Nanoline-gap controlled self assembly of plasmonic nanoparticles inside plasmonic nanolines

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Abstract

This paper presents plasmonic substrates fabricated by a gap—controlled, template-assisted self assembly of plasmonic nanoparticles—such as spherical nanoparticles and nanorods—inside one dimensional plasmonic nanoline templates fabricated using Deep-UV lithography. This hybrid fabrication process—which combines the bottom-up process of capillary-force self assembly with the top-down process of Deep-UV lithography—can potentially be employed for large-area fabrication (6 inch or 12 inch wafers) of plasmonic substrates with sub-10 nm gaps. These small gaps lead to a high electromagnetic enhancement which can be highly beneficial if these substrates are employed for sensing based on surface enhanced Raman scattering (SERS). We demonstrate that the templates of plasmonic nanolines act as lithographed traps and direct the capillary-force assembly of metallic nanoparticles. The gaps between the nanolines, along with the shape and dimensions of the nanoparticles, together determine the interparticle distance, packing pattern and the orientation of the assembled nanoparticles inside these nanolines. Moreover, the electromagnetic behavior of these substrates is exhaustively analyzed using Finite Difference Time Domain (FDTD) modeling. Thus, we demonstrate template-directed, capillary-force assembly of plasmonic nanoparticles inside plasmonic nanolines such that the assembly can be controlled by modulating the structural parameters of the template or the assembled nanoparticles, and can be potentially carried out on a large area.

1. Introduction

It is well known that plasmonic substrates based on engineered metallic nanostructures lead to the enhancement of optical phenomenon such as Raman scattering [1, 2], and fluorescence [3] due to the excitation of surface plasmons, localized surface plasmons, and coupled plasmons [4, 5]. More specifically, these plasmonic substrates can be employed for surface enhanced Raman scattering (SERS), which allows the inherently weak Raman signals from trace amount of analytes to be sufficiently enhanced for efficient detection. Moreover, plasmonic nanostructures with sub-10 nm gaps lead to a very high electromagnetic (EM) enhancement of SERS signals due to the formation of highly localized electromagnetic hotspots and thus, can be employed as highly sensitive SERS-based chemical or biological sensors [6–10]. However, for employment as efficient SERS based sensors, these plasmonic substrates must have the capability to be fabricated controllably and reproducibly. In addition, the fabrication should be scalable to a large area (wafer-scale) to make the sensors cost-efficient.

In the past, the fabrication of such sub-10 nm gaps has been carried out by employing top-down nanofabrication methods or bottom-up nanofabrication methods [11–14]. In the top-down approach, nano-scale features are fabricated by employing either lithographic methods [11, 12] or focused ion beam milling [13] to directly fabricate nanostructures on thin films. Unlike the top-down approach, a bottom-up approach works by integrating smaller atomic or molecular level components into nano-scale features [14]. A top-down nanofabrication approach offers a high degree of control, precision and reproducibility, but may be limited by the resolution of the lithography process. The few reports of fabrication of nano-scale devices with sub-10 nm dimensions in the past decade have described that sub-10 nm fabrication is generally complex, and requires modifications to the existing lithography processes.
In cases where sub-10 nm resolution is possible, lithography processes are slower (with large writing times) and may therefore not be suitable for large-area and cost-efficient fabrication. Sophisticated and advanced optical lithography at shorter wavelengths like the extreme UV lithography offers high resolution and quick fabrication but comes at a very high cost. Bottom-up fabrication, on the other hand, can be used for large area fabrication due to low fabrication time and cost-efficiency. However, it suffers from problems like randomness and non-uniformity of the chemical species involved. Therefore, a preferred nanofabrication strategy lies mid-way between the top-down and the bottom-up approach to nanofabrication. Top down approaches such as optical lithography processes or milling can be used to define slightly larger nano-patterned templates (i.e., templates with larger gaps) followed by the bottom-up processes to bridge these larger gaps. This hybrid approach leads to a cost-efficient fabrication with smaller fabrication times than the top-down approach alone, as well as to a a higher degree of control than the bottom-up approach alone.

