Plasmonic properties of silver nanocube monolayers on high refractive index substrates

Adam Bottomley[1], Daniel Prezgot[1], Anatoli Ianoul[1]

[1]Department of Chemistry, Carleton University, Canada
*corresponding author, E-mail: anatoli_ianoul@carleton.ca

Abstract

Extinction spectra of nanocubes supported by a symmetry breaking dielectric substrate are very different from those in solution. In this work we varied the refractive index of the substrate in order to optimize the refractive index sensitivity (RIS) of supported silver nanocube monolayers. We found that on thin (5-7 nm) silicon films the RIS is characterized by the figure of merit (FOM) for the quadrupolar plasmonic mode as high as 5.0, making silicon supported silver nanocube monolayers a promising sensing platform.

1. Introduction

Localized surface plasmon resonances (LSPR) of noble metal nanoparticles have been studied intensely in recent years. The ability to control and tune LSPRs is crucial to both understanding and application in the field of plasmonics [1]. Progress made in fabrication methods [2] and theory for metal nanoparticles has allowed for development of novel optical and sensing materials [3]. When the LSPRs of these particles are excited, a strong enhancement of their local electric fields occurs at the surface of the particles. This field enhancement allows for increased signal from optical techniques such as Raman [4,5], IR [6], and fluorescence [7-10] spectroscopy. The spectral extinction spectra of LSPRs are also very sensitive to the refractive index of their local environment making them an excellent platform for sensing [3,11]. The plasmonic signature of metal nanostructures can be influenced in several ways by modifying their size, shape, and material [1,12], but also through interparticle interactions [13] and particle substrate interactions [14,15]. Such investigations have shown unique properties such as collective modes and Fano like resonances [16].

Plasmonic signatures of nanoparticles that are supported by a dielectric material exhibit significant changes in their LSPRs when compared to particles in colloidal solutions. The most notable change is the splitting of a single dipolar plasmonic mode into two distinct modes [16-18]. When dealing with spherical nanoparticles these two new modes correspond to dipolar oscillations with orthogonal polarizations [18]. However, when nanocubes are deposited on a dielectric support their substrate interaction leads to plasmon mode hybridization, resulting in two distinct bands with corresponding charge oscillations located at the opposite sides of the nanocube [14,16-18]. Separation between the bands in the case of cubes was found to be greater than that for the spherical particles dependent on the size [17], edge and corner sharpness, as well as distance from the substrate [19]. Each of these hybrid bands present in the nanocubes is sensitive to the refractive index of their respective environments, one being the substrate and the other the surrounding medium in which the supported layer is immersed [14,16,17]. In the present work we fabricated quasi-periodic arrays of silver nanocubes on substrates with varying refractive indices. This allowed for a series of refractive index sensitivity measurements that relate the changes in refractive index of the substrate to changes in the surrounding medium.

2. Experimental

2.1. Chemicals

Silver nitrate 99+%, polyvinylpyrrolidone (PVP) with a molecular weight of 55000, anhydrous 99.8% ethylene glycol (EG), anhydrous sodium sulfide, and chloroform were purchased from Sigma-Aldrich and used as obtained. 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) was purchased from Avanti Polar Lipids, Alabaster, AL. Ethanol (95%) were obtained from Brampton and used without further purification.

2.2. Preparation of Nanocubes

Silver nanocubes (NC) with an edge length of 55 nm were synthesized according to the procedure described in the literature [20]. Typically, a 100 mL round bottom flask containing 35 mL of EG and a clean stir bar was placed in an oil bath set to 150°C and allowed to heat for 1 h. Using a glass syringe 5 mL of EG containing 0.4 g of dissolved PVP was injected. Five minutes later using a micropipette 400 μL of 3 mM sodium sulfide dissolved in EG was added. After an additional 5 min 2.5 mL of 282 mM silver nitrate dissolved in EG was injected slowly using a glass syringe. Upon addition of the silver nitrate the solution immediately turned black, slowly became a transparent yellow, and then changed to an ochre colour while some plating in the flask occurred. The reaction was monitored by periodically

taking small aliquots out of the reaction flask using a pasture pipette and dispersing it in a cuvette filled with ethanol for UV-visible spectroscopy. The reaction was quenched by placing the flask in an ice bath when the appearance of a small but distinct peak at 350 nm was observed in the spectra.

