The 3D Design of Multifunctional Silver Nanoparticle Assemblies Embedded in Dielectrics

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1. Introduction

Under light excitation, noble metal (as Au, Ag, and Cu) nanoparticles (NPs) are the seats of plasmonic resonance that permits to conﬁne, exalt, and control light/matter interaction at the nanometer scale. For more than 20 years, the interest of the scientiﬁc community in plasmonic materials has been intensifying with more than 8000 referenced articles and 175 000 citations, conﬁrming that plasmonics is a rising ﬁeld. Surface plasmon resonance (SPR) can be deﬁned as a collective oscillation of charge carriers induced by the electromagnetic wave at the interface between two materials having positive and negative permittivities as, for example, a dielectric and a metal. When the electron oscillations propagate along a planar interface, they are called surface plasmon polariton (SPP), and when they are conﬁned on a subwavelength-sized architecture, they are deﬁned as localized surface plasmon resonance (LSPR). Once excited, both can trap the incident electromagnetic ﬁeld at a deep sub-wavelength scale, leading to an exceptional exaltation of the local electromagnetic ﬁeld, hence permitting the control of light well below the diffraction limit. Consequently, plasmonic materials are promising for a wide range of applications such as photonics,[1] nonlinear optics,[2] chemistry,[3] energy,[4] and life sciences[5] but also in plasmoelectronics[6] and photocatalysis.[7,8]

Many applications as optical spectroscopy, photothermal therapy, photovoltaics, or photocatalysis take advantage of the localized surface plasmon resonance of noble metal nanoparticles (NPs). Among them, AgNPs are multifunctional nano-objects that can be used not only as efﬁcient plasmonic antennae but also as electron reservoirs for charge transfer or ion reservoirs with strong biocide activity. Herein, the 10 years’ efforts on the safe-by-design synthesis of multifunctional nanocomposites consisting of 3D patterns of small AgNPs embedded in dielectrics are presented by coupling low-energy ion implantation and stencil masking techniques. Their multifunctional coupling with different objects deposited on top of the dielectric surface is also presented through three examples. The twofold role of this single plane of AgNPs as the embedded plasmonic enhancer and charge carrier reservoir is ﬁrst tested on few-layer graphene deposited in speciﬁc areas at a controlled nanometer distance from the AgNPs. These buried AgNPs are also coupled to light emitters coimplanted in the dielectric matrix in speciﬁc regions, showing light emission enhancement. Finally, these AgNPs also provide an efﬁcient biocide activity on green algae when submerged in water, with the amount of Ag⁺ release simply controlled by the thickness of the silica cover layer.
composition, geometry, and spatial arrangement has been extensively studied. The recent keen interest for active plasmonic nanostructures (for which the LSPR can be actively controlled) has boosted the search of the ideal embedding matrix for an additional control of SPR in plasmonics structures. The most efficient metals for electromagnetic field exaltation are silver, gold, or copper, among which silver presents the highest LSPR in the visible range with a very elevated quality factor. Even if AgNPs are the best plasmonic antenna, their reactivity in air has strongly delayed their widespread use for plasmonic devices. Indeed AgNPs, when exposed to ambient atmosphere,  

In this feature article, we present our 10 years’ efforts on the safe-by-design synthesis of multifunctional nanocomposites consisting of 3D patterns of small AgNPs embedded in dielectrics by low-energy ion implantation (LE-II) and dedicated to both optical spectroscopy and controlled biocide action. Different architectures made of 3D arrays of AgNPs embedded in a dielectric matrix are designed to concomitantly take advantage of the optical interference phenomenon in the embedding multilayer and LSPR of AgNPs. These structures are elaborated by LE-II through stencil masks and consist of a 2D delta layer of AgNPs having controlled size distribution, surface density, and spatial position and buried in a thin thermal silica layer on top of a silicon substrate. The embedding amorphous dielectric matrix protects the AgNPs not only from aging but also from eventual dissemination in a safe-by-design approach, meanwhile keeping efficient plasmonic properties and maintaining a smooth and reusable surface for further molecule deposition and coupling.

