Biosensors and Bioelectronics 117 (2018) 32–39

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Mutual promotion of electrochemical-localized surface plasmon resonance on nanochip for sensitive sialic acid detection

Shuang Li[a,b], Jinglong Liu[a], Yanli Lu[a], Long Zhu[b], Candong Li[b], Lijiang Hu[c], Jun Li[c], Jing Jiang[d], Szeshin Low[a], Qingjun Liu[a,b,*]

[a] Biosensor National Special Laboratory, Key Laboratory for Biomedical Engineering of Education Ministry, Department of Biomedical Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] Collaborative Innovation Center of TCM Health Management, Fujian University of Traditional Chinese Medicine, Fuzhou 350108, PR China
[c] Heye Institute for Intelligent Healthcare, Zhejiang Heye Health Technology Co., Ltd, Anji, Zhejiang 313300, PR China
[d] Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

ARTICLE INFO

Keywords:
Localized surface plasmon resonance (LSPR)
Nanochip
Electrochemistry
Mercaptophenyl boronic acid (MPBA)
Sialic acid

ABSTRACT

Localized surface plasmon resonance (LSPR) induced charge separation were concentrated on the metal nanoparticles surface, which made it sensitive to the surface refractive index changes during optical sensing. Similarly, electrochemical detection was based on the electron transformation on the electrode surface. Herein, we fabricated a nanochip by decorating a nanocone-array substrate with gold nanoparticles and silver nanoparticles for dynamic electro-optical spectroscopy. Mercaptophenyl boronic acid (MPBA) was immobilized firmly on the nanochip by the metal-S bond for sensitive sialic acid sensing. Owing to the high stability of gold nanoparticles and the high sensitivity of silver nanoparticles, the nanochip showed good performance in LSPR detection with rich and high responses. Besides, the nanochip also showed sensitive electrical signals during electrochemical detection due to the excitation of the energetic charges from the nanoparticles surface to the reaction system. The dynamic electro-optical spectroscopy was based on a unique combination of LSPR and linear sweep voltammetry (LSV). On the one hand, electrochemical signals activated the electrons on the nanochip to promote the propagation and resonance of surface plasmon. On the other hand, LSPR concentrated the electrons on the nanochip surface, which made the electrons easily driven to enhance the current in electrochemical detection. Results showed that mutual promotion of electrochemical-LSPR on nanochip covered a linear dynamic range from 0.05 mM to 5 mM on selective sialic acid detection with a low detection limit of 17 μM. The synchronous amplification of the electro-optical response during electrochemical-LSPR, opened up a new perspective for efficient and sensitive biochemical detection.

1. Introduction

Induced by the matching between the frequencies of incident photon and the oscillations of metal nanoparticles, localized surface plasmon resonance (LSPR) shows excellent capability of surface condition monitoring for analyzing intermolecular interactions (Hoa et al., 2007; Sepúlveda et al., 2009). With the development of lab on chip, researches have been focusing on LSPR-based nanochip, in which arrays of nanoparticles were fixed on a solid nanostructured substrate (Saleem et al., 2017; Jiang et al., 2017). Compared to isolated nanoparticle, nanochip with the relaxed constraints of nanoparticle morphological variations, would contribute to accelerate data acquisition and improve signal to noise ratio (Acimovic et al., 2014; Lopez et al., 2017; Oh et al., 2017). Therefore, LSPR-based nanochip provided promising feature of uniform spatial structures, which could be considered as a beneficial tool for stable and sensitive LSPR detections. Other than the good performance in optics, nanochip could also be applied as electrode in electrochemical detections due to its superior electron transfer capability and large superficial area. Considering the compatibility of nanochip in LSPR detection and electrochemical detection, a new technique was established, which is, dynamic electro-optical spectroscopy. Studies have showed that LSPR coupled with electrochemistry have advantages on electron photocatalysis (Clavero, 2014; Wang et al., 2017), dielectric tuning (Ma et al., 2017; Llorente et al., 2017; Kawawaki et al., 2017; Di Martino et al., 2017), and light-matter interactions control (Kato et al., 2018).

