A Recognition-functionalized Gold-nanoparticle-attached Electrode Applied in the Detection of Dopamine

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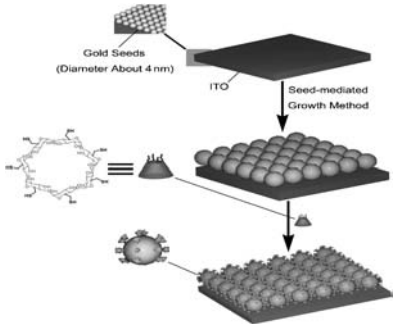
A kind of recognition-functionalized electrode which combined the advantages of two kinds of functional materials (gold nanoparticles and β-CD) was prepared and used for sensitive and selective detection of dopamine.

In recent years, molecular recognition of analytes at the surface of solid materials by host–guest chemistry is a promising approach to chemical sensing.[1] Use of selective inclusion complexation is the main strategy for preparing synthetic host molecules, which recognize structure of guest molecules.[2] Natural and chemically modified cyclodextrins (CDs), which can selectively bind various organic, inorganic, and biological molecules into their hydrophobic cavities to form inclusion complexes, could be used as selective molecular receptors.[3] This well-known inclusion complexation has brought great interest in the design of electrodes modified with CDs, which exhibited preconcentration and selective detection function.[4]

Nanomaterials exhibit attractive properties in electrode modification by enhancing the electrode conductivity, facilitating the electron transfer and improving the analytical sensitivity and selectivity.[5] The catalytic activity of these nanosized particles results from a band gap of a metallic–insulator transition in the few nanometer range, high surface area and interface-dominated properties that differ from those of the bulk counterparts.[6] In particular, gold nanoparticles (AuNPs) have been an intensive research subject for the design of nanostructured electrodes.[7] The use of AuNP superstructures for the creation of electrochemical devices is an extremely promising prospect.

Dopamine (DA) is an important neurotransmitter and extracellular messenger in biological systems. Extreme abnormalities of DA concentration levels may lead to Parkinson's disease.[8] So determination of DA is significant for neurochemistry and brain-science studies. As DA is electrochemically active, electrochemical detection becomes one of the feasible methods. The major problem of electrochemical determination is the interference from ascorbic acid (AA), which is oxidized at a similar potential and usually exists in real systems in large amount.[9] Thus, selectivity and sensitivity are important in the electrochemical determination of DA.

Based on these studies, the aim of our work was to develop a kind of recognition-functionalized electrode which combined the advantages of two kinds of functional materials (gold nanoparticles and β-CD) and could exhibit high sensitivity and selectivity for the determination of DA. Scheme 1 displays the schematic representation for the preparation of the recognition-functionalized electrode. First, the seed-mediated growth method[10] was applied to prepare the Au-nanoparticle-attached ITO (AuNP/ITO). Then, the AuNP/ITO electrode was immersed in 1.0 mM DMF solution of Per-6-thio-β-cyclodextrin[11]



Scheme 1. Schematic illustration of β-CD/AuNP/ITO electrode fabrication.

for 24 h to obtain the recognition-functionalized electrode (β-CD/AuNP/ITO).

Figure 1A shows the SEM image of the β-CD/AuNP/ITO electrode. As can be seen, the AuNPs attached on the electrode included gold nanorods and gold nanospheres. Most of the AuNPs had a nearly spherical shape and their size distribution was between 50 and 100 nm. The AuNPs were randomly distributed throughout the network and could be considered as ensembles of nanoelectrode.

Figure 1B shows the cyclic voltammograms at bare ITO, AuNP/ITO, and β-CD/AuNP/ITO, respectively, in 5.0 mM $[Fe(CN)_6]^{-3/-4}$ with 0.1 M KCl. $[Fe(CN)_6]^{-3/-4}$ exhibited a quasi-reversible one-electron redox waves at bare ITO (Figure 1B, curve a) with a peak–peak separation (ΔE_p) of 970 mV at 100 mV s^{-1}. After the AuNPs were deposited on ITO electrode, ΔE_p reduced to 410 mV, and a notable increase in the amperometric response of the electrode was observed (Figure 1B, curve b). This result indicated that the AuNPs deposited on the ITO substrate provide the necessary conduction pathways, besides acting like nanoscale electrodes in promoting

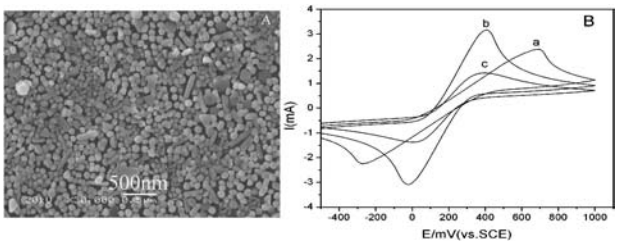


Figure 1. (A) SEM image of the β-CD/AuNP/ITO electrode. (B) CVs of bare ITO (a), AuNP/ITO (b), and β-CD/AuNP/ITO (c) electrodes in 0.1 M KCl containing 5 mM $K_3Fe(CN)_6$ and 5 mM $K_4Fe(CN)_6$. Scan rate: 100 mV s^{-1}. The effective area of the electrode is 0.5 cm^2.