In the following sections, we will first describe the safe-by-design synthesis of 3D assemblies of AgNPs embedded in dielectrics using LE-II. A focus will be done on the key parameters for tuning the NP size, surface density, and depth position in the silica matrix. The NP morphology and aging processes will also be discussed and the vibrational and optical properties of the embedded AgNPs will be presented. As far as applications are concerned, we will show how we can take advantage of these embedded AgNPs as substrates for surface enhanced Raman effect (SERS) and light absorption/emission enhancement, respectively, through two examples consisting of hybrid structures combining silver NPs and 1) few-layer graphene (FLG) and 2) semiconductor (Si) NPs embedded in dielectrics. The Ag$^+$ release and antibacterial action from these embedded AgNPs submerged in water will finally be presented, based on their impact on the photosynthesis of green algae used as an efficient detector of ionic silver.

2. Safe-by-Design Synthesis of 3D Assemblies of AgNPs Embedded in Dielectrics by Low Energy Ion Beam Synthesis

2.1. Ion Beam Direct Synthesis of AgNPs Embedded in Silica

A large variety of methods are used in the literature for the synthesis of metal NPs, from top-down techniques, as electron lithography, to bottom-up routes. Among the latter, chemical methods are simple and inexpensive routes have been widely used for the fabrication of metal NPs such as a colloid dispersed in aqueous solution or an organic solvent obtained by the reduction of their metal salts. Different metallic salts are used to synthesize metallic spherical NPs made of gold, silver, platinum, iron, etc. Two main methods have emerged, namely the Brust–Schiffrin synthesis (BSS) and the Turkevich method. Then, the NPs can be stabilized by capping agents/surfactants to avoid their agglomeration or even embedded in a matrix by the deposition of a cover layer. Hence, AuNP and AgNP colloids have been sandwiched between two silica layers deposited by the sol-gel method, allowing a controlled spatial and size distribution. Concerning physical routes, several techniques can be cited, from the synthesis of AgNPs evaporation-condensation
approach, the laser ablation technique, plasma deposition process, and ultra-LE-IBS, as in this work. Concerning ion implantation, this route is a process of material engineering that has been used for ages for semiconductor doping. This technique has been diverted from its initial use to introduce high doses and perform ion beam synthesis (IBS). Hence, tiny nanostructures of controlled compositions can be formed in virtually any matrix. The nucleation of the AgNPs occurs during the implantation process of silver ions in silica matrix without the requirement of any further heating process. This NPs formation occurs when the introduced Ag amount exceeds the solubility limit and the high diffusion coefficient of Ag in SiO₂ allows the nucleation process to take place during the implantation step. The IBS of AgNPs embedded in dielectrics is therefore a one-step process. This is one of the main advantages of the IBS method compared with the chemical routes that involve several steps for the synthesis of the “naked” NPs and the further embedding process. In addition, IBS is fully compatible with the Si microelectronics technology and can be easily implemented for the design of future devices. The implantation can be processed on large surfaces (i.e., standard wafer sizes of today’s microelectronics industry). IBS also maintains flat, chemically inert, and uniform surfaces, offering opportunities for the development of efficient and reusable substrates for SERS or antibacterial coating applications for instance. This flatness can be obtained even for very low implantation energy at which the NPs nearly touch the dielectric free surface; meanwhile, conformal and, therefore, rough cover layers are obtained for such thin cover layers, with any other kind of deposition process. Finally, patterning in the plane and 3D self-organization of AgNP assembly can be obtained by implanting across micrometric masks. Finally, all these strengths could easily compensate the highest cost of this technique compared with bare chemical methods.

