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The facile approaches to asymmetric modification of glassy biconical microchannel wall with silver, copper or gold

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ABSTRACT

The modification of inner surface has significant influence in the properties of the nano or microchannel based on various materials, especially for the ionic current rectification (ICR) that arises from the selective interaction between ions in solution and the inner surface. Herein, we demonstrate a simple strategy to asymmetrically modify the inner wall of a glassy biconical microchannel with silver, copper or gold by means of silver mirror reaction and polydopamine platform, respectively. And the bidirectional ionic current rectification phenomena were observed in all of the modified biconical microchannels. All of the modification methods are simple, facile and low-cost, and can be applied in the modification of other glassy pipettes.

1. Introduction

In the past decade, the glassy capillary-based nano- or micropipette for which the fabrication only requires a relatively inexpensive laser puller has been attracting more and more attention as an exciting novel tool for liquids manipulating [1,2] and biomimetic researches [3–5]. Interestingly, if the laser puller is stopped before the capillary breaks into two sections, a biconical microchannel would be fabricated instead of originally two almost identical pipettes, and such a system based on the integration of a biconical microchannel, working electrode and reference electrode may have potential and realistic value for studying the two-way ionic transport through the cell membrane [6]. As a matter of fact, the modification of inner surface has substantial influence on the properties of the nano- or microchannel, especially for the ionic current rectification (ICR) that arises from the selective interaction between ions in solution and the inner surface. ICR is related closely to the selective transport of ions and molecules [7–10]. Actually, the degree and even the direction of rectification in the modified channel can be dramatically different from the bare one [8]. Therefore, with the aid of different modification materials, many research purposes can be achieved such as simulating the gating effect of ion channels [11,12] or realizing metal nanoparticles [13] and protein detection [4,14], investigating biomolecular interactions [15,16], etc.

Various materials have been applied in the modification of nano- or microchannel including metal [11,17], small molecule [18], surfactant [6,8,19], polyelectrolyte [20] and biomacromolecule [21]. Of particular interest is the modification by metal. For instance, a novel electroporation technique for molecular delivery into a single cell has been developed based on the nanopipette with its outside edge being coated by Ag sputtering [22]. Another novel technique of local Cu electrochemical plating with a micropipette probe filled with an electrolyte can make nanometer-scale Cu dots electrochemically deposited on the Si surfaces [23]. Additionally, it is well known that the Au modified wall can make the glass nano- or microchannel more biologically friendly and allow it more facile functionalization through the Au-S bonds [17,24]. However, in practice, ion sputtering system generally requires complex apparatuses like a vacuum needing high cost and complicated operation [11,22]. More importantly, such a technique is not applicable for the modification of glassy capillary-based channel because the sputtering ions cannot survive a long cylindrical channel. As far as plating is concerned, its application in modifying the inner surface of nano- or microchannel would be a nontrivial task. As a consequence, finding new, facile and low-cost strategies to modify the nano- or microchannel wall is of paramount importance for further expanding the potentialities of such a channel.

In this work, silver mirror reaction and polydopamine platform were applied in the modification of biconical microchannel wall. On one hand, the classical silver mirror reaction is the chemical process of coating glass with a reflective silver layer, which mainly refers to the reaction of Tollen's reagent namely the silver-ammonia solution reduced by aldehyde compound and the generated silver deposited on the glass of the container forming bright layer like a mirror. On the other hand, mussels have been shown to attach to many types of surfaces even the adhesion-resistant materials poly tetrafluoroethylene, and it

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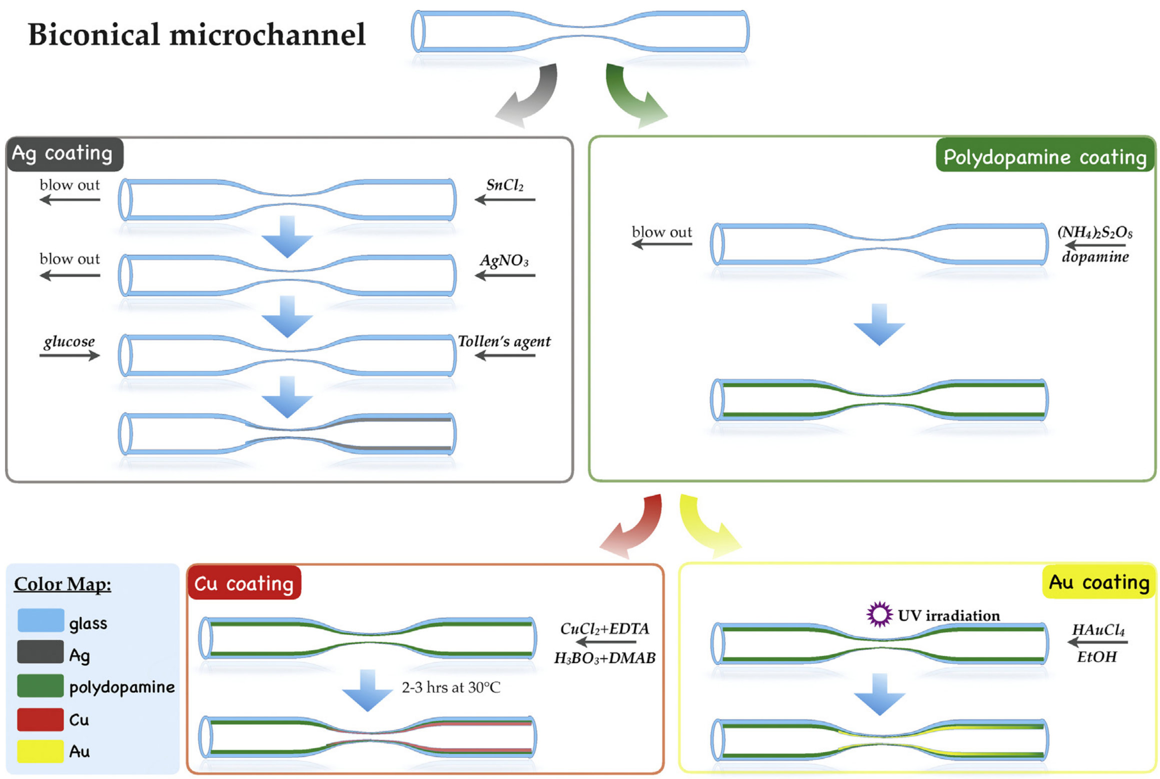

