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Dual-responsive electrochemical immunosensor for detection of insulin based on dual-functional zinc silicate spheres-palladium nanoparticles

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ABSTRACT

In this study, described an electrochemical immunoassay for insulin that is based on the use of zinc silicate spheres loaded with palladium nanoparticles (Zn_2SiO_4-PdNPs) that act as dual-function labels. The Zn_2SiO_4-PdNPs display high electrocatalytic activity towards the reduction of H_2O_2 and high sensitivity in chronoamperometry. The Zn_2SiO_4-PdNPs decrease the electron transfer rate between the electrolyte and the surface of the electrode, which can increase the changed current and enhance the sensitivity of the immunosensor as detected by square wave voltammetry (SWV). Electrodeposited gold is used as the matrix material. The icosahedral gold nanocrystals are coated with the primary antibodies formed a 3D mode to against abundant of insulin. Under optimal conditions, the assay has a linear response in the 0.1 pg mL^{-1} to 50 ng mL^{-1} insulin concentration range, and the limit of detection of the SWV and CA methods are 0.25 fg mL^{-1} and 80 fg mL^{-1}, respectively. Moreover, the immunosensor holds an outstanding analytical performance for the insulin detection and has promising potential in clinical diagnosis.

1. Introduction

The morbidity of the diabetes is on the rise throughout the world. Diabetes can cause the diseases of blindness, renal failure, heart disease and stroke. In clinical research, it had been clearly confirmed that insulin deficiency can induce diabetes [1]. Therefore, the concentration of insulin in serum is the cornerstone for diagnosis, screening and treatment of diabetes [2,3].

In the past years, diverse analytical methods have been developed for the sensitive detection of insulin, such as radioimmunoassay [4] and chemiluminescence [5]. While the electrochemical immunosensor method has been widely applied in product safety [6], environmental detection [7], clinical medicine [8], and so on. This method provided a rapid, accurate and quantitative technique for protein biomarker detection.

The signal amplification strategies of the conventional electrochemical immunosensors are almost used the multifunctional nanomaterial as the label [9,10]. There are a lot of advantages of the nanomaterials for the fabrication of biosensors, such as, enlarging the area of sensing surface, improving the power to conduct electricity and amplifying the output signal [11–15]. The zinc silicate spheres (Zn_2SiO_4) are easy to synthesize, economically available and environmentally friendly nanomaterial [16]. The Zn_2SiO_4 spheres are amorphous structure, exist much unoccupied position and the oxidation number of Pd (II) is same with Zn (II), the Pd (II) is easier to insert gaps than other metal ion by the ion-exchange adsorption [17]. The palladium nanoparticles (Pd NPs) are obtained by the *in situ* reduction, which has a good catalytic activity towards the reduction of H_2O_2 and conjugate secondary antibodies (Ab_2) by the chemical band of Pd-NH_2 [18]. The high sensitivity of the designed immunosensor can be attained when detected by the CA [19,20]. What is more, when the immunosensor was detected by square wave voltammetry (SWV), the label of the Zn_2SiO_4-Pd nanocomposite can hinder the electron transfer and increase the changed signal which have a positive effect on the SWV sensitivity. With the increase of the concentration of insulin, the electrochemical signal will decrease because the antigen can depress the electron transfer. The Zn_2SiO_4-Pd-Ab_2 and insulin can decrease the current response under SWV and increase the change of electrochemical signal subscribe to the sensitivity of the developed immunosensor. As a consequence, Zn_2SiO_4-Pd was used as dual-functional labels to developed immunosensor.

Electroplated gold was used as the matrix material for the construction of immunosensor. The primary insulin antibodies (Ab_1) are firmly connected to the electrode through the chemical binding of Au-

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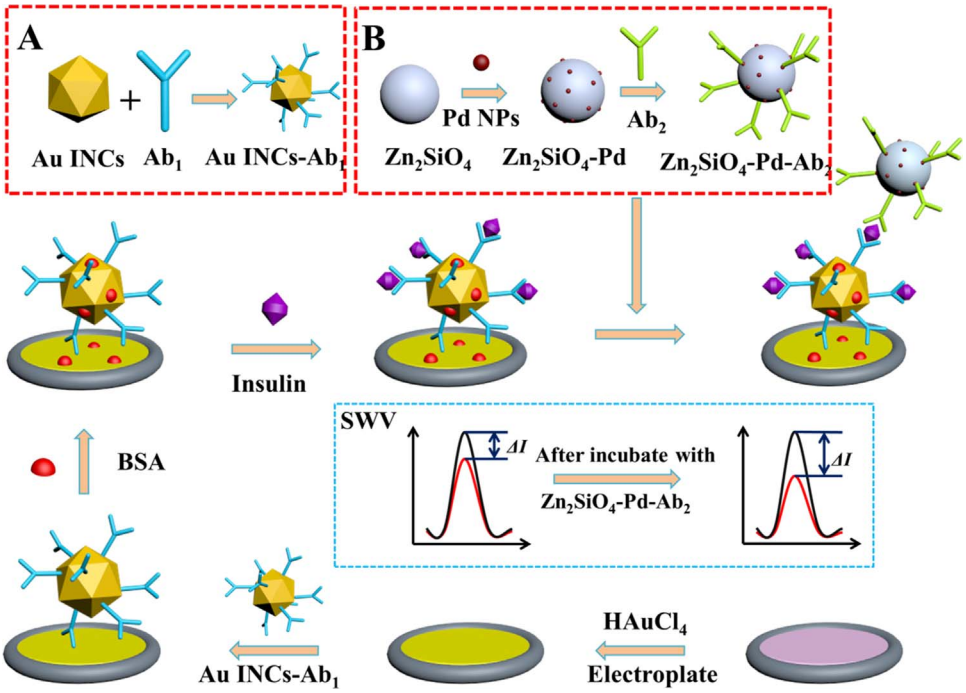