In our synthesis method, typical substrates are composed of the thermal silica layer grown on top of a Si wafer. The thickness of the dielectric has been chosen to be an antireflective layer (90 nm) to simultaneously exploit the LSPR and optical interference phenomena, taking advantage of a maximum of the electric field close to the surface, i.e., in the NP region. More details on the interest of using such antireflective layers are given in the study by Bayle et al.

Ag⁺ ions are implanted for a fixed energy (in the range from 0.6 to 20 keV), which determines the projected range of the implanted profile. In this energy range, the implanted profile is narrow and a quasi-2D array of NPs can be formed at a nanometric distance from the matrix surface. In this low energy range, tuning the implantation energy permits tuning the AgNPs theta layer spatial position under the silica-free surface in the nanometer range. Consequently, the distance of the AgNPs to the surface can be shifted from 3.5 to 12 nm when increasing the ion kinetic energy from 0.6 to 10 keV. The ion dose is varied approximately from $10^{15}$ to $10^{16}$ cm⁻² and fixes the amount of Ag introduced in the matrix, corresponding to Ag concentrations at the mean projected range (Rp) larger than 10 at%. The main drawback of our method consists of the saturation of the Ag amount introduced in the matrix when high doses are reached, thus limiting the further control of the diameter, density, and surface (or volume) fraction of the AgNPs.

This is because of the concomitant effect of sputtering and Ag diffusion toward the surface during the implantation process. Patterning in the plane of such AgNPs assembly can be obtained by the implantation of Ag⁺ ions across a stencil mask clamped onto the SiO₂ surface. Hence diverse plasmonic structures (lines or dots arrays, gratings) embedded in a dielectric matrix and made of AgNP arrays can be synthesized. The stencil mask is elaborated by means of milling with a focused ion beam (FIB) of 200 nm-thick Si₃N₄ membranes. After implantation, the mask is taken off from the substrate, leaving the implanted arrays for investigation. More details on this masking process can be found in the study by BenAssayag et al.

**Figure 1a** is a typical cross-sectional transmission electron microscopy (TEM) image of an implanted sample showing the presence of small AgNPs (typically 5 nm mean size, see size histogram in Figure 1c) located in a single plane (delta layer) placed at a few nanometers under the surface. They are spherical, homogeneously distributed, as shown in the plan-view image (see Figure 1b). The NPs are crystalline and made of pure silver, as revealed by high-resolution electron microscopy (HREM) observation (Figure 1d).

### 2.2. AgNPs Aging

In the study by Benzo et al., we have shown that these AgNPs, yet coated in SiO₂ matrices, encompass aging under ambient conditions after some months. This aging process has been detected by Raman spectroscopy: Raman signal originating from samples with embedded AgNPs measured some months after
implantation is much weaker compared with the one measured some days after implantation. On the contrary, this optical signal decrease is not detected on samples further annealed in the 400–500 °C range under N₂. X-ray photoelectron spectroscopy (XPS) measurements show the presence of silver oxide for “aged” samples. This is confirmed by HREM observations, which evidence the presence of hexagonal Ag₂O nanocrystals (NC). On the contrary, only pure metallic Ag nanocrystals are observed for the annealed ones. Hence, the annealing at 400 °C recovers the SiO₂ layer damage due to the ion implantation process without significantly modifying the main characteristics of the NPs population (size distribution, position with respect to the surface, and density). This heating process has been shown to be effective for the metal NPs stabilization, hampering any form of oxidation and maintaining their plasmonic properties.