A bottom-up fabrication technique which has been widely employed for the fabrication of nanostructured substrates is the self-assembly of nanoparticles. In general, nanoparticles self assemble as closed-packed arrays with minimum free energy, such that the complexity of the final assembly cannot be controlled, except for a variation in the shape and size of the nanoparticles. More recently, to make the process controllable, a combination of the top-down and bottom-up processes, i.e., template-directed self assembly of nanoparticles has been employed where templates or underlying structures are first fabricated as scaffolds into which the smaller components such as nanoparticles can be assembled. The introduction of a template leads to the manipulation of the interaction potentials, thus directing the process of self assembly, such that the nanoparticles can be arranged into structures that are complementary to the template. Thus, the engineered templates provide the freedom to create self assemblies of predictable and complex forms. In the recent past, many such hybrid substrates have been proposed.

In this paper, we demonstrate hybrid plasmonic substrates based on the nanoline-gap controlled template-directed self assembly of gold nanoparticles inside one dimensional plasmonic gold nanolines which can be potentially fabricated on a large area. The nanolines act as lithographed traps and direct the capillary assembly of gold nanoparticles, such that the gaps (G) between the nanolines as well as the shape and dimensions of the nanoparticles together determine the interparticle distance, the number of assembled nanoparticles, the packing pattern, and the orientation of the nanoparticles assembled inside these nanolines. We demonstrate that the desired number of gold nanoparticles can be assembled in the desired orientation inside the nanolines by modifying the size of the gap between adjacent nanolines, or by varying the size and shape of the nanoparticles assembled inside the nanolines.
In the last decade, various substrates fabricated by employing the self assembly of micro and nanoparticles inside lithographic templates have been demonstrated by various researchers. Such substrates can be characterized by the material of the template, the geometry of the lithographed traps in the template, the lithographic method used to fabricate these templates, and the material and size of the particles used in self-assembly. There has been extensive work related to the assembly of polystyrene beads [28, 29], other micro-sized particles [30–32], and non-plasmonic nanoparticles [33, 34] inside lithographed templates. However, in this paper, we focus on the assembly of plasmonic nanoparticles inside lithographed templates, as the employment of plasmonic nanoparticles can lead to the usage of such substrates for various nano-plasmonic applications including surface enhanced Raman scattering (SERS).

The capillary driven self-assembly of plasmonic nanoparticles inside templates has been demonstrated by many researchers in the last few years. Cui et al demonstrated a facile method for formation of large scale device arrays by assembling gold nanoparticles in trenches and holes made in resist on top of a silicon substrate by employing E-Beam lithography [33]. Flauraud et al demonstrated large area precise placement of anisotropic gold nanoparticles, i.e., nanorods inside rigid substrates precisely nanomachined with 3D traps for hosting single or double nanorods [35]. Kuemin et al fabricated linelets on a PDMS substrate by molding liquid PDMS against a patterned silicon master fabricated by E Beam Lithography. In these linelets, they demonstrated the self assembly of oriented gold nanorods [36]. Tebbe et al used dip coating to organize nanorods into single, double and triple assemblies onto a wrinkled PDMS substrate [37]. Holzner et al demonstrated the assembly of single gold nanorods on a thermally sensitive polymer film which was lithographed using scanning probe lithography. After the assembly of the gold nanorods, the polymer was decomposed by heating, and the pattern was transferred to the underlying target substrate [38]. Asbahi et al used gold nanoparticles suspended in hexane for self assembly onto nanospots or cavities patterned on HSQ coated Silicon substrates patterned using E-beam lithography [39]. Zhou et al demonstrated the shape selective assembly of nanoprisms and cubes inside patterned PDMS substrates [40]. Besides this, there are many other reports [41, 42] of capillary driven self assembly of plasmonic nanoparticles inside polymeric or resist coated silicon substrates.

Although many researchers have shown the self-assembly of plasmonic nanoparticles and nanorods inside polymeric templates, lithographed resists, or silicon substrates, this paper reports an assembly of plasmonic nanoparticles and nanorods inside plasmonic nanolines. The presence of a plasmonic gold template, instead of a polymeric or silicon substrate, leads to stronger interactions between the nanoparticles and the underlying template and leads to potentially high electromagnetic enhancements. Further, Deep-UV lithography, which has been employed for the fabrication of the template in this paper, is far better than E-beam lithography or scanning probe lithography (which have been used for the template development in previous works) due to its capability for fabrication of large-area templates in a small writing time.