2.3. Purification of Colloidal Silver Nanocubes

The as-synthesized colloidal nanocubes contained unreacted EG, an excess of PVP. EG and PVP were removed by diluting the colloidal solution with ethanol (1:1 by volume) followed by centrifugation at 12 000 rpm. The precipitate was collected and redispersed in ethanol by sonication. This process was repeated 30 times for complete removal of EG and PVP. The purified silver NC solution was further subjected to washing with chloroform by centrifugation (at least 3 times) prior to LB film preparation. The final volume of the nanocube solution was 4 mL.

2.4. Preparation of LB Monolayers

Nanocube substrates were prepared according to the procedure reported previously [21]. Briefly, a NIMA 311D trough, filled with Milli Q water (18.2 mΩ cm), was used to prepare the Langmuir monolayers of different NC samples. In order to form monolayers, an appropriate amount of each sample was deposited onto the water surface using a micro syringe. Each monolayer was left for 20 min to allow chloroform evaporation. The surface pressure of the monolayer was measured with a paper Wilhelmy plate. Before transferring the monolayer onto solid supports several isotherm cycles were performed to anneal the films to surface pressures in the solid phase. Monolayers of nanocube/DOPC mixtures were transferred onto substrates cleaned with aqua regia and subsequently with mixture of chloroform and methanol at various surface pressures by vertical upward dipping at 2 mm/min at room temperature.

2.5. UV-Vis Measurements

UV-vis spectra of monolayers deposited on the substrates were recorded using a Shimadzu UV-2450 UV-vis spectrophotometer. Spectra were analyzed using GRAMS/AI spectral data processing software. Spectral deconvolution was performed using an appropriate number of mixed Gaussian-Lorentzian functions as well as a linear baseline to achieve the best fit to the original trace while minimizing χ^2 values. To determine the refractive index sensitivities (RIS), the monolayer slides were immersed in water/EG solutions with varying volume percentages and the extinction spectra measured. The refractive indices of the mixtures were calculated from the volume percentages of the ingredients according to the Lorentz-Lorenz equation [22]. The refractive indices of the pure solvents were 1.3334 and 1.4318, for water and EG respectively [22]. The plasmon shifts were plotted as a function of the refractive index. The refractive index sensitivities were obtained from the slope of the linear fitting.

2.6. Topographical Measurements

The topography of the NC monolayers, transferred onto substrates at different surface pressures, was obtained using an Ntegra (NTMDT, Russia) atomic force microscope in semi contact mode in air at 23 °C with 512x512 points per image. A 100x100 μm^2 scanner (Ntegra) and cantilevers with rotated monolithic silicon tips (125 μm long, 40 N/m spring constant Tap 300Al, resonance frequency 315 kHz, Budget Sensors) were used for all topographic measurements. The typical scan rate was 0.5 Hz. AFM images were further processed by Nova image processing software.

3. Results and Discussion

Colloidal silver nanocubes of ~55 nm edge size used in the present study are characterized by an extinction spectrum with a single dipolar LSPR peak at 443 nm, and a small peak at 350 nm [23]. Applications exploiting plasmonic properties often require nanoparticles to be deposited on a solid substrate. We have previously shown that Langmuir Blodgett monolayer technique allows not only effective deposition but also control of plasmonic properties of monolayers of silver nanocubes [14,15,17]. Such monolayers are proven to be effective in enhancing surface enhanced Raman scattering (SERS) signal but also in probing refractive index change in the environment, and therefore represent a powerful sensing platform. Plasmonic properties of supported by a dielectric nanocubes however differ significantly from those in a suspension [1,3,14,23]. LSPR- induced charges in such dielectric substrates disturb the nanocube electric field leading to plasmon mode hybridization with the appearance of two new bands: dipolar (D) and quadrupolar (Q). The charge oscillations for these new bands are located at the opposite sides of the cube: dipolar near the substrate and quadrupolar away from the substrate [1,3,14,23]. The degree of spectral separation between the two bands and the refractive index sensitivity depend on the distance between the substrate and the cubes, contact area and the refractive index (n_{RI}) of the substrate (Figure 1) [1,14,23].

