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On the importance of optical contacts in gold hybrid structures for enhancement of localized surface plasmon resonance sensing

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ABSTRACT

Gold/polymer hybrid structures consisting of gold-coated dielectric particles resting on a thin gold mirror layer are investigated in view of their optical sensitivity toward molecular adsorption. Three different methods, i.e., metal evaporation, sputtering, and wet chemistry, are used to prepare metal coatings of different roughness and different extent to which the dielectric cores are engulfed by the metal. Further, the presence of contacts between the dielectric cores is varied. As a well-understood organic monolayer system, the sensitivity of the different hybrid structures toward adsorption of octadecanethiol is studied from ethanolic solution. Thereby, it is found that besides surface roughness, core–core contacts are important for the layers' optical response, which is governed by surface plasmon effects. The system prepared by means of wet chemistry that allows for core–core contacts achieves an about 4 fold higher sensitivity toward molecular adsorption as compared with that prepared by evaporation.

1. Introduction

Surface plasmon resonance (SPR) sensors based on the excitation of surface plasmon oscillations in thin gold films or gold nanoparticles have become well-established and highly reliable tools in modern biochemical and biomedical analysis [1]. Besides ease of application that requires only moderate experimental efforts, it is particularly the inertness of the gold layer used as sensing surface toward biochemical substances and buffer solutions that accounts for the success of this label-free transducer technology [2].

SPR comes about by confinement of the free electrons of a metal by geometrical means, i.e., at a surface or within a metal nanoparticle. In these cases, oscillations of the free electron system, i.e., the plasma, exist that are bound to said surface or nanoparticle. Those oscillations with frequencies located below the bulk plasma frequency ω_0 may become visible as additional features in the optical spectra of these systems. Plasmon excitations at surfaces travel along the metal-dielectric interface and therefore are called "freely propagating surface plasmons" (PSPs), while plasmon oscillations of a nanoparticle are necessarily localized at that particle and thus are called "localized surface plasmons" (LSPs). While PSPs impose some particular conditions on their excitation by optical means in view of the angle of incidence and thus on the rigidity of the experimental set-up applied, LSPs are observable in the optical spectra of the nanoparticles, e.g., obtained by transmission or reflection measurements from nanoparticle assemblies, at arbitrary incidence.

For LSPR sensing, particularly surface-adsorbed nanoparticles are of interest due to more comfortable handling in multiple-step process protocols. Monolayers of basically spherical metal nanoparticles, however, show typically only weak extinction of the order of about 0.1 O.D. units [3], thereby limiting the dynamic range of the sensor as well as its practical application, and thus leaving the commercial field of SPR sensing mainly to systems based on PSPs so far.

About one decade ago, a new approach has been suggested for surface plasmon sensing, in which gold nanoparticles are formed above a thin gold film, however electrically isolated from the latter by an interlayer of dielectric nanoparticles [4]. Such "hybrid structures", which seem to combine the physical properties of PSPs and LSPs, show an amazingly strong optical extinction of up to 3 O.D., when interrogated by visible light in reflection [4,5]. Thus, while the optical extinction is in the range of that observed with PSPs, the effect is observable under basically arbitrary angles and thus resembles the most important property of LSPs [6]. Most interestingly, the sensitivity of these structures toward molecular

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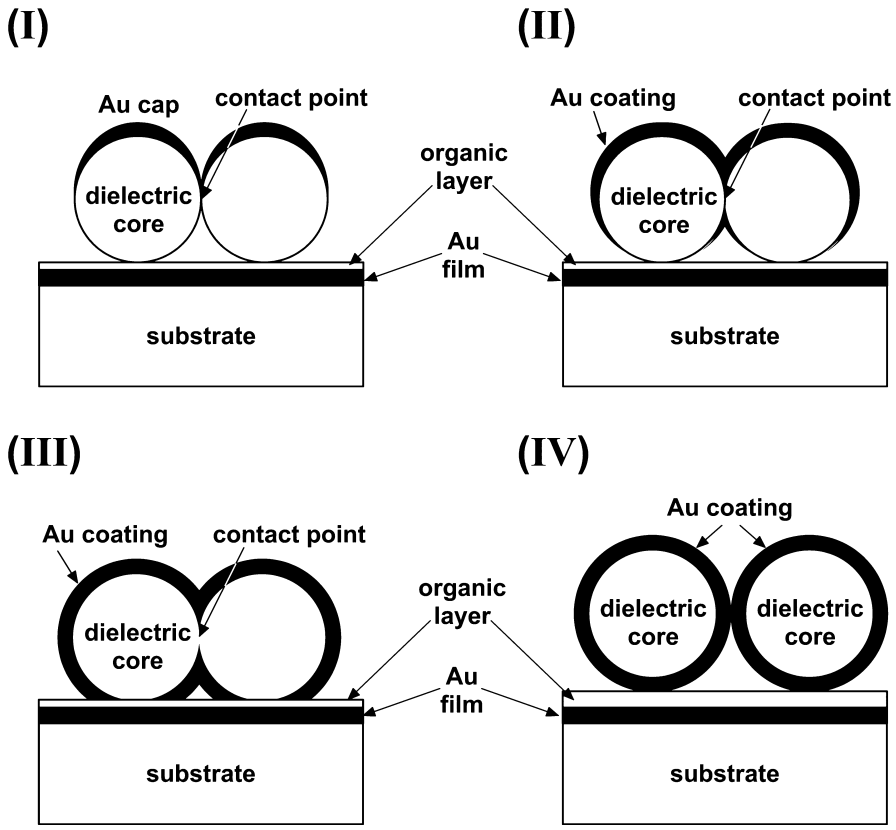

