Research Article

Growth Kinetics and Sensing Features of Colloidal Silver Nanoplates

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Received 29 July 2018; Revised 10 October 2018; Accepted 28 October 2018; Published 15 January 2019

Academic Editor: William Yu

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This paper presents the growth mechanisms and the plasmon sensing features for a large class of silver nanoplates obtained in the colloidal form. The synthesis is conducted by seed-mediated growth and leads to plates with aspect ratios as large as 20, having localized surface plasmon resonances extending deeply into the infrared spectral region (1000 nm and above). We measure plasmon sensitivity by varying the colloidal local refractive index, and $\Delta \lambda / \Delta n$ sensitivity values up to 500 nm/RIU are obtained. Theoretical considerations regarding the correlation between the refractive index sensitivity and the position of the main localized plasmon resonance band demonstrate that plasmon sensitivity does not depend directly on the nanoparticle shape and aspect ratio.

1. Introduction

1.1. Metal Nanoparticles for Sensing. Metal nanoparticles catalyzed a large research interest because of their applications in several fields such as photonics, electronics, catalysis, sensing, and biological labeling [1–3]. One of the most important features of this kind of nanostructures is interacting with an external electromagnetic field through their conduction electrons, exciting plasmon resonances [4]. The plasmonic behavior of a metal nanoparticle depends on the composition (e.g., the dielectric functions of the material), on the refractive index of the surrounding medium and on several geometrical features, such as shape and size. In a collection of particles, the resonance frequencies are also driven by their spatial arrangements including the distance between them [5–7]. All these facts contribute to determining the quality of nanoparticle response towards a large number of phenomena such as enhanced spectroscopic signals [8–10] or enhanced catalysis [11–13]. In advanced sensing applications, a highly localized field induced by plasmon resonance excitations makes metal nanostructures sensitive probes to detect local variations in the surrounding environment at a molecular level. For example, local changes in the refractive index, due to adsorption of proteins or biomolecules onto the nanoparticle’s surface, can be easily detected by spectral changes. For these reasons, nanoplasmonic sensing is emerging as a simple and extremely sensitive strategy for real-time detection of biological or chemical interactions and it is also suitable for device miniaturization and multiplexing due to the small dimensions of metal nanoparticles [14, 15].

1.2. Seed-Mediated Approach for Nanoparticle Growth. In the last decade, different approaches to produce gold and silver nanoparticles with different plasmonic features have been developed [11, 16, 17]. One of the most used is the so-called “seed-mediated growth” method [18] which is recognized as an easy, straightforward, and low-cost strategy, also suitable for scale up production. The optimization of any synthetic protocol is a fundamental step for tailoring the shapes and sizes of noble metal particles as it gives the possibility to act on a temporal separation of the nucleation and growth stages. In fact, the basics of the seed-assisted
generation of silver nanoplates regard the ability to drive silver platelet growth onto preexisting seeds, thus disfavoring homonucleation events [19]. Different parameters such as seed concentration, nature and concentration of surfactants, nature and concentration of impurities and additives, growth temperature, growth time, and pH values determine the final colloidal features. Herein, in the frame of a seed-mediated growth procedure, we investigate the role played by the reactant addition rate and the concentration of seeds in order to control silver nanoplate aspect ratio and shape. Once we have obtained a range of different colloidal samples having plasmon resonances from near UV (below 400 nm) to near IR (above 1000 nm), we have verified their specific sensing features in terms of refractive index sensitivity, as the dielectric constant of the surrounding medium varies. We have also compared these sensitivities with an analytical model which, up to now, has been tested only computationally.

2. Materials and Methods

2.1. Silver Nanoparticle Preparation. Silver nitrate (AgNO₃, 99.9%), tri-sodium citrate (TSC, 99%), sodium borohydride (NaBH₄, 99%), and hydrated hydrazine (50–60%) have been purchased from Sigma-Aldrich and used as received without further treatment. Deionized water (>18.4 MΩ·cm) was used in all of the synthesis processes. Silver seed solution is obtained by reducing a silver nitrate solution by using sodium borohydride (E₀ = −0.78 V), in the presence of TSC as a stabilizing agent. In particular, we added 0.5 mL of a 20 mM NaBH₄ solution to 10 mL of a 59 mM AgNO₃ one, in the presence of TSC (1 mL, 35 mM). The reaction is conducted at 293 ± 1 K under strong stirring. The as-prepared colloid was then aged for 24 hours before use to ensure a complete reduction of AgNO₃.

