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Combining localized surface plasmon resonance with anodic stripping voltammetry for heavy metal ion detection

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ABSTRACT

In this proof-of-concept study, we proposed a dual detection method for heavy metal ions based on nanostructured sensor device. This sensor device, named nano Lycurgus cup array, was characterized with hybrid structure of nano-scaled cups and gold nanoparticles. The hybrid periodic nanostructure could trigger localized surface plasmon resonance (LSPR) phenomenon, which was highly sensitive to refractive index changes. Then electrochemical measurement of anodic stripping voltammetry (ASV) was combined with LSPR for synchronous heavy metal ions detection, i.e., galvanizing metal ions onto the surface of the nanodevice whilst quantitatively recording electrochemical signals. Combining the electrochemical method with LSPR measurement, the dual detection system demonstrated a detection limit of part-per-billion level for aqueous heavy metal ions, such as lead, copper, and zinc. The LSPR measurement demonstrated a higher signal to noise rate (SNR) than electrochemical measurement and promising accuracy even with the presence of mixed solution, and was proved immune to the mechanical fluidic disturbance during the stripping phase which would deteriorate electrochemical signal in traditional electrochemical voltammogram. By presenting electrochemical signals on the dimension of LSPR, our method could be applied in highly integrated detection systems for on-spot detection.

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1. Introduction

Heavy metal ions, such as lead, zinc, and copper pose great threats to the public health when traces of these elements presented in soil and water exceed regulation level. Long-term exposure to heavy metal contaminated environment, even at very low exposure extent, usually could result in serious physiological compromises, such as neural disorder and cognitive deficits [1]. For qualitative and quantitate determination of heavy metal ions, numerous methods have been proposed, including inductively coupled plasma mass spectroscopy (ICPMS) [2,3], atomic absorption/emission spectroscopy (AAS/AES) [4–6], quantum dots [7–9], X-ray fluorescence reflection [10,11], and even immunoassay-based surface plasmon resonance [12–14]. However, these technologies required either bulky expensive equipment or complicated biomaterial binding processes. For point-of-care heavy metal detection, these devices were not widely used due to their cost or instability, especially for biomaterial-modified sensors. Low-cost, label-free, and reliable point-of-care monitoring devices are still in great need for pollutant detection and health care.

One of the most common utilized techniques in laboratory for detection of heavy metal ions was anodic stripping voltammetry (ASV) [15,16]. ASV is capable of determining the categories of heavy metal ions with the corresponding concentrations, based on different stripping potential and the corresponding peak height. Nevertheless, there still were several limitations to ASV [17,18]. First, for the stripping process of ASV measurement, like most of the electrochemical measurement processes, a totally quiescent environment was often required in order to avoid any possible mechanical disturbances, which might result in artifacts like sudden spikes. In other words, ASV can only detect metal ions in quiescent liquid environment, which usually could not be applied in most systems that requires dynamic measurement. Secondly, for anodes of different materials and structures, the stripping peaks presented in the results also variates [15,16]. Finally, the working electrodes for ASV were usually made of mercury, which may contaminate the environment.

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Surface plasmon resonance (SPR), as well as localized surface plasmon resonance (LSPR) spectroscopy of metallic nanoparticles was one of the highly sensitive techniques that could respond to refractive index changes on the contacting surface [19]. Surface plasmons are coherent delocalized electron oscillations on a metallic surface. Based on the interface condition, resonance can be triggered between the surface plasmon and an incident light beam, resulting in energy absorption in certain regions of the light spectrum [20]. Noticing that LSPR is extremely sensitive to the interface's boundary condition, which is largely determined by the refractive index of medium adjacent to the metallic surface, theoretically the molecular changes on the surface can be detected [21,22]. On such basis, many efforts have been made to combine SPR or LSPR with electrochemistry in detecting heavy metal ions. Wang et al. firstly purposed to detect heavy metal ions by combining SPR and ASV [23]. By observing the coupling of SPR angular shift and electrochemical current signal, they were capable of measuring the concentrations of divalent copper in solution. However, the entire detecting device was too bulky for point-of-care environmental monitoring since SPR often employed complex optical pathways. Recently, Cheng et al. utilized a dual-detection platform for divalent copper ions in early Parkinson's disease diagnosis [24]. The immobilization of α-synuclein, a protein reported to bind strongly to divalent copper ions, onto an Au nanostructured indium tin oxide (ITO) surface enhanced differential peak voltammetry (DPV) peak current intensity, meanwhile provided a bathochromic shift in absorbance spectrum. This technique, despite being very sensitive to divalent copper ions, was faced with the challenge of maintaining the vitality of α-synuclein and insensitivity to other heavy metal ions.

