

Ion selective gate based on silica/gold cavity array for electrochemical detection of dopamine



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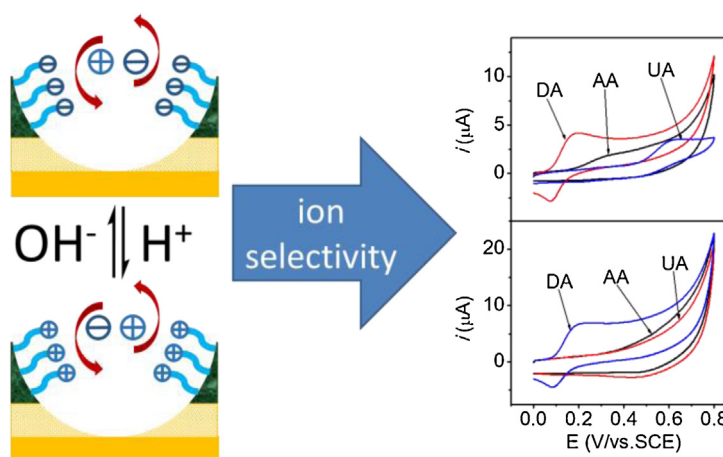
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HIGHLIGHTS

- Silica/gold cavity array microelectrodes were fabricated.
- Silica surface was sulfonated to provide negative charges.
- The modified cavities exhibited excellent ion selectivity.
- The ion selective gate of the cavities selectively detected dopamine in the presence of ascorbic acid and uric acid.

GRAPHICAL ABSTRACT



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ABSTRACT

A silica/gold (SiO₂/Au) cavity array microelectrode was fabricated on a gold film-coated glass slide by using highly ordered monodispersed polystyrene spheres as a template. The surface of the silica, as the upper part of the cavity, was sulfonated by 1,3-propanesultone, providing negative charges on the surface of the cavities in a media with pH > 2. The ion selectivity of the sulfonated SiO₂/Au cavities was revealed by voltammetric response of potassium ferricyanide and methyl viologen dichloride as the electrochemical probes. Due to the electrostatic interaction, the positively charged methyl viologen cations can transport through the negatively charged SiO₂ gate and react on active sites at the bottom of the cavities, whereas the diffusion access of the negatively charged ferricyanide anions into the cavities is blocked by the SiO₂ gate. The ion selective gate of the cavities enables the electrode to selectively detect dopamine in the presence of ascorbic acid and uric acid, giving a linear range from 15 μM to 160 μM and a low detection limit of 85 nM.

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Abbreviations: SiO₂/Au CAME, silica/gold cavity array microelectrode; SEM, scanning electron microscope; PS, polystyrene; CV, cyclic voltammetry; DA, dopamine; AA, ascorbic acid; UA, uric acid; DPV, differential pulse voltammetry; PB, phosphate buffer.

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1. Introduction

Selective separation and detection of molecules is an attractive field in fundamental research and technology [1]. Materials with micro/nano porous structures have been proven to have the capability to selectively separate species, and thus, to achieve selective detection, due to the fact that micro/nano porous materials possess unique features, including adjustable pore size, easily modification by various functional molecules and high transport rate of target molecules. Recently, highly ordered SiO₂-based porous structures have been received increasing attention, benefitted from its well biocompatibility and manipulable surface modification [2]. In general, highly ordered micro/nano porous structures of SiO₂ can be achieved by templating method, which involves solidification of SiO₂ sol-gel that is infiltrated into the voids of a template through electrochemical or physical approaches [3]. The removal of the templates leads to the formation of diversified SiO₂ structures, such as bowl or cavity arrays, column arrays, crescent arrays, linear or zigzag chains, and circular rings [4]. The porous SiO₂ membranes can also be fabricated without template. For example, the porous structures or interstices can be spontaneously formed among the well-arranged SiO₂ colloidal spheres by self-assembly, sputter-coating, and electrodeposition of SiO₂ colloidal spheres [5,6]. Technologies based on the micro/nano porous SiO₂ have been used in drug and DNA delivery, detection of cancer, molecular recognition, and selective isolation [7–9]. Molecular transport and selectivity can be controlled by the surface functional groups that respond to environmental stimuli, including pH, light and temperature [10,11]. Nevertheless, in most of the studies, the systems were composed of multilayer SiO₂ membranes, which frequently bring about structural defects, and consequently the difficulty in controlling of the transport or selectivity of the target molecules.