In this work we prepared a monolayer of 55 nm silver nanocubes on several substrates with varying refractive indices. The samples were found to be very homogeneous with very uniform nanocubes (Figure 1a). In addition, to minimize interparticle dipolar coupling the monolayer was prepared from a mixture of nanocubes and a phospholipid DOPC. We have previously shown that by using mixtures consisting of nanocubes and lipids of different kind it is possible to pattern the nanocubes in monolayers. Depending on the lipid properties we were able to obtain homogeneously dispersed nanocubes, as shown in figure 1a. It turns out

that in such monolayers separation between the nanocubes was maintained at ~130 nm (Figure 1b). As a result extinction spectra of supported nanocubes contained only small long wavelength peaks corresponding to dipole-dipole coupling between adjacent cubes, observed at Figure 1c in the 550-700 nm spectral region. We used four substrates with increasing refractive indexes: glass, sapphire, 5 nm Si film deposited on glass, and a 7 nm Si film deposited on glass. Due to plasmonic band hybridization two bands visible in the spectra are observed and assigned to Q and D modes.

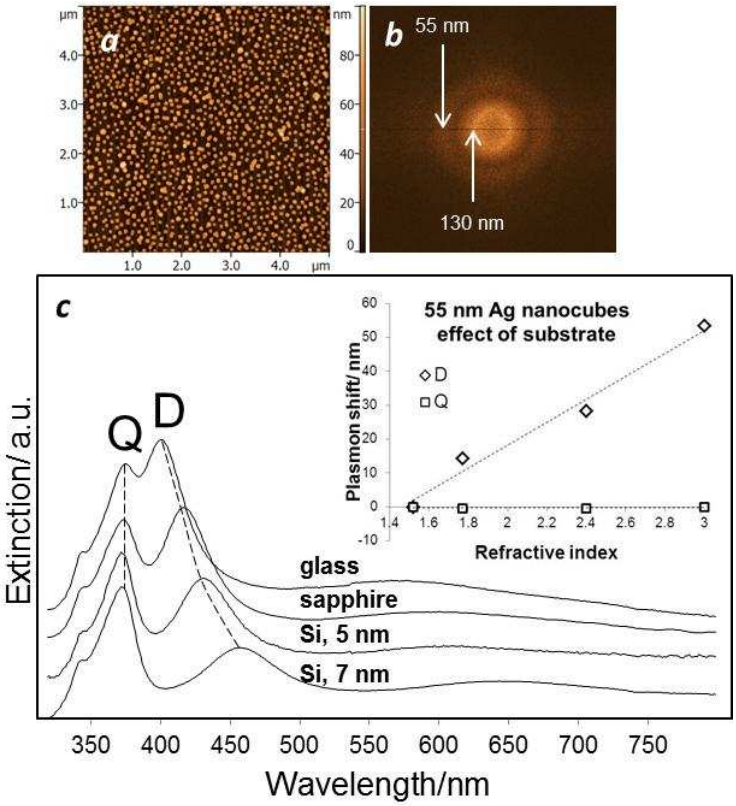

Figure 1: Supported silver nanocube monolayer prepared by Langmuir Blodgett technique: (a) AFM topography and (b) Fast Fourier transform (FFT) images indicate the size (55 nm) and the average inter-particle distance (130 nm); (c) extinction spectra of supported silver nanocube monolayers indicate strong dependence of the dipolar (D) but not quadrupolar (Q) mode on the substrate refractive index.

Since charge oscillations corresponding to the D mode are located near the substrate surface the dipolar band shows strong dependence on the substrate refractive index, and red-shifts by more than 50 nm when the refractive index of the substrate changes from 1.52 for glass to ~3.0 for a 7 nm silicon film (Figure 1c inset). In contrast the quadrupolar mode is insensitive to the substrate refractive index.