To our knowledge, no reported research has been conducted to study the LSPR response of nanostructured surfaces to heavy metal ions. In this paper, we report a dual-detection method combining ASV with LSPR to analyze trace aqueous heavy metal ions. We based our detection system on a previously-reported nanostructured device called nano Lycurgus Cup Array (NanoCA) [25,26]. Firstly we calibrated the NanoCA by performing ASV while recording the LSPR response simultaneously. We then respectively examined heavy metal ions of lead, zinc, and copper for their ASV and LSPR responses. Finally we tested our detection system by analyzing an unknown mixed sample, and the results derived from the electrochemistry and LSPR response show promising integrity. Our detection system can be developed into portable micro-sized devices for point-of-care environment and healthcare monitoring relating to heave metal ions.

2. Experiment

2.1. Nanodevice fabrication

In order to reduce fabrication cost, NanoCA was obtained using the replica molding process where the master nanocone pattern (nanocone heigh was 500 nm, and pitch 350 nm) was fabricated on a glass substrate using the laser interference lithography patterning and reaction ion etching technique [24,26]. Cleaned and silanized with dimethyl dichlorosilane solution for 30 min and rinsed in ethanol and deionized water, the two-dimensional square lattice was transferred to a flexible and optically transparent polyethylene terephthalate (PET) film using nanoreplica molding process: 5 μL of UV-curable polymer (NOA-61) was evenly spread on the top of the nanocone master and a PET sheet of 250 μm thick was carefully put on top of the polymer, to avoid the bubble formation and to act as a substrate. The UV polymer was cured with a UV light-curing flood lamp system (Dymax EC-Series) with average power density of 105 mW/cm^2 for 60 s at room temperature. The

nano-patterned PET substrates was then peeled off carefully from master mold. Finally in order to make the structure surface plasmon active, a thin adhesive layer of Titanium (5 nm) was deposited and followed by 90 nm of metal layer of gold, and the gold nanoparticles were deposited onto the sidewalls synchronously using a six pocket e-beam evaporation system (Temescal). (Appendix A in Supplementary material is the Schematic overview of the replica molding fabrication process.)

Fig. 1a and b shows the scanning electron microscope (SEM, XL30-ESEM, Philips, Netherlands) image of the device in normal view and cross-sectional view respectively. In the normal view, two-dimensional periodical pattern was observed. Whilst in the cross-sectional view, the cup structure and the deposited gold nano particles (marked with white arrows) were observed. The SEM images demonstrated that cup arrays of nanoscale (average diameter of a single nanohole is ~100 nm) were successfully imprinted onto the substrate and gold particles (average diameter is ~10 nm) were deposited to the structural surface. The NanoCA film was finally pruned to size of 2 mm × 4 mm, serving as the sensing component.

2.2. LSPR measuring system

As shown in Fig. 1c, the LSPR measuring system mainly consisted of two parts: the light source and the spectrophotometer receptor. The light source used in LSPR detection was a halogen cold light source (DT-MINI-2, Ocean Optics Inc., Dunedin, USA). A light emitting probe with fiber bundle attached to the light source, allowing small region illumination on the NanoCA. Similarly, the spectrophotometer (USB2000+, Ocean Optics Inc., Dunedin, USA) was connected to a light receptor probe with fiber bundle to allow the regional transmission spectrum recording. Both the emitting probe and the receptor probe were immobilized with optical brackets, and vertically placed 1 cm away from the electrochemical reactor chamber. Collimating lens was utilized to ensure the light path was vertical straight. (Appendix B in Supplementary material is the photograph of the experimental apparatus.) During the entire experiment, the spectrophotometer recorded the transmission spectrum every second. The transmission spectrum, by the virtue of plasmonic tuning, would reveal the refractive index changes of the NanoCA surface caused by electrochemical interactions. The recorded transmission spectrum ranged from 300 nm to 1000 nm with 0.5 nm increment.

Preliminary experiments, which measured the LSPR responses during electrochemistry process on centre and margin of the NanoCA, indicated little differences among those sampling spots. Actually, according to published reports [27,28], the deposition period of ASV was capable of forming homogeneous atomic coverage by ions reductions, and was one of the electrochemical atomic layer epitaxy (ECALE) methods for compound semiconductors formation. Therefore the central spot was believed to represent the entire atomic activities of the electrode, and was therefore used for location of data acquisition. Also the central region of NanoCA was less likely to suffer from deformations, nanocup distortion and substrate distortion, for example, caused during fabrication.

2.3. Electrochemical measuring system

Another component in Fig. 1c is the electrochemical measuring system. The measuring system for heavy metal detection included a standard three-electrode system and a perfusion system. Instead of using traditional gold electrode for working electrode (WE), the NanoCA device was utilized as working electrode whilst platinum and Ag/AgCl were used as counter-electrode (CE) and reference electrode (RE), respectively. Original electrochemical data and primary data processing were based on electrochemical workstation