The detection of dopamine (DA) is important to neuroscientists and chemists for that a loss of DA-containing neurons may result in some serious disease such as Parkinson's disease and schizophrenia [12]. Usually, the detection of DA is interfered by the presence of ascorbic acid (AA) and uric acid (UA). These three biomolecules can be electrochemically oxidized, but their oxidation peaks are overlapped seriously at ordinary electrodes when they coexist in the samples [13]. In order to extract the detection signal of DA, various electrode materials, including single-wall and multi-wall carbon nanotubes, reduced graphene oxide, nanostructured metals and polymers, have been used to modify the surface of the electrodes [14–16]. Nonetheless, improvement in sensitivity and selectivity of DA detection is still desirable for the complex systems.

Herein, we report the fabrication of highly ordered SiO₂/gold (SiO₂/Au) cavities on a gold film-coated substrate to generate an array microelectrode. By modification of the SiO₂ gate with sulfonic acid groups, selective electrochemical reactions occurring on the active sites at the bottom of the cavities can be achieved by the electrostatic interaction between the transporting species and the SiO₂ gate of the cavities. Only DA can be selectively detected in the co-existence of AA and UA molecules due to the difference in electrostatic interaction between those molecules and the SiO₂ gate under physiological pH conditions.

2. Experimental

2.1. Materials

LUDOX®SM-30 colloidal SiO₂ (7 nm, 30 wt.% suspension in H₂O, Sigma-Aldrich), dopamine hydrochloride (DA, 98.5%, Sigma-Aldrich), methyl viologen dichloride (MVCl₂, 98%, TCI), 1,3-propanesultone (99.5%, Ourchem), uric acid (UA, 99%, Ourchem), ascorbic acid (AA, 99%, J&K) were used in the experiments with-

out further purification. All the other chemicals are reagent grade. Styrene was distilled under reduced pressure to remove the antipolymerizer before use. All solutions were prepared with Millipore-Q water.

2.2. Instruments

A FEI Quanta 200 FEG high-resolution scanning electron microscope (SEM) was used to measure the surface morphologies of the PS template and the SiO₂/Au cavity array microelectrode (SiO₂/Au CAME). A high vacuum multi-target magnetron sputtering coating machine (JCP-350M2, Beijing Technol) was used to deposit the Au film on the glass substrate.

A three-electrode cell was employed with a SiO₂/Au CAME (diameter of 5 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum sheet as the auxiliary electrode. All the electrochemical experiments were performed on a CHI660D electrochemical workstation. The electrolytic solutions were purged with N₂ to remove dissolved O₂ prior to the measurements.

2.3. Fabrication of highly ordered SiO₂/Au cavity array microelectrode

Firstly, PS particles with diameter of 400 nm were synthesized by an emulsion-free polymerization method [17]. The fabrication process of PS spheres monolayer colloidal template was according to the protocol reported previously [18]. A small amount of PS colloidal suspension was dispersed onto the surface of deionized water in a Petri dish. The monolayer of the PS spheres was spontaneously formed on the air/water interface. In order to make the PS spheres closer than their van der Waals distance, a few drops of 2% sodium dodecylsulfate solution were added into the Petri dish to change the surface tension.

Then, a glass slide (25 mm × 9 mm) was sequentially cleaned in an ultrasonic bath with acetone, ethanol and pure water, and dried by flowing pure argon. A ca. 30 nm Cr layer and ca. 100 nm Au layer were deposited on the glass substrate in sequence by using the high vacuum multi-target magnetron sputtering coating machine to form a conductive substrate. The gold film-coated electrode was tilted about 30° and immersed into the solution in the Petri dish through the clear area. At a controlled rate of water drainage, the monolayer of the close-packed PS spheres was transferred onto the surface of the electrode. The electrode was dried at room temperature to remove the remaining solvent in the monolayer. A highly ordered template of close-packed PS spheres was formed as shown in Fig. 1.

Next, the PS spheres were fixed on the substrate by heating at 84 °C for 30 min before use.

After that, a multi-current step method was employed to electrochemically deposit Au nanoparticles (AuNPs) in the interstices among the PS spheres on the template according to the literatures [19,20]. The electrolyte was a solution containing 12 g/L HAuCl₄, 5 g/L C₁₀H₁₄N₂O₈Na₂·2H₂O (EDTA), 160 g/L Na₂SO₃ and 30 g/L K₂HPO₄. A Pt sheet and a SCE were used as the auxiliary and the reference electrode, respectively. The method involving two processes: the first was a large-amplitude current step (20 mA, 100 ms) that carried out one time to grow Au crystal seeds; the second was 100 times of small-amplitude current step (5 mA, 50 ms) with an interval of 1 s to grow AuNPs on the crystal seeds.

In addition, the colloidal SiO₂ was infiltrated into the upper part of the interstices, and drying at room temperature for one or two days.

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