Moreover, this paper presents the first systematic study of the capillary driven self-assembly of plasmonic nanoparticles on a plasmonic lithographed template which shows that the pattern (face-to-face or hexagonally packed), the number (single, double, and triple), and the orientation of the nanoparticles inside the long channels/gaps between the nanolines, are dependent on the nanoline-gap, shape, and size of the nanoparticles. Additionally, these substrates can potentially be applied for large area fabrication as the fabrication of the template is done using Deep-UV lithography. Furthermore, we report for the first time a mixed assembly (longitudinal and angular) of plasmonic nanorods inside templates of plasmonic nanolines—such that the angle of the assembled nanorods can be controlled by changing the inter-nanoline gap. It must be noted that gold nanoparticles and nanorods were chosen for this study due to their chemical stability and ease of surface functionalization. For the different plasmonic substrates fabricated by employing the template-guided self assembly of metallic nanoparticles inside metallic nanolines, we systematically analyzed the effects of varying inter-nanoline gaps. Additionally, the electromagnetic behaviour of the fabricated substrates was numerically analyzed through Finite Difference Time Domain (FDTD) simulations.

2. Methods

2.1. Fabrication of nanoline-gap controlled plasmonic substrates

The nanoline substrates were fabricated using deep-UV lithography followed by deep reactive ion etching (RIE) and E-beam evaporation (see figures 2(a)–(c)). A 6-inch silicon wafer was patterned with nanoline patterns with varying inter-nanoline gaps, using deep-UV Lithography at 193 nm by employing an ASML 5500/950B scanner. Thereafter, the patterned wafer was etched using Deep-RIE (Alcatel AMS 100) to obtain the periodic nanolines structures with a depth of 50 nm. Following this, a layer of ~100 nm gold was deposited on the substrates using E-Beam evaporation (Kurt Lesker PVD 75) to obtain the gold-coated plasmonic nanoline substrates. It must be noted that the inter-nanoline gaps can be decreased by depositing more gold on the fabricated substrates.
Non-functionalized gold nanoparticles and gold nanorods were purchased from Nanopartz and employed for the self-assembly. It must be noted that nanoparticles which have been functionalized with SERS dyes can also be employed for self assembly if such substrates are to be used for specific applications like surface enhanced Raman scattering. A constrained evaporation-based method was employed for the self-assembly of gold nanoparticles inside the gold-coated nanolines (see Figure 2(d)). The templated nanoline substrates were cleaned by dipping and agitating them slowly in acetone followed by IPA for 30 s. Thereafter, the substrates were rinsed three times with DI water, and dried. For the self-assembly, two pieces of a thick film were placed on the sides of the substrate (see Figure 2(d)) to create a spacer layer of uniform thickness. A 10 μl drop of the concentrated nanoparticle solution was dropped onto the substrate. Thereafter, a cover-slip was placed onto the substrate, spaced from the substrate by means of the two spacer layers on either side of the substrate. This leads to the formation of a parallel cell-like structure with the nanoparticle droplet trapped between the substrate and the cover-slip. The small pressure induced by the cover-slip on the nanoparticle droplet leads to a mild spreading of the droplet over the substrate. Following this, the nanoparticle droplet was allowed to evaporate overnight, at room temperature and at a humidity of ~35%. The receding meniscus led to the capillary-force driven self-assembly of the nanoparticles inside the nanoline templates (Figures 2(e)–(f)). During the self-assembly of the nanoparticles, the geometric confinement by the plasmonic nanolines breaks the isotropic symmetry of the interaction forces on the nanoparticles into an anisotropic symmetry, and leads to a guided assembly of the nanoparticles along the nanolines—such that the nanoparticles are physically trapped as organized arrays between the plasmonic nanolines.

