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Au nanoparticles decoration of silica nanowires for improved optical bio-sensing

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ABSTRACT

In this work we study the potential of silica nanowires (NWs) decorated with Au nanoparticles (NPs) as novel optical platform for plasmonic biosensing. These composite materials combine the high white-light scattering of silica NWs with the selective absorption of the localized surface plasmon resonances (LSPRs) of the metal NPs, generating efficient light trapping just at the LSPR wavelengths. In addition, the NWs offer a macroporous framework for a three-dimensional (3D) distribution of the Au NPs, easily accessible by biomolecules. These optical and morphological pecularities, make the decoration of silica NWs with metal NPs a promising strategy for improved plasmonic biosensing. We fabricated silica NWs by thermal oxidation of silicon (Si) NWs, grown by plasma enhanced chemical vapor deposition (PECVD). The silica NWs were decorated with Au NPs by evaporating and then de-wetting via thermal annealing Au thin films. The biosensing ability of these materials was studied and compared with the performances of similar Au NPs deposited on glass substrate, forming a planar (two-dimensional, 2D) distribution. A careful morphological analysis about the NWs and their Au NP coverage, including their vertical distribution across the NW film, was performed by high resolution scanning electron microscopy (HR-SEM) and energy dispersive X-ray spectroscopy (EDS) experiments. The morphological information was used for building a theoretical model through 2D finite element modeling (FEM) able to describe the optical behavior of the new transducers and their functional properties, as well as to predict the evolution of the sensing performance of the transducer when passing from a 2D to a 3D distribution of plasmonic NPs. The Au NPs decorated NWs were finally modified with a self-assembled monolayer of BSA (bovin serum albumin) and the specific binding with the related antibody monitored during the time.

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1. Introduction

The need for rapid, specific, sensitive, inexpensive, in-field and real-time detection of biomolecules analytes has increased biosensors importance especially in fields such as environmental monitoring, pollutant detection, medical diagnostics, and biological warfare defense.

The phenomenon of Localized Surface Plasmon Resonance (LSPR), which results from the plasmonic response of noble metallic nanoparticles to incident electromagnetic waves [1], can be exploited in the label-free sensing of analytes. Binding of analytes on metallic surfaces causes a change in the local refractive indices (RIs) of the surrounding dielectric, resulting in either a shift in the spectral extinction peak or a change in the peak intensity [2–4].

When compared to other optical transducing platform based on plasmon phenomena such as Propagating Surface Plasmon Resonance (SPR) [5,6] or Surface Enhanced Raman Spectroscopy (SERS) sensors [7,8], LSPR systems have some advantages including the use of a simple analytical set-ups in addition to being portable and practical. Transmission spectrometry, which is relatively simple and inexpensive, can be used for LSPR sensing of 10–100 nm particles in the UV–vis region [9].

Much work has been devoted to develop sensors from silver and gold NPs suspended in solution [10,11]. However, the strong demand for rapid, cost-effective, and high-throughput measurements has led to the development of a chip-based assay consisting of metal NPs immobilized on a substrate, a so-called two-dimensional (2D) chip [12–14]. To this purpose, chemical immobilization can be achieved via compounds such as alkanethiols [15,16], but also physical immobilization techniques as well gave successful results [17–19]. Well-ordered 2D arrays of monodisperse particles have the advantage of presenting narrow

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well defined extinction bands so that an easy theoretical prediction of optical response of such systems using the discrete dipole approximation (DDA) method is possible [20,21].

However, such plasmonic devices that rely solely on changes in the dielectric permittivity of the environment often suffer from low sensitivity (typically <10 nm spectral shift for spherical nanoparticles) [22,23] that originates from fairly small variations in the refractive index because of the low density of nanoparticles in the defined surface area.

Recently we have showed as silica nanowires (NWs) decorated with Au and Ag NPs can act as efficient RI sensors [24], due to their morphological and optical features, which are also very attractive for biosensing applications. First, they form a dense three-dimensional (3D) ensemble of metal NPs, easily accessible to liquids, vapors, or biomolecules due to the macroporous structure of the NW forest and the large interparticle distance. Second, they offer absorption enhancement at the LSPR wavelengths because of light trapping effects in the NW forest. To the best of our knowledge, only a few attempts have been made to create three-dimensional (3D) LSPR structures to increase the sensing performance of metal NPs transducers.

