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Aluminum nanopyramid array with tunable ultraviolet–visible–infrared wavelength plasmon resonances for rapid detection of carbohydrate antigen 199

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ABSTRACT

Aluminum-based localized surface plasmon resonance (LSPR) holds attractive properties include low cost, high natural abundance, and ease of processing by a wide variety of methods including complementary metal oxide semiconductor process, making itself having an edge over conventional ones induced by noble metal. However, the inherent drawbacks of plasmonic mode limited on UV–green wavelength, low refractive index sensitivity, as well as heavy-shape-dependence greatly prevent aluminum plasmonics from real-life biosensing. Here, we demonstrated a uniform quasi-3-dimensional Al nanopyramid array (NPA) structure with tunable ultraviolet–visible–infrared (UV–vis–NIR) plasmon resonances for biosensing. By changing the reflection measuring angle, we could easily obtain typical peaks simultaneously exhibited on the reflectance spectrum across UV–vis–NIR wave region. The Al NPAs carried out high refractive index sensitivities which even comparable with that of noble metal, and can be used as a biosensor for directly detecting cytochrome c and carbohydrate antigen 199 in air after the sensing surface was washed cleanly and dried; the limits of detection were determined to be 800 nM and 29 ng/mL, respectively. Our proposed work therefore initiates the low-cost, high-performance biosensing using aluminum plasmonics, which would find wide applications in rapid diagnosis, mobile-healthcare and environmental monitoring.

1. Introduction

Localized surface plasmon resonance (LSPR) in metallic nanostructures and nanoparticles has been playing a pivotal role in various fields, including sensing, imaging, color display, information processing, and energy harvesting, due to its unique and outstanding manipulation of light (Atwater and Polman, 2010; Schuller et al., 2010; Yokogawa et al., 2012). One of the most conspicuous applications empowered by such plasmonic resonance is biosensing, which is regarded as a crucial component for bio-interaction analysis, early diagnosis, and portable medical supervision in mobile healthcare (Free et al., 2013; Li et al., 2015). Recent years have seen achievements of exquisite size and shape control in the synthesis of noble metal nanoparticles (Ament et al., 2012; Guo and Kim, 2011; Sannomiya and Vörös, 2011) and nanostructures (Gordon et al., 2008; Li et al., 2015; Stewart et al., 2006; Wang et al., 2014) (i.e. gold, silver, and platinum), and their extensively applications in biological and chemical sensing. Unfortunately, the intrinsic properties and high price of these noble metals, as well as their incompatibility with the popular manufacturing scheme that incorporates complementary metal oxide semiconductor (CMOS) process, present significant limitations for their large-scale use (Lohse et al., 2014; O Brien et al., 2014; Schade et al., 2014). Moreover, for Au-mediated plasmonic resonance, interband transitions are supposed to cause a dissipative channel at wavelengths below 550 nm, while the nanostructures made of Ag are extremely vulnerable to color degradation resulting from oxidation and sulfidation (Naik et al., 2013; Tan et al., 2014). These factors practically prohibit the adoption of those precious metals as a material candidate for widespread use.

Meanwhile, aluminum (Al) holds attractive properties including low cost, high natural abundance, high stability (because of the surface oxidation layer), and ease of processing by a wide variety of methods including CMOS process, making Al LSPR having an

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edge over conventional noble plasmonic materials (e.g. Au and Ag). Additional optimistic aspects of Al encompass neutral tint, broad resonance, and good adhesion to diverse substrates (Clausen et al., 2014; Knight et al., 2014; Olson et al., 2014; Zheng et al., 2014). Taking into account the aforementioned appeal of Al, researchers have paid increasing interests on exploring the possibility of biosensing on Al materials, such as surface enhanced fluorescence (SEF) (Chowdhury et al., 2009; Ray et al., 2007) and surface enhanced Raman scattering (SERS) (Liao and Stern, 1982; Zhang et al., 2006), by taking advantages of its excellent optical properties of LSPR in the region from deep ultraviolet (UV) electromagnetic spectrum (Knight et al., 2014). Despite its potential, the exploitations of Al in plasmonics, especially for refractometric biosensing, are still in their infancy and facing a variety of problems and challenges.

On one hand, recent investigations have been focused on tailoring the plasmonics into the deep UV region, which, when applied to biosensing, are beneficial for the SEF and SERS, however, bring about troubles for refractometric biosensing, including the photo-toxicity to biological components and the detection noise from absorption band and auto-fluorescence by bio-molecules, because UV or blue plasmons match the general electron transition energy for the organic molecules. On the other hand, Al plasmonic nanostructures have been rarely applied to refrectometric biosensing, owning to the limitations of low refractive index (RI) sensitivities of plasmon resonance located in the UV to green wave region (Barrios et al., 2014; Canalejas-Tejero et al., 2014; Norek et al., 2014; Skinner et al., 2008). The inhomogeneity of nanostructures, as well as the oxidization of outer Al layer (Bisio et al., 2014; Chan et al., 2008), decrease the RI sensitivity of Al nanostructure (Bisio et al., 2014; Langhammer et al., 2008). These impacts are even huge on the smaller NPs. The RI sensitivities of plasmonic Al nanostructures are not comparable with that of conventional noble metal, making it difficult for detection trace analytes with concentration range from pM to fM, which are crucial for rapid diagnosis. Therefore, Al plasmonic nanostructure with high RI sensitivities from UV to infrared wave regions for on-demand high-performance biosensing is still a challenge for real-life application.