Fig. 1. Schematic presentation of the immunosensor fabrication and the preparation process of Au INCs-Ab_1 (A) and Zn_2SiO_4-Pd-Ab_2 (B).

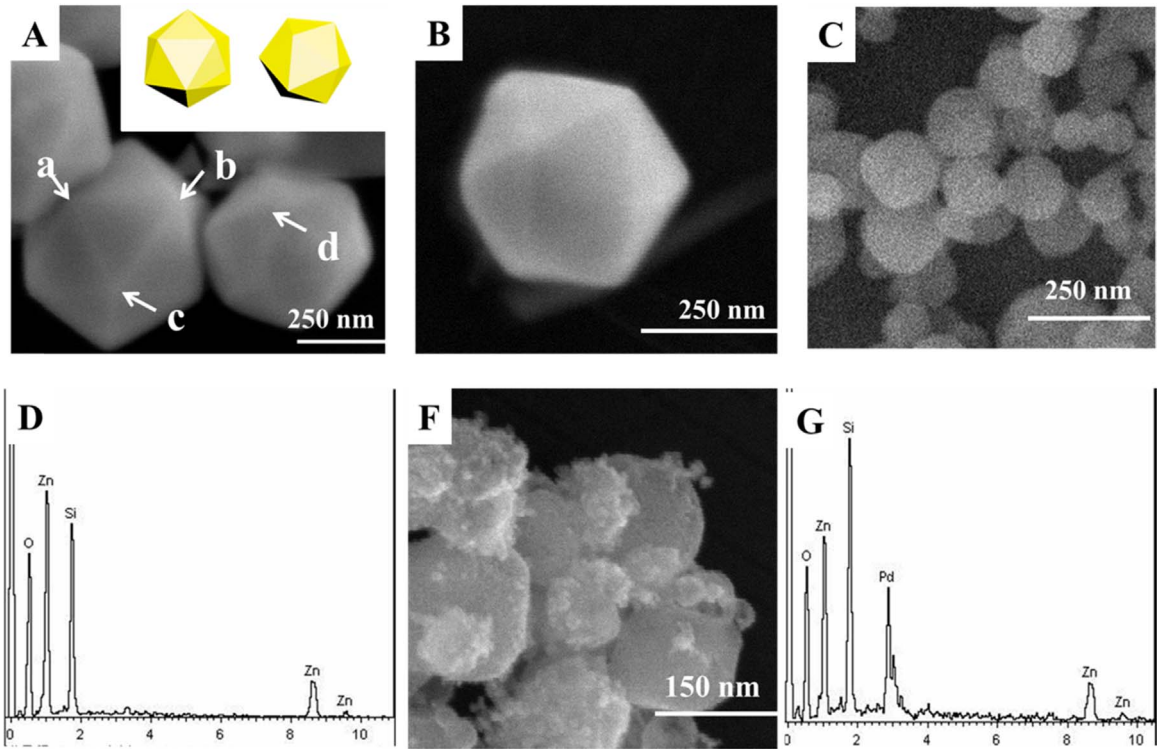

Fig. 2. The SEM images of Au INCs (A and B); the SEM image (C) and EDS (D) of Zn_2SiO_4, the SEM (F) and EDS (G) of Zn_2SiO_4-Pd.

NH_2 with the amino groups of the Ab_1 [21,22]. The Ab_1 have immobilized on the gold icosahedra nanocrystals (Au INCs) by the chemical binding of Au-NH_2 before the modification of immunosensor. There are some advantages with this strategy. Such as, the Au INCs own twenty spots and every spot can link the biomolecules more tightly than the point-of-touching of nanospheres and the chemical binding of Au-NH_2, the Ab_1 are linked strongly to Au INCs [23,24]. At the same time, the previously reported immunosensors were linked Ab_1 directly on matrix and formed a 2D mode. While, in this part, the Ab_1 linked on the Au INCs can form a 3D structure and linked more insulin than the Ab_1 linked on the gold matrix directly.

In this work, we designed a new mode immunosensor based on zinc silicate spheres-palladium nanoparticles as dual-functional labels and gold icosahedra nanocrystals as multifunctional strategy material for the detection of insulin. Under this circumstance, the sensitivity of the developed immunosensor is improved.