3. Optical and Vibrational Properties of Embedded AgNPs

3.1. Vibrational Properties

The experimental details and set-up are described in the studies by Bayle and coworkers.[43,45] The dynamics of both lattice modes (Lamb modes and bulk phonons) and electron modes (plasmon modes and electron–hole excitations) have been explored. The Raman signal is made of three components. At a high-frequency range, we can distinguish optical phonons of the Si substrate emerging from a “background” (electronic Raman scattering (ERS)). A thorough study of this “background” is detailed in the work by Carles et al.[45] This signal appears as an intrinsic effect, which is directly linked to the SERS effect. At intermediate frequencies, we find “bulk phonons” that reflect the vibrational density of states (VDOS) of the AgNPs. Finally, if we focus in the low-frequency regime (Figure 2), a particularly intense peak is visible at the frequency of 0.27 THz, with two shoulders to 0.5 and 0.9 THz. These last contributions are attributed to the elastic deformations of the NPs (“Lamb modes”). In resonance conditions as here, these modes strongly interact with the plasmon oscillations. The highest and lowest frequency peaks are attributed to the fundamental quadrupole mode and the shoulders to its harmonics. These modes are the function of the NP size that can be deduced from these measurements. These values are in good agreement with TEM observations.[43]

3.2. Plasmonic Response of the Embedded AgNPs

UV–vis reflectivity spectra measured in backscattering geometry (θ, ≈ 0) on a SiO₂/Si multilayer are shown in Figure 3 (blue spectrum). Three reflectivity minima (E₁ = 2.63 eV, E₂ = 4.1 eV, and E₃ = 5.7 eV) are observed, corresponding to the interference effects in the SiO₂ layer. The presence of embedded AgNPs can be detected in the reflectivity signal (red line) by an amplification of the reflectivity minima. We can see that a single plane of AgNPs, provided it is located at a maximum of the electric field, strongly modifies the antireflective effect. This strong effect can be clearly highlighted by measuring the contrast of the reflectivity signal (black spectrum in Figure 3), which efficiently renders the absorption process by both the AgNPs and the underlying Si substrate, due to the optical changes in the SiO₂/Si multilayer induced by the AgNPs plane.[29] In addition, the signature of NPs in the reflectance contrast will be strongly amplified close to the antireflection condition because the reflectivity of the unimplanted sample (R₀) is minimum. Finally, the LSPR of the single layer of AgNPs is characterized by a well-defined peak located at around 3.0 eV (Figure 3). This energy perfectly fits with the theoretical value for absorption by an individual and spherical AgNP buried in silica.[45] Hence, retardation or collective processes are supposed to be unimportant for such nanometer-sized and low-density NP assemblies.

3.3. AgNPs Morphology

Figure 1c shows a high-resolution transmission electron microscopy (HRTEM) micrograph of an isolated nanocrystal of 8 nm size oriented along <110> and characteristics of the NC population obtained by implanting Ag at a low energy and high dose in silica. The face-centered cubic (FCC) Ag structure can be deduced from the measured interplanar distances and angles. In addition, the NP surface is clearly bounded by four {111} and two {100} facets, which are features of a truncated octahedron equilibrium shape.[47] In the study by Sauceda and Garzon[48] the VDOS calculated by atomic scale simulations has been compared with the one measured on our samples through plasmon resonance Raman scattering and described in the study by Sauceda et al.[45] The best agreement between the calculated and measured density of states is obtained for the icosahedral morphology and not for the truncated octahedron shape, which is the one observed in HRTEM. Nevertheless, we can argue that the theoretical model used in the study by Iravani et al.[19] is based on a perfect individual NP located in vacuum. This configuration is far from the real experimental conditions consisting of a population of size-distributed AgNPs embedded in a matrix. In particular, the model does not consider the
different effects that affect the measured VDOS, such as surface disorder, binding heterogeneities, and very local strain. In particular, a high number of AgNPs, even of small sizes, present stacking faults that can be imaged in HRTEM. Finally, even if the synthesis of large icosahedral AgNPs has been demonstrated using out-of-equilibrium deposition techniques, they remain metastable.