Fig. 1. Technology roadmap visualizing the overall picture of the developed methods.

was discovered that their adhesive versatility should lie in the adhesive proteins which are rich in 3,4-dihydroxy-L-phenylalanine [25,26]. Inspired by this clue, researchers used dopamine self-polymerization to construct thin and surface-adherent polydopamine films onto various inorganic and organic materials [27]. With the polydopamine coating as a platform for secondary surface-mediate reaction, many other adlayers can be created on the materials, including metal, self-assembled monolayer, and grafted polymer coatings. This two-step method of surface modification has really promising application for a wide variety of materials.

Herein, we report three facile electroless metallization methods to form Ag, Cu or Au coatings through simple injection of corresponding aqueous solution into the biconical microchannel. The technology roadmap shown in Fig. 1 visualizes the overall picture of the developed methods. In brief, the Ag coating depends on classical silver mirror reaction, while the best choice for Cu or Au coating is to fabricate the polydopamine coating as a platform for the following secondary surface-mediate reaction. The success of metal modification was confirmed via the ICR behaviours of the biconical microchannel. That is to say, differing from the nearly straight current-voltage curves in the bare biconical microchannel [6], the asymmetrically modified microchannel clearly rectify the ionic current, and the directions of ICR would be opposite if the working electrode located in the modified or bare conical regions.

2. Materials and methods

2.1. Apparatus

Current-voltage curves were obtained with CHI 760 electrochemical workstation (Shanghai, China). Two Ag/AgCl electrodes were inserted inside of the left and right cone of the biconical microchannel separately, acting as the working electrode and auxiliary/reference electrode, respectively. After a linear sweep voltammetry (LSV) scanning, the connection between electrodes and electrochemical work station was exchanged and another current-voltage curve was recorded with the Ag/AgCl electrode in the right cone acting as working electrode. The microscope image was obtained with Olympus BX-51 optical microscope (Japan).

2.2. Reagents

KCl (Beijing Chemical Works), $AgNO_3$ (West Long Chemical Works), $NH_3{\cdot}H_2O$ (Beijing Chemical Works), $C_6H_{12}O_6$ (Glucose, Sigma Aldrich), $SnCl_2{\cdot}2H_2O$ (Beijing Chemical Works), $C_8H_{11}O_2N$ (Dopamine, Alfa Aesar), $C_4H_{11}NO_3$ (Tris, Sinopharm Chemical Co. Ltd), NaOH (Beijing Chemical Works), $(NH_4)_2S_2O_8$ (Beijing Chemical Works), $CuCl_2$ (Alfa Aesar), H_3BO_3(West Long Chemical Works), EDTA (Beijing Chemical Works), $C_2H_{10}BN$ (dimethylamine borane, DMAB, Aladdin), $HAuCl_4$ (Alfa Aesar), C_2H_5OH (Beijing Chemical Works). All aqueous solutions were prepared with pure water pruchased from Wahaha Group Co. Ltd. (Hangzhou, China). All chemicals were used as received without further purification.

2.3. Asymmetric modification process

The asymmetric modification process of biconical microchannel wall is as follows.

Silver modification: (1) The $SnCl_2$ solution (0.2%) was injected into the biconical microchannel for 30 s and was blown out. (2) After washed with water, 118 mM $AgNO_3$ solution was injected into the channel. And before the silver mirror reaction, the solution was removed out. (3) 2% $NH_3{\cdot}H_2O$ solution was added into $AgNO_3$ solution (118 mM) drop by drop until the generated precipitate disappeared. And immediately, the solution was injected into the right conical region of the channel, followed by the glucose solution (10%) being injected from the left channel. Then, the bright silver layer formed on the inner surface of the right channel.

Copper modification: (1) Before injected into the biconical microchannel, 0.2 g/L $(NH_4)_2S_2O_8$ was added into the dopamine solution