* Corresponding author at: Biosensor National Special Laboratory, Key Laboratory for Biomedical Engineering of Education Ministry, Department of Biomedical Engineering, Zhejiang University, Hangzhou 310027, PR China.
E-mail address: qjliu@zju.edu.cn (Q. Liu).

https://doi.org/10.1016/j.bios.2018.05.062
Received 5 April 2018; Received in revised form 16 May 2018; Accepted 31 May 2018
Available online 01 June 2018
0956-5663/ © 2018 Elsevier B.V. All rights reserved.

Sialic acid, a negatively charged 9-carbon monosaccharide derivative, is normally found in blood serum as the integral part of ganglioside structure in synaptogenesis and neural transmission (Varki, 2007). The detection of sialic acid has been shown to play an important role in early brain development, skeletal growth, and the diagnosis of cardiovascular disease as well as cancers (Narayanan, 1994; Gopaul and Crook, 2006; van Karnebeek et al., 2016). Generally, the detection of sialic acid is based on specific enzymatic reactions. However, instability for long-term preservation and limited repeatability may influence the detection sensitivity. Therefore, the usage of a stable recognition molecule, such as boronic acid, has been drawing wide attention in sialic acid sensing (Sankoh et al., 2016; Wang et al., 2016). By esterification, the amide NH or CO located at the C-5 position of sialic acid, could form a B-N or B-O linkage with boronic acid at proper pH, resulting in good selectivity for sialic acid detection.

In our study, a nanochip was designed for electrochemical-LSPR detection of sialic acid. The nanochip consisted of a cone array structure with gold and silver nanoparticles, fabricated by green and nontoxic physical control and electrochemical reduction. The bio-sensitive molecule, mercaptophenyl boronic acid was immobilized on the nanochip through metal-S bond. The nanochip showed excellent performances in LSPR, electrochemistry, and electrochemical-LSPR detections. Among them, electrochemical-LSPR is the most advantageous as it realized the mutual amplification of the electro-optical response, and also attained high efficiency and good sensitivity during biochemical analysis.

2. Materials and methods

2.1. Chemicals and reagents

In this study, sialic acid (SA, $C_{11}H_{19}NO_9$, MW: 309.28) and mercaptophenyl boronic acid (MPBA, $C_6H_7BO_2S$, MW: 153.99) were purchased from Sigma-Aldrich. The phosphate buffer solution (PBS, 10 mM, pH 7.4) was prepared by dissolving PBS tablets in deionized water. Silver nitrate ($AgNO_3$, MW: 169.87) and potassium nitrate (KNO_3, MW: 101.1) for electrochemical reduction and deposition of silver nanoparticles (AgNPs) on the nanochip, were all analytical grade and purchased from Sigma-Aldrich. Sodium chloride (NaCl, MW: 58.44), potassium chloride (KCl, MW: 74.55), L-Glutamic acid (Glu, $C_5H_9NO_4$, MW: 147.13), human serum albumin (HSA, MW: 66.47 K), Uric acid (UA, $C_5H_4N_4O_3$, MW: 168.11), Lactic acid (LA, $C_3H_6O_3$, MW: 90.08), and Ascorbic acid (AA, $C_6H_8O_6$, MW: 176.13) used for specific detection were also purchased from Sigma-Aldrich.

2.2. Fabrication of the nanochip

Nanochip consists of nanocone array, where the top and side of the walls are closely packed with gold nanoparticles and (AuNPs) and silver nanoparticles (AgNPs). First, the nanoarray structure was fabricated by nanoreplica molding technique. The original mold was a nanocone array on the flexible (poly)ethylene terephthalate (PET) substrate, fabricated by laser interference lithography and reaction ion etching techniques. A 4-in. silicon oxide with the thickness of 100 nm was sputtered on the nanocone array using K-J-Lesker-PVD-75 system to make the surface hydrophilic. Then, gold nanoparticles were deposited onto the nanocone array by electron beam evaporation with a six pocket system (FC/BJD-2000, Temescal Inc., USA). Silver nanoparticles were deposited by electrochemical reduction.