It must be noted that the surface chemistry in the grooves between nanolines is extremely critical for the successful assembly of the nanoparticles and the nanorods. When a drop of the nanoparticle solution is dropped on the gold coated nanoline substrate, it forms a three-phase contact line corresponding to a contact angle. As evaporation happens, the nanoparticles, under the right conditions, are driven towards the wedge-shape edge of the evaporating droplet—the meniscus, forming a nanoparticle rich accumulation zone. The capillary assembly is based on the dragging of these nanoparticles in the accumulation zone—over the surface of the substrate—due to the receding three-phase contact line. As the meniscus drags over the templated substrate, the nanoparticles tend to get trapped inside the grooves between the nanolines. However, successful assembly is dependent on the shape of the meniscus. For the proper formation of a wedge-shaped meniscus which can

Figure 2. Fabrication of hybrid plasmonic substrates. (a) Large area patterning of nanoline patterns, with different inter-nanoline gaps, on a 6-inch wafer using Deep-UV Lithography, (b) Deep RIE to etch nanoline patterns on the patterned Si substrate, (c) E-beam evaporation to deposit gold on the etched nanolines, (d) Self assembly of gold nanoparticles on the fabricated nanolines, using a constrained evaporation based method, (e) SEM image of the fabricated nanolines (Scale bar is 1 μm), and (f) SEM image of the hybrid substrate with nanoparticles assembled inside nanolines (Scale bar is 500 nm).
support an accumulation zone, it is imperative that the substrate surface has a low wettability, but is not completely hydrophobic. Further, even after the formation of a properly shaped meniscus, trapping of nanoparticles inside the grooves is not ensured. As this meniscus encounters a groove, the nanoparticles get trapped inside the groove due to the component of the capillary force pointing in the downward direction. However, as the evaporation proceeds, the groove must offer enough resistance or energy barrier to keep the nanoparticles trapped inside the grooves. Furthermore, the nanoparticles must not get dislodged from the grooves during the process of drying. Therefore, the surface chemistry and the geometry of the grooves are both critical in determining the success of this self assembly process.

2.2. Numerical methods
The effect of the ratio of the inter-nanoline gap to the dimensions of the nanoparticles or the nanorods—on the electromagnetic behaviour of these substrates was also studied through Finite Difference Time Domain (FDTD) modelling [43]. The simulations were carried out by employing Numerical FDTD solutions. Perfectly matched layer (PML) boundaries were employed in the Y-direction, and periodic boundaries in the X- and Z- directions. The coordinate system is shown in figure 4(a). The metals employed in the simulations were modelled using the Lorentz Drude dispersion model [44]. The diameter of the nanospheres and of the nanorods was taken to be 50 nm. The simulations were carried out for both X- and Z- polarizations.

3. Results and discussion
The nanoline-gap controlled self assembly of spherical nanoparticles inside the nanolines substrate is based on the ratio of the inter-nanoline gaps (G) and the size of the nanoparticles (D) being assembled. Nanoline patterns, with varying inter-nanoline gaps, as shown in figure 3, were fabricated by employing Deep-UV lithography, Deep-RIE and E-beam evaporation such that the inter-nanoline gaps were varied from 70 nm to 140 nm. It is clear by the geometry of the fabricated nanolines (see figures 1(a) and 3), that, to accommodate a single spherical nanoparticle (SNP), a dimer of SNPs in hexagonal configuration, and a dimer of SNPs in face to face
configuration, the inter-nanoline gap (G) must be atleast ‘D’, ‘1.5D’ and ‘2D’ respectively, where ‘D’ is the diameter of a SNP. For values where G > 2D, a hexagonal assembly of SNPs inside the nanolines is expected. We verified that the assembly of the SNPs completely followed these simple geometric rules. With a G:D ∼ 0.67 (G = 70 nm, D = 103 nm), i.e., for G < D, a bead like assembly of single SNP chains on the underlying nanoline bed was observed (figure 3(a)). Although, the inter-nanoline gap (G) was smaller than the diameter (D) of the SNPs, it was sufficient enough to allow the SNPs to partially sink-and-stick into the gaps. As the G:D ratio was increased to ∼1.36 (G = 140 nm, D = 103 nm), i.e., for D < G ≤ 1.5D, single SNP chains were formed inside the nanolines (figure 3(b)), as two SNPs could not be accommodated inside the nanolines in any form. On further increasing the G:D ratio to 1.7 (G = 90 nm, D = 53 nm), i.e., for 1.5D < G ≤ 2D, a hexagonal assembly of SNPs inside the nanolines was observed (figure 3(c)). When the G:D ratio was increased to 2.6 (G = 140 nm, D = 53 nm), i.e., for 2D < G ≤ 3D, a face-to-face assembly of a dimer of SNPs was observed (figure 3(d)). For all cases, when G > 3D, a hexagonal assembly of multi-SNP chains was observed (figures 3(e)–(f)).