4. Application to Plasmon-Enhanced Scattering

4.1. Coupling with 2D Layers (Graphene)

We can take advantage of the arrays of embedded AgNPs as substrates for enhancing light scattering, diffraction, or imaging efficiency. Our first attempt consisted of a classical test, i.e., their coupling with a micrometer droplet of pyridine molecules deposited on the top of the surface of our plasmonic architectures. The Raman signal recorded in implanted regions (with AgNPs) has been compared with that measured on unimplanted areas (without AgNPs). If we assume that the signal mainly comes from the volume of the droplet situated close to the focal point of the microscope objective (around 1 μm thick), the exaltation of the signal arising from pyridine molecules situated in the surrounding area of the substrate is in the range $10^4$–$10^5$. Nevertheless, the calculation of any enhancement factor was hazardous, due to the difficulty in evaluating the number of molecules implied in the SERS process.

More recently, we associated our embedded Ag nanostructures to FLG, the 0D nanostructures, and the 2D layer being located at the vicinity of the AgNPs (see Figure 5b,c). The strong enhancement of the semiconducting NPs light emission induced by the presence of AgNPs is due to plasmonic effect. Such architectures are appropriate for light conversion layers in third-generation photovoltaics devices.
5. Application to Ag\(^{+}\) Release and Toxicity

In parallel, we have also assessed the toxic effect on algal photosynthesis of the same experimental system made of small (size <20 nm) AgNPs embedded in silica layers. For this experiment, two physical routes were used for the elaboration of the nanocomposite structures: 1) LE-II as already presented in this article and 2) combined silver sputtering and plasma polymerization as described in the study by Pugliara et al.\[27\]. The measurement of the silver release from the NPs for 20 h immersion in buffered water was carried out using inductively coupled plasma mass spectrometry (ICPMS). We obtain values ranging between 0.02 and 0.49 μM. In addition, the short-term toxicity of Ag during the photosynthesis of green algae (Chlamydomonas reinhardtii) was measured by fluorometry spectroscopy. We demonstrated that embedding AgNPs in a silica matrix efficiently minimizes their interaction with the buffered water media, thereby preserving the AgNPs from fast oxidation. This study also reveals that the release of bioavailable silver (i.e., the one impacting algal photosynthesis) is governed by silica cover layer thickness or in other words, by the spatial position of the AgNPs under the host matrix surface (see Figure 6).\[28\] In addition, the toxicity of silver released from these embedded AgNPs during the photosynthesis of green algae is similar to equivalent concentrations of Ag\(^{+}\) released from silver nitrate salt (AgNO\(_3\)). For elucidating the origin of the observed silver toxicity (silver ions Ag\(^{+}\) and/or AgNPs) to algae, fluorometry measurements in the presence of cysteine (known as an equimolar silver ligand) have been carried out, and we demonstrate that the addition of this protein totally eradicates the Ag\(^{+}\) toxicity during algal photosynthesis. This observation is in good agreement with previous works\[35,36\] and confirms that all the toxicity coming from the solution after contact with specimen containing embedded AgNPs is due to the presence of ionic silver in the suspension. In addition, the analysis of TEM micrographs taken after plunging in buffer water shows that Ag liberation is accompanied by the dissolution of

Figure 4. a) Raman spectra associated with the five characteristic regions labeled in (b); b) Optical image of a SiO\(_2\)/Si sample implanted with Ag and after graphene deposition, with the different regions of interest; c) second-order Raman signatures of a multilayer (three layers) graphene flake: on the unimplanted SiO\(_2\)/Si (green curve), in the AgNPs region (red curve), and at the boundary between these two zones (purple curve). In all spectra, the background (electronic scattering) has been subtracted and spectra have been shifted for sake of clarity. The image in the inset of (c) is the integrated intensity of the 2D band. Reproduced with permission.\[37\] Copyright 2018, IOP Publishing Ltd.