Defined aliquots of colloidal seeds, ranging from 20 µL to 1 mL (±1 µL), are mixed with a freshly prepared 20 mL solution of hydrated hydrazine (N₂H₂·2H₂O) and TSC. Each of these former colloids is a reactor (solution A) for the growth of specific silver nanoplates. From here on, a 59 mM solution of AgNO₃ (solution B) is added dropwise to solution A, by varying the addition rate from 0.1 mL/min to 10 mL/min. The addition rate has been controlled by using a peristaltic pump with an error below 0.01 mL/min. All the experiments have been performed at 293 ± 1 K in a thermostatically controlled room. The obtained colloidal dispersions have colors which change from yellow to orange, pink, red, green, and finally to blue (Figure 1), according to the shape and size of the nanoplates (from here on AgNPTs). The blue color corresponds to the biggest AgNPTs.

2.2. Characterization Methods. Once the colloid has been produced, a range of spectroscopic and morphologic characterizations has been performed. Some of them involve the colloid itself, and others have been performed after the deposition of some drops of the colloid under investigation onto a suitable surface (flat and conductive). In particular, extinction spectra have been obtained in the range 250–1100 nm using an Agilent Cary 60 UV-Vis spectrophotometer. A fraction of the colloids was deposited on nickel grids to carry out scanning transmission electron microscopy (STEM) characterization. STEM images were taken by a scanning electron microscope (ZEISS; model Merlin Gemini 2) operating at an accelerating voltage of 30 kV and at a working distance of 4 mm. AFM analyses have been performed using a WITec alpha300 R5 machine in contact mode. Plasmon sensing has been evaluated by varying the refractive index of the medium through the addition of specific sucrose solution aliquots to the initial colloidal suspension (1.33–1.46 in refractive index units (RIU)).

3. Results and Discussion

3.1. Growth of Silver Nanoplates. In principle, the optical response of spherical silver colloids is predicted by Mie theory [18]. This theory defines a critical size for controlling the plasmon signal: for silver nanoparticles (in water), this limit is ~50 nm in diameter. Below this value, the applied optical field is uniform across the width of the nanoparticle and free electrons move as a single-electron cloud in resonance with light [20]. This condition is spectroscopically indicated by the appearance of characteristic plasmon resonance peaks whose wavelength is independent from the particle diameter. For particles larger than this critical size, however, the applied optical electric field begins to vary substantially in magnitude and phase from one end of the particle to the other. The electron cloud no longer oscillates as a single dipole unit. Consequently, the dipole peak shifts to longer wavelengths while quadrupole and octupole peaks begin to emerge at higher energies. Plasmon resonances change significantly moving from spherically to anisotropically shaped particles. The Mie theory and its extension to ellipsoids (Mie-Gans) fail to predict the plasmonic spectra. Accordingly, a number of computational approaches must be used and can be found in literature to model the optical response [21]. Typical extinction spectra of colloidal aqueous solutions containing spherical silver seeds (diameters below 40 nm) and silver nanoplates (AgNPTs) are reported in Figure 2.

Besides interband transition signals located below 300 nm, the resonance spectra of spherical nanoparticles and those of platelets deeply differ. The former has single sharp resonances at around 395 nm (red line) while the latter presents many plasmon modes which are generally attributed to the following [20]:

**Figure 1:** Some of the colloidal dispersions obtained. Different colors correspond to different plasmon resonance features.
from the solution. In any case, there is a specific concentration at which sizes can be appreciated in Figure 3(b). TEM data reported in Figure 3(b) give an idea of the situation, once the AgNO₃ nutrient solution addition rate is increased. Initially (high addition rates), the plates are quite small and the presence of spherical nuclei is evident. As the addition rate decreases, the signal at 400 nm is reduced in intensity and the longitudinal in-plane dipole mode moves towards the infrared and increases in intensity because of the plate breadth modification.