The effect of the ratio of gap to the diameter of the nanoparticle, i.e., G:D, on the electromagnetic behaviour of these substrates was studied through Finite Difference Time Domain (FDTD) modelling [32]. In the FDTD simulations (see figure 4), the diameter of the spheres was taken to be 50 nm. To allow a comparison between various substrates, all the simulations were carried out such that the NP-NP gaps, i.e., the gaps between any two SNPs, and the NP-NL gaps, i.e., the gaps between the SNPs and the nanoline wall, were taken to be 2 nm. The gaps are shown as insets in figure 4. The simulations were carried out for both X- and Z- polarization of the incident optical radiation, as shown in figure 4.

The average and peak E-field enhancement (∣E/|E0∣), calculated using FDTD, for the various substrates shown in figure 3 are shown in figure 4. For single NP chains, it was observed that the peak E-field enhancement is ∼90 for the X-polarization, and around ∼70 for the Z-polarization. For X-polarized light, the nanolines on either side of the NPs lead to a higher enhancement than when Z-polarized light is incident on the substrate. The spatial distribution of the E-field enhancement, at the respective resonance wavelengths for the two states of polarization, are also shown in figure 4(a). It is well known that the SERS electromagnetic enhancement factor is proportional to ∣E/|E0∣4. Thus, the SERS EM enhancement with such substrates (single NP chain) is of the order of ∼107. When combined with the chemical enhancement of ∼107 in SERS, a total SERS enhancement of ∼1014 can be obtained from these substrates, which is a moderately high value for SERS enhancement factor.

Figure 4(b) shows the case when two particles are assembled in a hexagonal configuration inside the nanolines (see inset of figure 4(b)). Due to the creation of multiple hotspots (NP-NP and NP-NL), the average E-field enhancement in this case is different from the peak E-field enhancement. However, it must be noted that

Figure 4. Peak and average E-field enhancement versus wavelength graphs; and the field profiles at the respective plasmon resonance wavelength for the two states of polarization when (a) single nanoparticle array is assembled inside nanolines, (b) arrays of two nanoparticles are assembled in a hexagonal pattern inside the nanolines, (c) arrays of two nanoparticles are assembled in a face-to-face pattern inside the nanolines, (d) arrays of three nanoparticles are assembled in a hexagonal pattern. The insets in the graphs show the corresponding interparticle gaps, and nanoparticle-nanoline gaps. The direction of polarization is marked in the figures. The color bar on the right shows the values of E-field enhancement for the field profile maps.
there is no significant difference between the EM enhancement obtained for X- and Z- polarized light. This is due to the creation of angular hotspots at 45 degrees to both X and Z-axes. A component of the incident field is always coupled into these hotspots for both X- and Z-polarization. Figure 4(c) shows the case when the internanolines gaps are such that face to face assembly of nanoparticles occurs. In this case, the E-field enhancement is higher for the X-polarized light due to the confinement by the nanolines on either side of the nanoparticles. Figure 4(d) shows the peak and average E-field enhancements for the hexagonal assembly of three nanoparticle arrays inside the nanolines.

As the self-assembly of plasmonic nanoparticles inside nanolines depends upon many process conditions such as the uniformity of the fabricated template, the uniformity in size of the nanoparticles, or any other fabrication defects, the placement of the nanoparticles inside the nanolines is not always symmetric. Although, the packing pattern and the number of nanoparticles is broadly dependent on the G:D ratio, the gaps may be slightly asymmetric due to perturbations along the X-, Y- or both axes. To understand the electromagnetic effects of such perturbations on the E-field enhancement, a set of simulations, for one of the substrates with $2D < G < 3D$, were performed with various gap combinations along the X axis (see figure 5(a)).