Figure 5. a) Energy filtered TEM image at 17 eV (Si plasmon) of the hybrid structure coupling two delta layers (AgNPs in black contrast and SiNPs in white contrast); b) associated room-temperature PL exciting with a 532 nm laser and mapping along X–Y of the emission intensity obtained by the signal integration in the range 600–750 nm with a scan step of 0.2 μm; c) PL spectra obtained by averaging the signal arising from SiNPs in the region with AgNPs (A) and without AgNPs (B). Reproduced with permission.\[33\] Copyright 2017, AIP Publishing LLC.
AgNPs that are situated in the close vicinity of the silica surface; meanwhile, the NP density does not vary. This finding suggests that the AgNPs are the reservoirs of Ag⁺ ions released into the solution. Moreover, the reusability of the samples has been tested and the released Ag amount from the reused nanocomposite samples is comparable with the one measured on pristine nanocomposites.

For the fine tuning of the Ag⁺ release, the understanding of the basic processes associated with both the separation of Ag⁺ from the NPs and their propagation through the silica layers is mandatory. A first advance consists of a deep study of the interface between the NPs and their SiO₂ surrounding shell. In this purpose, periodic density functional theory (DFT) modeling has been conducted on model systems characteristics of the interfaces between amorphous SiO₂ and the crystalline facets of nanocrystals that have been observed in TEM (Figure 1d). Unforced breaking of Si—O bonds and the creation of two O—Ag and one Si—Ag bonds are found in half of the studied interfaces. In addition, the study of the electronic structure of the interfaces sheds light on the covalent character of the bonds between Ag and O and between Ag and Si.[41]

6. Conclusions

This work is a compilation of results demonstrating that the patterning in three dimensions of nanocomposites consisting of AgNPs embedded in a SiO₂ matrix can be successfully achieved in a single-step process involving LE-II through micrometric masks. With this technique, arrays of plasmonic nanostructures can be localized at nanometer distance under the dielectric surface. The near-field coupling of these embedded AgNPs with molecules or nano-objects on top of this surface has been demonstrated on two examples, i.e., a 2D graphene layer and an array of luminescent SiNPs. The study of Raman scattering (both vibrational and electronic components) in FLG flakes deposited on top of our plasmonic substrates has demonstrated intensity exaltation that can be ascribed to the electromagnetic mechanism. In addition, the plasmon-assisted optical injection of electrons in the graphene layers has been evidenced. The design of the hybrid structure, containing both plasmonic antenna (AgNPs) and luminescent centers (SiNPs), has been successfully obtained using the same technique, and a strong enhancement of light emission from the semiconducting NPs is induced by the plasmonic NPs. Finally, an original method allowing the measurement of ionic silver release from these AgNPs buried in silica matrices has been proposed, involving the Ag biotoxicity during green algae photosynthesis. The Ag⁺ release from the NPs is simply controlled by the thickness of the silica cover layer.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Ag nanoparticles, biocide effects, plasmonic antennas

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References

[1] D. Dregely, R. Taubert, J. Dorfmüller, R. Vogelgesang, K. Kern, H. Giessen, Nat. Commun. 2011, 2, 267.
[2] J. Toudert, H. Fernandez, D. Babonneau, S. Camelio, T. Girardeau, J. Solis, Nanotechnology 2009, 20, 475705.
[3] M. D. Xiao, R. B. Jiang, F. Wang, C. H Fang, J. F Wang, J. C. Yu, Mater. Chem. A 2013, 1, 5790.
[4] S. C. Warren, E. Thimsen, Energy Environ. Sci. 2012, 5, 5133.
[5] O. Tokel, F. Inci, U. Demirci, Chem. Rev. 2014, 114, 5728.
[6] P. Spinelli, A. Polman, Opt. Express 2012, 20, A641.
[7] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, N. J. Halas, Nano Lett. 2013, 13, 240.
[8] A. Mezni, N. Ben Saber, M. M. Ibrahim, N. Hamdaoui, A. Alrooqi, A. Mlayah, T. Altalhi, Mater. Chem. Phys. 2019, 221, 118.
[9] N. J. Halas, S. Lal, W.-S. Chang, S. Link, P. Nordlander, Chem. Rev. 2011, 111, 3913.