In Figure 4, we present the evolution of the longitudinal dipole mode position (localized surface plasmon resonance wavelength, \( \lambda_{\text{LSPR}} \)) which is related to the growing silver platelets, as a function of the nutrient solution addition time. The plot regards three different reactors (solution A) with three different concentrations of seeds. For all of them, the data show a classical saturation behaviour, which can be well presented by the empirical relation:

\[
\lambda_{\text{LSPR}} = \lambda_{\text{sat}} + (\lambda_{\text{sat}} - \lambda_0)e^{-kt}.
\]  

We identify a saturation value \( \lambda_{\text{sat}} \), a kinetic constant \( k \), and the parameter \( \lambda_0 \) which represents the plasmon wavelength position at \( t = 0 \). \( \lambda_{\text{sat}} \) gives the final position of the longitudinal dipole mode, once the growth is finished. Saturation changes significantly by changing the seed concentration and reaches values above 1000 nm in the case of very diluted reactor colloids (below 80 \( \mu \)L). The kinetic constant \( k \) indicates how fast the growing process is. Of course, the smallest the breadth of the final particles is, the faster is the growing process, as can be seen in Table 1, where we report the fitting results obtained using equation (1).

The empirical relation in equation (1) clearly originates from a first-order kinetics. Xia et al. [23] have recently proposed the use of such a law in seed-mediated growth of colloidal metal nanocrystals. They considered that in all those cases in which the reductant is supplied in excess and the types of reagents and temperature involved are fixed, the reductant concentration remains relatively constant throughout the synthesis and so the instantaneous precursor concentration at time \( t \) can be modelled using a
pseudo-first-order law. These data reflect some features of the growing mechanism.

On the other hand, it is to be considered that a seed-mediated growth (heterogeneous nucleation) is always in competition with a homogeneous nucleation procedure. However, if we maintain the growing driving force sufficiently low, homogeneous nucleation can be prevented and heterogeneous nucleation prevalently occurs. This is the core
the nature of the plasmonic nanoparticles (i.e., size, shape, and Shape). Nanoplasmonic refractometric sensing enables the detection of small refractive index (RI) changes in the dielectric medium surrounding the metal nanostructure [12, 21]. This happens through the changes of either the plasmon peak position or the intensity per refractive index units (RIU). In this work, we have defined a refractive index sensitivity $S$ [25] as follows:

$$S = \frac{d\lambda_{LSPR}}{dn} = \frac{de_{LSPR}'}{d\epsilon(\lambda)/d\lambda},$$  

where $n$ is the refractive index of the host matrix, $\lambda_{LSPR}$ is the wavelength at the maximum plasmon resonance (in-plane dipole, in our case), and $\epsilon'$ is the real part of the dielectric function of the metal constituting the nanoparticle. These measurements are generally performed by monitoring the spectral changes that occur when the plasmonic material is exposed to solutions with various well-known RIs. Literature data [26] largely report the RI sensitivity as highly dependent on the nature of the plasmonic nanoparticles (i.e., size, shape, and metal composition), so we expect to find a variety of different efficiencies in our class of silver nanoplates. For this reason, we have tested the sensitivity of our particles by controlling the surrounding refractive index with sucrose solutions prepared at different concentrations. Indeed, sucrose molecules do not interact chemically with the nanoparticles, and, at the same time, the correlation between the solution refractive index and its sucrose concentration is well established in the range between 1.333 (pure water) and 1.46 (70% w/w). Table S1 in the Supplementary Material reports the refractive index dependence on sucrose concentration [27].

Figure 6(a) reports some results after an investigation of the dipole plasmon sensitivity for some of the colloidal nanoplates under study. We have limited our study to different initial seed concentrations after a sufficiently slow AgNO$_3$ addition (saturating conditions). In the figure, $\Delta\lambda_{\text{max}}$ is the difference between the in-plane dipole plasmon resonance position of the nanoparticles at a given sucrose concentration (and then at a given refractive index) and that found in pure water. At first glance, it seems that the higher the platelet aspect ratio is (ratio between the breadth and the thickness of the particle), the better is the observed dipole plasmon resonance sensitivity. Indeed, it reaches $\Delta\lambda_{\text{max}}/d\lambda = 450$ nm/RIU for the particles prepared using 20 $\mu$L of seed solution. Some authors have observed that this trend is misleading and that the sensitivity changes are merely due to a variation of the spectral position of the plasmon resonance. In particular, Saison-Francioso et al. [28] determined an analytical expression of $S$ in the quasistatic approximation. They found that $\Delta\lambda_{LSPR}/dn$ is related to the LSPR wavelength position, the refractive index of the host matrix, and the wavelength dispersion of the real part of the dielectric function on the
nanoparticles. Under the hypothesis of a quadratic dependence of $\varepsilon'(\lambda)$ as [25]