Herein, we reported a uniform quasi-3-dimensional Al nano-pyramid array (NPA) structure with tunable ultraviolet–visible–infrared (UV–vis–NIR) plasmon resonances for biosensing. The Al NPA with large-area uniform nanosutructure was fabricated through an electrochemical etching method. By changing the reflection measuring angle, we could easily obtain typical peaks exhibited on the reflectance spectrum from UV–vis to NIR wave region. Taken as example, we conducted RI-resolved peak shifts of these LSPRs at 15°-measuring angle, and found that the Al NPAs hold high RI sensitivities which even comparable with that of Au plasmonics. We further demonstrated the Al NPA as a biosensor for one-step detecting cytochrome c (Cyt c) and carbohydrate antigen 199 (CA199) through nonspecific and specific interaction systems, with detection limits up to 800 nM and 29 ng/mL, respectively.

2. Materials and methods

2.1. Materials

Al foil with a thickness of 0.25 mm (99.99%) was bought from Alfa Aesa. Cytochrome c (Cyt c, from horse heart) was from Genview Scientific (US). 1-Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride (EDC) was purchased from Fluka Analytical (US). N-Hydroxysuccinimide (NHS) and polyacrylic acid (PAA, molecular weight=350,000, 35 wt% in water) were supplied by Sigma Aldrich Company (US). NaH_2PO_4 and Na_2HPO_4 were from Da-Mao chemical reagent (Tianjin, China). Ethanol, glycerol, ethylene glycol, isopropyl alcohol, and acetone were obtained from Fuyu chemical reagent (Tianjin, China). Phosphoric acid, citric acid, chromic acid, and perchloric acid were all from Zhiyuan reagent (Tianjin, China). All chemicals and solvents were of analytical grade and were used as received. Phosphate buffer solutions (PBS, 0.1 M) were prepared by mixing the stock solutions of NaH_2PO_4 and Na_2HPO_4, and then adjusting the pH to 7.2 or 2.0. carbohydrate antigen 199 (CA199) antibody, CA199 antigen standards, and alpha-fetoprotein (AFP) antigen standards were all from Fapon Biotechnology (Shenzhen, China) and stored at 4 °C as received. Double distilled water was used throughout all experiments.

2.2. Fabrication of Al NPA substrate

The Al NPA substrate was prepared through denting and then electrochemical etching. A flat aluminum sheet was ultrasonically washed with acetone and isopropyl alcohol, and then was electrochemically polished in the mixture contained perchloric acid and ethanol (v:v=1:3) for 2 min at 10 °C. Then the Al sheet was dented using a silicon mold with square ordered pillar array on its surface with a pressure of approximately 2×10^4 N/cm^2. After that, the pattern was transferred to the Al sheet. The dented substrates were then anodized in 240 mL solution composed of citric acid (2 wt%) and ethylene glycol (2 wt%) and H_3PO_4 (0.01%) at 10 °C with a voltage of 400 V. The Al NPA substrate was finally obtained by etching away the anodization layer in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 63 °C for 40 min.

2.3. Measurements of the reflectance spectra

The measurements were taken on an ultraviolet/visible/near-infrared spectrometer (Lambda 950, PerkinElmer). The incidence angle of the spectrometer can be changed from 8° to 68° at an accuracy of 0.5°. All reflectance spectra were corrected by dividing them with the reflectance spectrum of a silver mirror, which served as a reference only.

2.4. Refractive index (RI) sensitivity measurements

RI sensitivity measurements were performed by submerging the Al NPA in aqueous solutions of glycerine (Gl) with different concentrations (0, 25.96, 41.46, 62.50, and 86.57 wt%), which is a standard procedure for calibration and determination of the bulk RI sensitivity. The RIs are 1.333, 1.355, 1.386, 1.417, and 1.447, respectively. To obtain the 15°-measuring angle in the solutions with different concentrations, we adjusted incident angle of the wave from spectrometer according to the Snell's Law $n_1 \sin\theta_1 = n_2 \sin\theta_2$. The NPA surface was rinsed thoroughly with deionized water after each measurement. Three spectral measurements at each concentration were performed for the standard deviation (s.d.) calculation.

2.5. Cyt c and CA 199 detection in air

The Al NPA was firstly cleaned with UV/O_3 for 15 min, and then was treated with PAA solution (0.02 M, pH 5.0) for 30 min. These treatments ensured that the entire Al_2O_3 surface was covered by a self-assembled PAA layer containing pendent carboxyl groups. The unreacted PAA molecules were washed away with sufficient phosphate buffer (pH=7.2) and deionized water sequentially. Unless it was noted, the same wash-off procedures were conducted before all reflectance measurements in the following Cyt c and CA199 detections.

For Cyt c detection, reflectance spectrum of the PAA-modified