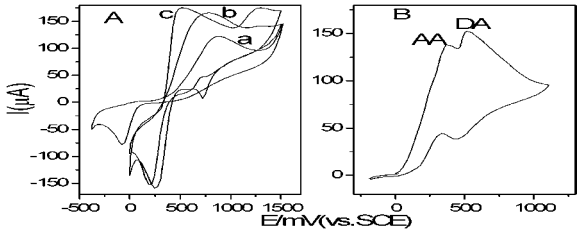


Figure 2. (A) CVs of 1.0 mM DA at bare ITO (a), AuNP/ITO (b), and β-CD/AuNP/ITO (c) in 0.1 M phosphate buffer (pH 7.0). (B) 1.0 mM DA + 10.0 mM AA at β-CD/AuNP/ITO. Scan rate: 100 mV s^{-1}.

the electron transfer between the analyte. The formation of the SAM of β-CD on the AuNP/ITO substrate was confirmed by the significant decrease in peak current of $[Fe(CN)_6]^{-3/-4}$ (Figure 1B, curve c) due to the presence of the CD ring between the bulk solution and the Au surface. The previous studies on a barrier effect of β-CD SAM to $[Fe(CN)_6]^{-3/-4}$ suggested that $[Fe(CN)_6]^{-3/-4}$ is sterically not permeable through the β-CD cavity but is permeable only through the space remaining between the surface-confined β-CD residues.[12] Therefore, the results indicated that the electrochemical reaction of $[Fe(CN)_6]^{-3/-4}$ was inhibited by the densely packed β-CD SAM.

The electrocatalytic behavior of the β-CD/AuNP/ITO electrode was evaluated by the oxidation of DA and the mixture with AA. Figure 2A shows the cyclic voltammograms of 1 mM DA in 0.1 M phosphate buffer (pH 7.0) at a scan rate of 100 mV s^{-1} at bare ITO, AuNP/ITO, and β-CD/AuNP/ITO, respectively. The oxidation peak of DA negatively shifted from 860 mV at the bare ITO electrode to 750 mV at the AuNP/ITO electrode accompanied with obvious increase in peak current, indicating a favorable catalytic activity of gold nanoparticle arrays toward the oxidation of DA. While at β-CD/AuNP/ITO (Figure 2A, curve c), the peak current of DA increased significantly and the peak potential decreased obviously, apparently β-CD with a hydrophobic cavity such a structure allows them to form inclusion complexes with DA.[4c,4d] The inclusion action further enhanced the accumulation effect of β-CD/AuNP/ITO electrode, accordingly increased the apparent concentration of analytes in the interface of modified electrode, which results in pronounced peak current. These phenomena suggested that the β-CD/AuNP/ITO electrode not only benefited from use of AuNPs but also from the ability of β-CD to form inclusion complexes with organic molecules. The β-CD/AuNP/ITO electrode thus gave the best analytical performance in the determination of DA compared with the other two.

It is well known that AA widely coexists with DA in real biological matrices. So, avoiding AA interference is an important target for any DA analytical methods. The interference of AA to DA detection arises from two aspects: one is the very similar oxidation potential of AA and DA at ordinary electrode; the other is the electrocatalytic oxidation of dopamine by ascorbic acid.[9] Namely, oxidized dopamine, i.e., dopamine–*o*-quinone, is chemically reduced by ascorbic acid. Thus, one would anticipate that the oxidation wave of DA will be affected by the concentration of AA. Figure 2B shows the cyclic voltammograms of 1 mM DA coexisting with 10.0 mM AA in 0.1 M phosphate buffer (pH 7.0) at a scan rate of 100 mV s^{-1} at β-CD/AuNP/ITO. The two separated oxidation peaks for DA and AA were clearly resolved, and a potential separation of 162 mV for the two oxidation peaks was achieved, suggesting the feasibility of reliable determination of DA free from AA interference. The reasons were as follows: Since β-CD could form stronger inclusion complexes with DA derivatives[13] than with AA[14] ($K_{DA} = 2000\,M^{-1}$, $K_{AA} = 130\,M^{-1}$), most of DA entered into the cavity of β-CD on the β-CD/AuNP/ITO electrode and then been oxidized. DA–quinone form, the oxidized product of DA, was retained in the β-CD cavity and protected from interaction with AA. On the other hand, AA was oxidized only in the defects of the electrode. So DA and AA were oxidized individually without interference. In addition, the oxidation peak current increased linearly with the concentration of dopamine in the range of 1.0×10^{-6} to 4.7×10^{-3} M and the detection limit was 3.1×10^{-6} M.

In conclusion, the electrode that has recognition function was successful prepared by assembly of β-CD on the gold-nanoparticles-modified ITO. The recognition-functionalized electrodes not only had high electrocatalytic oxidation activity toward DA but also high selectivity for determination of DA in the presence of AA. The reason for the excellent performance could be attributed to the combination of high electrocatalytic activity of the gold nanoparticles and the recognition function of β-CD.

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