Fig. 1. Schemes of the four different hybrid structures studied. Polystyrene (PS) nanoparticles are adsorbed on a thin gold film evaporated on a PS substrate. Subsequently, the PS particles are coated with gold by evaporation (**I**), sputtering (**II**), or wet chemistry (**III**). In the case of (**IV**), the PS particles were coated with gold by wet chemistry before surface adsorption and therefore do not allow for direct contact points between neighboring dielectric cores.

adsorption as determined by the shift in the LSPR extinction peak [5] is the same as that known from the well-established PSP resonance (PSPR) systems [7].

Accordingly, application of hybrid structures to SPR sensing facilitates the experimental requirements, allowing a simple fiber optical set-up for plasmon excitation and read-out. By applying single optical fibers, detection areas of only few microns have been reported [8], thus paving the way for multiple-analyte detection protocols on a single surface.

One drawback of the reported hybrid structures, however, is the need for repeated gold coating of the surface by means of ultrahigh vacuum (UHV) evaporation. This is tedious and costly, and therefore recently it was thought of replacing at least the second step of metal deposition, i.e., the formation of the gold nanoparticles on the dielectric nanoparticle interlayer, by a deposition method based on wet chemistry. Surprisingly, it was found, however, that such structures exhibit an even higher response toward molecular adsorption [8].

In this article, we aim at shedding light on these newly observed effects in hybrid structures by investigating four closely related systems. As sketched in Fig. 1, these structures differ in the way of forming the metal nanoparticle layer on the dielectric nanoparticle interlayer. In Fig. 1a, this is achieved by the previously mentioned method of gold evaporation, which yields cap-shaped nanoparticles coated with gold from top to down their equator (**I**). The second scheme as shown in Fig. 1b is achieved by sputtering of gold onto the surface-adsorbed dielectric nanoparticles, which yields coating also of the lower hemisphere of the dielectric nanoparticles, however, with decreasing layer thickness from top to bottom (**II**). The third structure shown in Fig. 1c is achieved by wet chemistry, which yields an even coating of the entire free surface area of the dielectric particles (**III**). The fourth structure as depicted in Fig. 1d, finally, is achieved by first coating the dielectric particles by means of wet chemistry in suspension, followed by their deposition on the gold surface (**IV**). This structure therefore circumvents direct contacts between the dielectric nanoparticles as unavoidable in the other three cases. In the case of structure **IV**, the flat gold films were first coated with organic layers to ensure that the gold nanoparticles deposited stayed electrically isolated.

All other parameters, such as the formation of the flat gold film on a polystyrene substrate, the deposition of the dielectric particles as well as their size, were kept identical for all prepared surfaces to allow direct conclusions about the effect of the differences in the preparation of the gold coatings on the dielectric nanoparticle interlayer.

2. Materials and methods

2.1. Materials

Polystyrene (PS) latex beads with a nominal diameter of 350 nm (standard deviation <5%, 2.6 wt% suspension in water) were purchased from Polysciences, Inc. (Warrington, PA). As substrates, the inner face of the lids of Falcon PS cell culture plates was utilized (FALCON cat. no. 3002, BD Co., Germany), which is divided in 96 wells of ~9 mm diameter with a rim height of ~1 mm. Ethanol (analytical grade), NaCl, disodium hydrogenphosphate (Na_2HPO_4), sodium dihydrogenphosphate (NaH_2PO_4), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4{\cdot}3H_2O$, 99.9 + %), polyethyleneimine (PEI, MW 25,000 Da), polysodium-4-styrenesulfonate (PSS, MW 70,000 Da), poly(allylamine hydrochloride) (PAH, MW 15,000 Da),