Optically and elastically assembled plasmonic nanoantennae for spatially resolved characterization of chemical composition in soft matter systems using surface enhanced spontaneous and stimulated Raman scattering

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We present a method to locally probe spatially varying chemical composition of soft matter systems

director n_0 (inset in Fig. 1

from the contrast of refractive index between uniform alignment of the far field and the LC distortions around NB particles, as well as the dependence of the effective refractive index distribution on the trapping beam's polarization.[19] Consequently, the average trap stiffness at a laser power of $= 32$ mW in a planar cell (~ 3.5 pN/μm) was found to be different from that in a homeotropic LC cell (~ 1.7 pN/μm). Additionally, the NB nanoparticle can be elastically attracted and trapped, as well as manipulated by use of local melting of the LC. In addition to the optical trapping of NBs, we observed a transfer of the angular momentum from the vortex LG beam to the nanoparticle resembling that discussed in earlier literature reports.[20] The NBs rotate around the beam's propagation direction [Fig. 3(c)]. The direction of rotation depends on the topological charge of the beam, being clockwise for negative and counterclockwise for positive [Figs. 3(c) and 3(d)]. The rate also shows dependence on laser power and [Fig. 3(d)]. The rotation rate increases with increasing laser power and with decreasing the integer $| | > 0$ and is, for example, ~ 0.5 Hz at $= 40$ mW and $= \pm 2$ [Fig. 3(d)]. The angular velocity is dependent on the angle between the line connecting the centers of the LG beam, NP and $\mathbf{n}$ [Fig. 3(c)].[21] This dependence is caused by the anisotropy of LC's viscous drag forces as well as by the complex dependence of laser trapping forces on the particle's position in such an experiment. The controlled trapping and dynamics of NB particles allow us to effectively use them as movable nanoantennae for the enhancement of weak spontaneous and stimulated Raman scattering signals, as discussed below.

B. Enhancement of Raman signals of 5CB by assemblies of NB particles

The ability to optically trap NB nanoparticles allows us to move them through the studied medium either through dynamically changing holograms displayed by the SLM or with the help of a motorized stage spatially translating the sample. Since the near contact-assembly of NBs yields even stronger field enhancement in the inter-particle regions, we can optically organize multiple particles into side-by-side assemblies, which in LCs are then held together by elastic forces, as shown in Figs. 2(d)–2(g). The electromagnetic field simulation for assemblies of NB particles [Figs. 2(b) and 2(c)] shows a strong electromagnetic field enhancement at the sharp edges of the particles, especially in the inter-particle region. The higher field enhancement at the adjacent edges of the particles and in the region between them is due to the coupled electromagnetic field emerging from the dipole and quadrupole interactions between the particles. Interestingly, the electromagnetic enhancement depends

When calculating the enhancement factor, to mitigate the influence of temporal fluctuations in the intensity due to positional and orientational fluctuations of the particles on the enhancement, each Raman spectrum was collected over a relatively long integration time of 0.5 s and then 1000 of such spectra were averaged using the EMCCD software. It is clearly evident from the comparison of Figs. 4(a) and 4(b) that the Raman lines corresponding to 5CB are enhanced considerably in the presence of NB. A close inspection of Fig. 4(b) reveals additional lines, which do not correspond to 5CB. In order to investigate the origin of these additional lines, a Raman spectrum was collected from NB particles spin coated on a glass substrate, Fig. 4(c), which indicates that these additional lines originate from the NSOL capping ligands of NBs. As compared to regular 5CB spectra, the average enhancement factor of Raman signal from 5CB molecules in the presence of NB particles is ∼500, although the values varies from 200–700 for different NB particles. The calculations of this factor were performed by taking the ratios of integrated intensities of SERS signal corresponding to the characteristic line at $1158 \, \mathrm{cm}^{-1}$ collected from the NB location and Raman signal collected after moving the beam away from NB particles in LC medium, normalized with respect to the number of 5CB molecules in the excitation volume, as commonly done in SERS literature and described in more details elsewhere.[7] The achieved enhancement factor is somewhat limited by the fact that the Raman spectra measured from the NB locations are convoluted because of the larger volume of the excitation beam as compared to NB assembly size, which is only about several hundreds of nanometers along the light propagation direction. The electromagnetic field enhancement is limited to a sample region very close to the NB particles and decays rapidly with the distance [Figs. 2(b) and 2(c)]. Consequently, Raman signals from 5CB molecules that are farther away from the NB particles are practically unaffected by the field enhancement, adding up together with the SERS maximally enhanced signal of 5CB molecules near NB and yielding the Raman spectra shown in Fig. 4(b). The enhancement factor calculated from the simulations was found to be dependent on the polarization of the incident electromagnetic wave, whether it is parallel or perpendicular to the line joining center of the particles. The calculated values of enhancement factor based on the simulated values corresponding to these two polarization were 115 and 194. The higher values of the enhancement factors observed experimentally can be explained by such factors as (1) the waist of the beam tightly focused by the high-NA objective is slightly smaller than the diameter of the volume used in simulations, (2) the local director field close to the NB particles [Fig. (1)] is distorted and complex, having a noticeable in-plane component, which may result in an additional increase of the intensity of the Raman signal, (3) each particle has its own unique roughness features which cannot be fully accounted for in experiments but can substantially influence the enhancement factor, especially

probing chemical composition. The optical trapping enables us to manipulate these nanoparticles through a soft matter medium with nanometer precision. We have demonstrated the use of such a system for studying the surface-enhanced Raman scattering of LC molecules with gold nanoparticles dispersed within the medium. Finally, we have also demonstrated probing of chemical inhomogeneity in the LC medium by using the optically trapped plasmonic particle as a probe of the Raman signal using the SERS effect.

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[3]

polymer chains (refer to dark diamond and star symbols) as depicted in Fig. 7(a). Higher intensities of the Raman lines of the polymer chains in Fig. 7(c) compared to Fig. 7(b) reveals higher concentrations of polymer chains inside LC defects as compared to the bulk regions away from defects. This indicates that the polymer chains segregate into the isotropic regions of the LC defects during the photopolymerization process, which is natural as they represent a lower cost of free energy when localized within defects as compared to the uniformly aligned LC host in which they induce energetically costly elastic distortions. This result shows that plasmonic metal nanoparticles are suitable for nanoantennae-like probes with the potential applications in exploiting nanoscale composition of soft matter composites.

IV. CONCLUSIONS

We have developed an experimental tool for spatially resolved characterization of chemical composition in soft matter systems by using surface-enhanced spontaneous and stimulated Raman scattering with simultaneous optical manipulation of particles with suitable nanometer-sized structures. These structures produce large surface electromagnetic field enhancements and, as such, can act as optically and elastically assembled plasmonic nanoantennae for