Jiang and co-workers [25] fabricated multilayer structures composed of Au nanoparticles (NPs) and polyelectrolyte by spin-assembly or spin-assisted layer-by-layer (SA-LbL) deposition techniques and discussed their optical properties by correlating them to the density of the metal NPs into the multilayer structure. Plasmon resonance peaks from isolated NPs and interparticle interactions were revealed in their UV–vis extinction spectra. In Refs. [26,27] metal-coated macroporous films were realized using silica spheres and used as transducer platform to measure a typical antigen-antibody binding event. Ye et al. [28] demonstrated the improvement of bulk refractive index sensitivity of 3D self-assembled Au NPs multilayer structures obtained by the alternate deposition of a bifunctional cross-linker and Au NPs. The number of deposition cycles, in this case, was crucial in obtaining the desired sensor performance. Analogously, Guo and coworkers [29] realized a 3D Au nanoarchitecture by layer-by-layer (LbL) deposition of Au NPs and multiwalled carbon nanotubes (MWCNTs). After demonstrating the improvement of the bulk refractive index (RI) sensitivity of these multilayered Au NPs with respect to a monolayer of AuNPs on a glass chip, they experimented the beneficial role of the 3D transducing platform also for the study of a biomolecular binding experiment.

In this work, we study the biosensing feasibility of silicon NW forests decorated with Au NPs. In particular, silica NW were obtained by thermal oxidation of Si NWs grown by plasma enhanced chemical vapor deposition (PECVD). The NWs were decorated with metal Au NPs by de-wetting thin metallic films evaporated on the NWs [24]. The proposed preparation techniques offer the stability and reproducibility typical of a physical deposition technique while keeping a degree of flexibility required for producing a functional transducer platform. In order to compare the sensing performance of the 3D plasmonic structure respect to a traditional 2D configuration, Au NPs on glass substrate were also prepared in the same conditions used for the decoration of the NWs.

Structural and morphological information were obtained by Scanning Electron Microscopy in normal and cross section configuration. They were used to build a theoretical model through a 2D finite element model (FEM) able to describe the optical behavior of the transducers and their functional properties. In the numerical model the scattering in the NWs framework and the plasmonic absorption of metallic NPs were taken into account. Numerical results found a confirmation in experimental optical characterization.

Finally, a functional characterization of the realized transducer platform was carried out thus demonstrating an increase of the bulk RI sensitivity in these 3D structure with respect to the classical 2D chip. The improved performances of the 3D structure with respect the 2D were also predicted by the theoretical model. After this calibration step, immobilization of BSA (bovine serum albumin) molecules was monitored, and the consequent binding with anti-BSA antibodies was detected. The label free detection of the interactions is easily achieved thus confirming the promising outcomes of the proposed optical sensor.

2. Experimental details

2.1. Silica NWs decorated with Au NPs

Forests of silica NWs were produced by thermal annealing of Si NWs grown by PECVD. First, gold-catalyzed Si NWs were grown by PECVD Si(1 0 0) substrates. To induce the NWs growth, a 1 nm thick Au film was evaporated onto the substrates prior to growth. The growth was performed by using pure SiH_4 as precursor at a total pressure of 1 Torr and substrate temperature of 360 °C. A 13.56 MHz radiofrequency with power density of 50 mW cm^{-2} was used to create the plasma. In these growth conditions 15–20 μm long Si NWs with average diameter of 150–200 nm at the bottom and tapered shape can be obtained [30]. After the growth, the Si NWs were oxidized to form SiO_2 (silica) NWs by means of a thermal treatment in a convection oven (controlled steam atmosphere) at 980 °C for 8 h. The decoration of the silica NWs with Au NPs was obtained by thermal evaporation of a thin film of Au on the silica NWs. The nominal thickness was fixed at 12 nm and estimated by considering the deposition rate obtained in the case of evaporation on a flat substrate. Au NPs were obtained as a result of metal de-wetting at high temperatures (∼800 °C) for 6 min.

In order to compare the sensing performance of the 3D plasmonic structure with respect to a traditional 2D configuration, Au NPs on glass substrate were also prepared in the same conditions used for the decoration of the NWs, i.e. thermal evaporation of a 12 nm thick layer of Au onto glass substrates and successive thermal treatment at 800 °C for 6 min.

2.2. Morphology

The morphology of the silica NWs decorated with metal NPs was investigated by SEM both in plan-view and cross-sectional geometry. EDS line scan profiles were acquired in cross-section in order to study the compositional distribution of gold, silicon and oxygen along the thickness of the NWs film. A Zeiss NVISION 40 dual-beam Focused Ion Beam machine, equipped with a high resolution SEM Gemini column and an Oxford 350 x-act EDS spectrometer, was used for SEM and EDS experiments. SEM observation were also performed onto 2D samples containing gold NPs deposited on glass substrates.

2.3. Modeling and simulation

The optical properties of the system were investigated through finite element simulations. A numerical model for the diffuse reflectivity of disordered NWs decorated with plasmonic nanostructures was developed with the RF Module of COMSOL Multiphysics platform. The model has taken into account the morphological characteristics of the system, the scattering events of the light in the NWs mats and the plasmonic absorption of metallic NPs. The model well described the reflectivity measurements and the ability of the system to perform real-time monitoring of molecular adsorption. We explored several key parameters in order to know how the optical properties of the local environment influence the LSPR conditions.

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