A few cases of geometrical perturbations in the gaps along the X-direction are shown in figure 5(a). The E-field profiles of these substrates, simulated with X-polarized light, are shown at the resonance wavelength of 788 nm in figure 5(b). The average E-field enhancement was calculated over the three electromagnetic hotspots and is plotted with respect to the wavelength in figure 5(c). It can be seen from this figure that the E-field enhancement varies from $\sim 35$ to $\sim 45$ amongst these four cases. This implies that the SERS EM enhancement ($|E|^4/|E_0|^4$) for all these four cases is of the order of $\sim 10^6$, which implies that this slight variability in the gaps will not affect the employability of these substrates for SERS applications. It must also be noted that there is a negligible effect of these geometrical perturbations in the X-direction on the E-field enhancement, if Y-polarized light is employed. The effect of geometrical perturbations in the Y-direction, and in both X- and Y- directions also shows only a slight variation in the E-field enhancement and is discussed in appendix.

To highlight the control of orientation through gap controlled self assembly, gold nanorods were also assembled inside plasmonic nanoline substrates. Although, nanorods have a tendency to assemble longitudinally, in the template-assisted assembly of nanorods inside nanoline substrates, it was observed that the nanorods exhibit mixed assembly—i.e., it was a mixture of longitudinal and angular assembly based on the relationship between the dimensions of the nanorods and the nanoline periodicity.

It is evident by the geometry of the substrate (figure 6) that for longitudinal assembly of X’ number of nanorods, the inter-nanoline gap (G) must be greater than diameter of the nanorods (D), i.e., for $G/D > X$. Additionally, for angularly stacked nanorods, the angle with the horizontal (A) can be roughly approximated as $\cos^{-1}(G/L)$, where L is the length of the nanorods. Multiple substrates were fabricated to observe the nature of mixed assembly of the nanorods. Nanorods with varying aspect ratios/dimensions were assembled inside nanolines with varying inter-nanoline gaps. When the G:D = 1.75, and G:L = 0.51 ($D = 40$ nm, $L = 135$ nm and $G = 70$ nm), longitudinal assembly of single nanorod chains was observed as $D < G < 2D$. This is shown

Figure 5. Effect of perturbations in the gaps along the X-axis for the case when $2D < G < 3D$. (a) The case of symmetric gaps of 5 nm between the nanoparticles and between the nanoparticle and the nanoline, are compared with a few asymmetric gap combinations which can occur during and after self assembly, (b) E-field enhancement profiles at the resonant wavelength of 788 nm for these gap combinations respectively, and (c) Average E-field enhancement from the electromagnetic hotspots is plotted against the wavelength for all the four cases.
Additionally, a few NRs were assembled angularly with the angle dependent on G:L such that \( A = \cos^{-1}(G/L) \). As the G:L ratio is large, steep angles with the horizontal were observed. When the G:D ratio was increased to 2.25 \((D = 40\text{ nm}, L = 135\text{ nm}, \text{ and } G = 90\text{ nm})\) such that \( 2D < G < 3D \), dimers of...
nanorods were assembled longitudinally (figure 6(b)). As the G:L ratio is 0.66, NRs were also assembled as angular stacks with $A \sim 45^\circ$. To further study the effect of the G:L ratio on the angular assembly of stacked NRs, the G:L ratio was further increased to 0.88 ($D = 40$ nm, $L = 135$ nm, and $G = 120$ nm). It was observed that the angle of the angularly stacked NRs reduced in approximate accordance with $\cos^{-1}(G/L)$. As the G:D ratio is increased to 3 such that $2D < G < 3D$, dimers of NRs was longitudinally assembled. When the G:L > 1, enough spacing is available between the nanoline walls to accommodate the NRs horizontally. This leads to a mixed assembly of perfectly horizontal and longitudinal stacks of nanorods.

Due to the creation of multiple hotspots both for the longitudinally and the angularly assembled NRs, these substrates lead to a high EM and hence, SERS enhancement. Figure 7 shows the E-field profiles at the respective resonance wavelengths—for the three different cases of template-assisted self assembly of gold nanorods inside gold nanolines—simulated with Lumerical FDTD Solutions. Figure 7(a) shows FDTD simulation results of the purely longitudinal assembly of dimer of gold nanorods (with a diameter of 40 nm and a length of 135 nm) inside nanolines. The inter-nanoline gaps were selected such that gaps of 2 nm are present between the two nanorods in the X-direction and between the nanorods and the nanolines on either side. It can be noted that when the X-polarized light is incident, a 2D EM hotspot is created all along the nanorod length. However, it can be seen that the highest EM enhancement is obtained when the NRs exhibit a mixed assembly such that the NRs are angularly stacked ($A \neq 0^\circ$ and $A \neq 90^\circ$). This case, where the diameter of the nanorod is 40 nm and their length is 135 nm, is shown in figures 7(c) and (d) for the X- and Z- polarizations, respectively.