Here, the electrochemical reduction and deposition were achieved by cyclic voltammetry on the electrochemical workstation (PARSTAT-4000 AMETEK Inc., USA). During the deposition, the nanochip was used as working electrode, platinum and Ag/AgCl were used as the counter electrode and reference electrode, respectively. The three electrodes were activated in PBS solution by applying anodic potentials (range: +0.2 V to +2.0 V, scan rate: 50 mV/s) for 10 circles. Then, cyclic voltammetry (range: −1.0 V to +1.0 V, scan rate: 50 mV/s) was proceeded for 20 circles for the reduction and deposition of silver nanoparticles. During the process, 0.9 mL of potassium nitrate (concentration 10 mM, solvent: PBS) was employed as the electrolyte and 0.1 mL of silver nitrate (concentration 0.1 mM, solvent: PBS) was employed as the precursor for silver nanoparticles. Finally, the nanochip was passivated with dimethyl dichlorosilane solution for 30 min and rinsed with ethanol and ultrapure water for cleaning. Scanning electron microscopy (SEM, HITACHI UHR FE-SEM SU 8010) images showed the micromorphology of the gold nanoparticles modified nanochip and gold/silver nanoparticles modified nanochip at an accelerating voltage of 3 kV.

2.3. LSPR detection and electrochemistry detection on nanochip

LSPR detection was carried out on a reflection spectrum system. The spectroscopy system includes a halogen cold laser (DH-mini UV–Vis–NIR, Ocean Optics Inc., Dunedin, USA) and a spectrophotometer (USB2000 +, Ocean Optics Inc., Dunedin, USA). The emitting probe with six fiber bundles delivered incident light to the nanochip. The receptor probe with one fiber bundle delivered reflected light to the spectrophotometer. Both the emitting probe and the receptor probe were fastened on the optical bracket and placed vertically 5 mm away from the reactor chamber. The range of the reflection spectra used was from 400 nm to 650 nm with 0.36 nm interval. Electrochemistry detection was carried out on a PARSTAT 4000 electrochemical workstation (AMETEK Inc., USA) with the nanochip as working electrode (WE), platinum as counter electrode (CE), and Ag/AgCl as reference electrode (RE). The electrochemical responses were monitored by linear sweep voltammetry (LSV). The range of the potential was from 0 to 0.3 V with a scan rate of 0.05 V/s.

2.4. Electrochemical-LSPR for sialic acid detection

The electro-optical spectroscopy system included a reflection spectrum system and an electrochemical system. The spectra and voltammogram were both recorded and saved every 6 s, simultaneously. In order to detect sialic acid, mercaptophenyl boronic acid a thiol containing boronic acid, was modified on the nanochip through stable metal-S covalent bonds. PBS with the pH value of 7.4 was taken as the solvent for sialic acid as the mercaptophenyl boronic acid has special binding affinity with sialic acid in physiological environment with pH value of 7.4. The sialic acid was prepared with different desired concentrations, 0.05 mM, 0.1 mM, 0.2 mM, 0.5 mM, 1 mM, 2 mM and 5 mM, respectively. For specificity detection, sodium chloride, potassium chloride, L-glutamic acid, human serum albumin, uric acid, lactic acid, and ascorbic acid were applied as control groups. The concentrations of these substances were all 1 mM with PBS as solvent. In addition, the same batch of the functionalized nanochip were tested with 1 mM sialic acid for 1 day, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 15 days, 30 days, and 50 days for stability verification. After each measurement, the nanochip was washed with 0.5 mL PBS for three times. Parallel experiments for each concentration were tested 5 times. All detections were performed at room temperature (~20 °C).

3. Results and discussion

3.1. Electro-optical spectroscopy system

The electro-optical spectroscopy system was based on gold/silver nanoparticles modified nanochip (Fig. 1A). The nanochip was used as the optical device in reflection spectrum system and also as the electrodes in electrochemical system (Fig. 1B). Plasmon induced charge separation were concentrated on the metal nanoparticles surface, which resulted in excited energetic charges of the hot-electrons and hot-holes (Fig. 1B inset). If the electrons energy exceeded the work function of the material, photoemission would be generated from the photoexcited

Download English Version:

https://daneshyari.com/en/article/7228982

Download Persian Version:

https://daneshyari.com/article/7228982

Daneshyari.com