$$\varepsilon'(\lambda) = A\lambda^2 + B\lambda + C,$$

the final expression for $S$ is given by

$$S = \frac{2(A\lambda_{LSPR}^2 + B\lambda_{LSPR} + C)}{n(2A\lambda_{LSPR} + B)}.$$  (4)

This simple correlation has been tested theoretically by comparing the analytical expression (equation (4)) with numerical simulations performed by using the well-known finite difference time domain (FDTD) method which has been used to simulate each single-plasmon resonance [28]. We want now to test such a theory with the colloidal samples previously described. We have first obtained the parameters $A$, $B$, and $C$ by fitting $\varepsilon'(\lambda)$ using equation (3) in the wavelength interval of interest (300–1500 nm) [29]. These results are reported in the Supplementary Material (Figure S3) and

![Graph showing plasmon resonances in a saturation condition for several reactors with different initial seed concentration.](image)

**Figure 5:** (a) Plasmon resonances in a saturation condition (very low addition rates) for several reactors, each with a different initial seed concentration. (b) The AFM profile for some of the platelets obtained.

![Graph showing refractive index sensitivity.](image)

**Figure 6:** (a) Results after an investigation of the dipole plasmon sensitivity for some of the colloidal nanoplates under study. (b) Sensitivity as a function of the plasmon resonance position.
have been obtained using the optical constants taken by ref. [26]. Once these parameters have been calculated, they are used to perform a final fitting procedure, using equation (3) as reported in Figure 6(b). The red curve represents a fitting with the method presented in ref. [21]. The hypothesis of Saison-Francioso et al. is respected, and a surrounding medium refractive index value of $n = 1.6$ is obtained by the fit. The value is not so far from the refractive index of water (1.33). Figure 6(b) also reports the behavior of the same curve at $n = 1.33$. We can ascribe this discrepancy to two different reasons:

(a) A deviation from the quasistatic approximation which is evident at high $\lambda_{\text{LSPR}}$

(b) Due to reaction by-products, the effective refractive index of the liquid surrounding the particle deviates from that of pure water

Further investigation is underway to clarify this point.

4. Conclusions

We have reported some specific experimental aspects in the synthesis of silver nanoplates by using a seed-mediated growth approach. We have described the kinetics of the platelet growth at different seed concentrations. The position of the LSPR maximum depends on both the initial seed concentration and the speed at which the seed solution is fed by the nutrient Ag⁺ one. With the lowest seed concentration, in saturation conditions, we were able to obtain colloidal suspensions with dipole in plane resonances which extend beyond 1000 nm. These colloids reach plasmon sensitivity values as high as 450 nm/RIU, and each single particle has aspect ratios as high as 20. Recent literature data [30] indicate that such a sensitivity remains unchanged even after 2.5 years, a major requirement for most industrial applications. Finally, the comparison of the experimental data with an established model has demonstrated that plasmon sensitivity does not depend directly on the nanoparticle shape and aspect ratio but merely on the position of the resonance. This last consideration opens the possibility to extend further the sensitivity of AgNPTs if particle geometries and the NIR region are further explored.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

The authors gratefully acknowledge the PON project Bionanotech Research and Innovation Tower (BRIT) financed by the Italian Ministry for Education, Universities and Research (MIUR). We also acknowledge G. F. Indelli (BRIT) for the technical support.

Supplementary Materials

Figure S1: spherical particles forming during secondary nucleation and growth give a characteristic signal which is markedly shifted towards the red with respect to small silver nanoparticles. Figure S2: (a) AFM image and profile of platelets obtained with 20 μL of seed solution once the colloid is suitably deposited onto a flat surface; (b) SEM image of the same colloids. Table S1: refractive index of a sucrose aqueous solution as a function of the concentration. Figure S3: fit of $\epsilon'(\lambda)$ using equation (2) in the wavelength interval of interest (300–2000 nm). (Supplementary Materials)

References


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