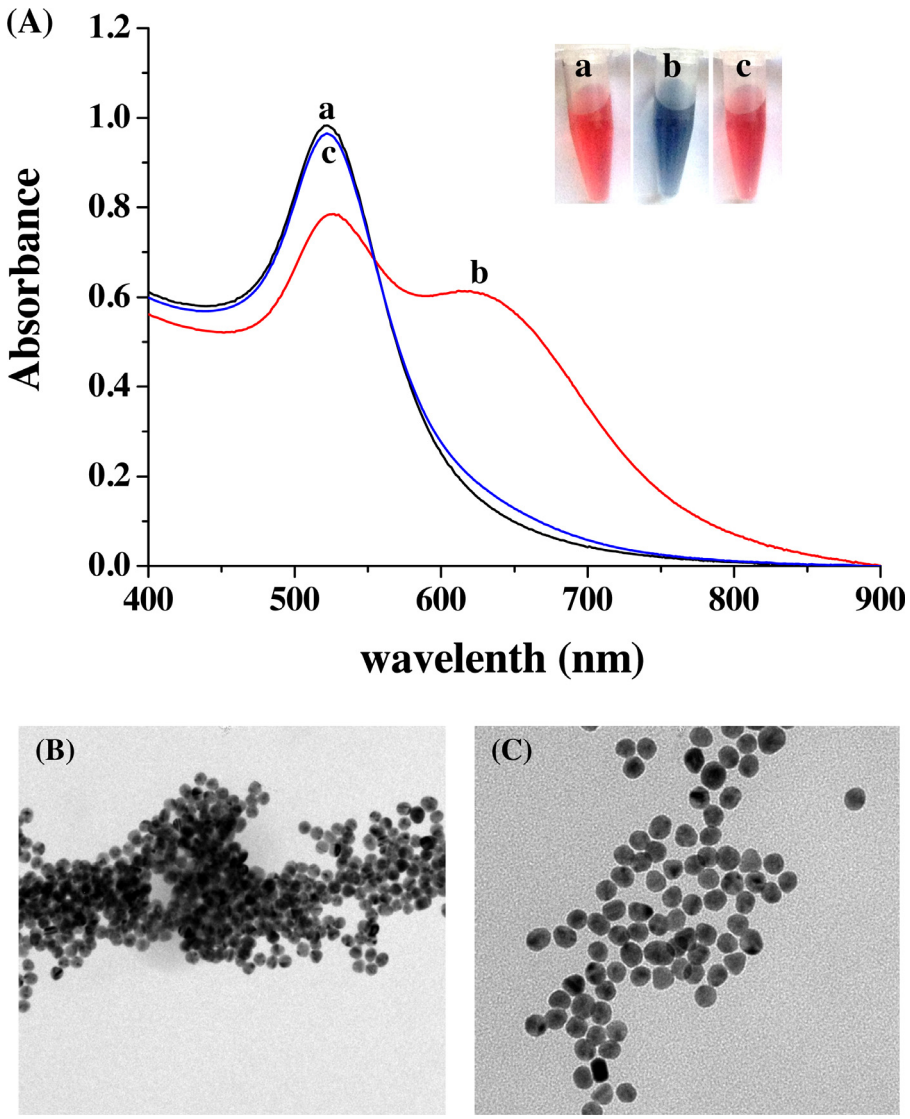

Fig. 1. (A) The UV–vis absorption spectra and photographic images of AuNPs in various systems (curve/tube a, AuNPs; curve/tube b, AuNPs + peptide; curve/tube c, AuNPs + peptide + hCG). The final concentrations of AuNPs, peptide and hCG were 3.6 nM, 1 μM and 50 IU/mL, respectively. TEM images of AuNPs in the presence of peptide (B) and peptide/hCG (C).

sensitivity by miniaturization of the sensor elements. For example, gold nanoparticles (AuNPs) possess distinct physical and chemical attributes (e.g. excellent conductivity, high surface area and catalytic properties) that make them excellent materials for the fabrication of novel chemical and biological electrochemical sensors [21–26]. These strategies included the use of AuNPs as carriers for probe/signal molecule loading and as indicators to induce the deposition of metals on AuNPs surface. It has also been suggested that the use of peptide probes as both the analyte binders and the AuNPs-aggregation inducers would enable the development of colorimetric assays [27–29]. After forming a complex with the analyte, the peptide probe lacks the other function as an inducer of AuNPs aggregation; then, the AgNPs remain dispersed. This methodology is a simple colorimetric sensing technique because it does not require modification of analyte binding molecules onto AuNPs. However, it shows low sensitivity and poor anti-interference ability for protein assay in serum samples. Since gold electrode exhibits a superficial microenvironment similar to that of AuNPs, we suggest that modification of gold electrode with peptide probe would allow for the deposition of increasing amounts of AuNPs on the electrode surface through the peptide-induced assembly of AuNPs. As a result, the liquid-phase colorimetric assay could be converted into enhanced surface tethered electrochemical analysis based on the peptide-induced formation of a network of AuNPs on electrode surface, that is to say, the aggregation of AuNPs in a solution was facilely initiated on a solid (electrode)–liquid (electrolyte) surface. The formation of a network of AuNPs on electrode surface would reduce the charge transfer resistance due to the excellent electrical conductivity of AuNPs [30–32]. However, if the peptide probe immobilized on electrode was bound with the target, it would lose the ability to trigger the formation of the AuNPs-based network architecture on electrode surface. To demonstrate the feasibility of our strategy, human chorionic gonadotropin (hCG), a hormone that is produced by the placenta and considered the major indicator of embryo implantation in pregnancy [33–35], was tested as the model analyte. Electrochemical impedance spectroscopy (EIS), a powerful electrochemical technique for studying various surface processes and properties, was employed to monitor the change of charge transfer resistance. Furthermore, amyloid-β oligomer (AβO), a reliable molecular biomarker and crucial target for the diagnosis and therapeutic intervention of Alzheimer's disease [36], was determined based on the proposed detection principle.