When the NRs are angularly stacked, highly localized 3D hotspots are also present in addition to the longitudinal 2D hotspots. These 3D hotspots, which lead to a very high EM enhancement, are formed between the nanolines and the spherical end of the nanorod (shown with an $'$ in figure 7(c)). Figures 7(e)–(f) show the E-field profile for the case when a mixture of longitudinal and horizontal assembly is present.

4. Conclusions

Thus, we demonstrate that potentially large area plasmonic substrates can be fabricated by template-directed capillary-force self assembly. It is shown that the number of nanoparticles, their packing pattern, and their orientation can be controlled by varying the relationships ‘G:D’ or ‘G:L’ between the inter-nanoline gaps in the underlying template (G) and the dimensions (D or L) of the nanoparticles of different shapes (nanospheres or nanorods, respectively). Moreover, the mixed assembly (longitudinal and angular) of plasmonic nanorods inside templates of plasmonic nanolines is demonstrated. It is shown that the angle of the assembled nanorods can be controlled by changing the relationship ‘G:L’. Furthermore, the electromagnetic behavior of these plasmonic substrates is systematically analyzed using Finite Difference Time Domain Modeling. It was found that large electromagnetic enhancement can be obtained which can be exploited for developing highly sensitive surface enhanced Raman scattering (SERS) based sensors.

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Appendix

Figure A1 (a) shows two cases of geometrical perturbation or aperiodicity in the Y-direction between the nanoparticles, and compares it with the case when the substrate is periodic with a gap of 5 nm in the Y-direction.
For these simulations, it is assumed that the gaps in the X-direction are symmetric and are 5 nm between the nanoparticles and between the nanoparticles and the nanoline.

The E-field profiles of these substrates, simulated with Y-polarized light, are shown at the resonance wavelength of 626 nm in figure A1(b). The average E-field enhancement was calculated over the electromagnetic hotspots and is plotted with respect to the wavelength in figure A1(c). It can be seen from this figure that the E-field enhancement varies only slightly as the gaps become aperiodic. These slight variations in the E-field will not change the order of the SERS enhancement achievable from these substrates. It must be noted that, as the gaps are being varied in the Y-direction, there is a negligible effect of these perturbations on the E-field enhancement, if X-polarized light is employed.

However, if the perturbations are present in both the X- and Y-directions such as those shown in figure A2(b), the E-field enhancement profile will change for both the X- and Y- polarized light (see figure A2(d)) as compared to the case when periodic or symmetric gaps are present (figures A2(a) and A2(c)). Figures A2(e)–(f) show a comparison of the average E-field enhancement for the uniform and non-uniform assembly of the nanoparticles when X- and Y-polarized light is incident. It can be seen from this figure that there is only a slight variation of the average E-field enhancement when the assembly of the nanoparticles is non-uniform compared to when it is uniform.

Figure A1. Effect of aperiodicity or perturbation in the gap along the Y-axis for the case when \(2D < G \leq 3D\). (a) The case of symmetric gap of 5 nm (in the Y-direction) between the nanoparticles is compared with a two asymmetric gap combinations which can occur during self assembly. The gaps in the X-direction are assumed to be constant and equal to 5 nm for all these cases. (b) E-field enhancement profiles at the resonant wavelength of 626 nm for these gap combinations respectively, and (c) average E-field enhancement from the electromagnetic hotspots is plotted against the wavelength for all the cases.
Figure A2. Effect of simultaneous perturbation in the X- and Y-direction, for the case when $2D < G \leq 3D$. (a) The case of symmetric gaps of 5 nm between the nanoparticles and between the nanoparticle and the nanoline, in both the X- and Y-direction. (b) The case of asymmetric gaps in both the X- and Y-directions. E-field enhancement profiles for X- and Y- polarizations of the incident light for: (c) symmetric i.e. uniform gap combinations, and (d) asymmetric i.e. non-uniform gap combinations. Average E-field enhancement from the electromagnetic hotspots is plotted against the wavelength for the two cases when: (e) X-polarized light is incident and (f) Y-polarized light is incident.

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