At the same time, both modes were found to be sensitive to the refractive index change of the medium (Figure 2). And, since change oscillations corresponding to the Q mode are located at the nanocube side away from eth substrate, it was found to have a stronger dependence than the D mode (Figure 2 inset) [14,23]. At the same time, the nature of the supporting dielectric substrates appears to play a crucial role in our ability to track spectral changes associated with the medium refractive index change. For example, when n_{RI} of the substrates is relatively low, as for glass, where n_{RI}=1.52, upon immersion in liquid plasmon mode hybridization disappears (Figure 2). This is due to insufficiently large refractive index change between the substrate and the medium to induce plasmon mode hybridization. As a result, plasmonic signature of glass supported silver nanocube monolayer immersed in water resembles that of colloidal nanocubes, mentioned before. The main band observed in such monolayer corresponds to dipolar oscillations and show modest sensitivity to the medium refractive index (Figure 2). At the same time, if the substrate has a sufficiently high n_{RI}, as with the 7 nm silicon film (n~3.0), the dipolar and quadrupolar bands remain clearly distinguished even when submerged in high refractive index liquids, such as ethylene glycol (Figure 2). The Q and D bands remain well separated in various solutions- pure water and ethylene glycol. By tracking the position of each band in solvents with increasing n_{RI} we were able to determine the refractive index sensitivity (RIS) of the quadrupolar band to be

~150 refractive index units/ nm, which is about twice as high as for the D mode (Figure 2 inset). Another parameter that is often used in evaluating sensitivity of various platforms to the refractive index change, namely the Figure of merit (FOM), was introduced as a ratio of RIS to the full width at half maximum for a band. From the data obtained in this work we were able to obtain the figure of merit for the quadrupolar band as high as ~5.0. This value is one of the highest reported so far for plasmonic nanostructures.

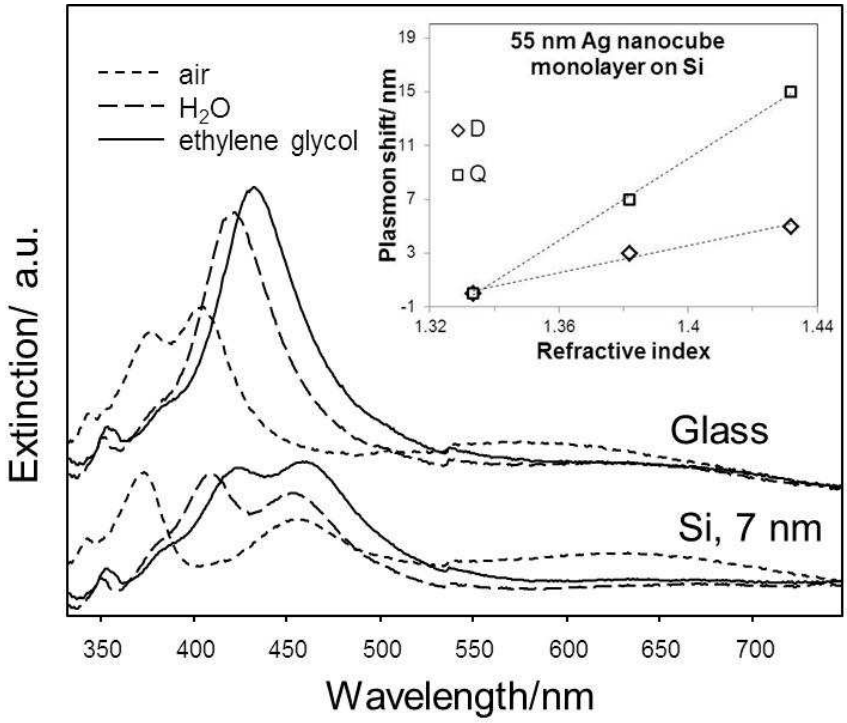

Figure 2: Solution refractive index sensing using nanocube monolayers deposited on glass and on a 7nm thick silicon film. Inset shows solution refractive index dependences of the dipolar (D) and quadrupolar (Q) peaks.

4. Conclusions

In this work we prepared monolayers of silver nanocubes on substrates with various refractive indexes in order to enhance the sensitivity of such plasmonic materials to the refractive index change. We found that by changing the refractive index of the substrate dipolar and quadrupolar plasmon mode hybridization can be carefully adjusted and fine-tuned. As a result, silicon supported silver nanocube monolayers are shown to represent a powerful platform for sensing the refractive index change.

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