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Electrically controlled surface plasmon resonance frequency of gold nanorods

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We have presented the voltage-controlled tuning of plasmonic response of absorption spectra of gold nanorods in liquid crystals. We observe that gold nanorods can be aligned along the rubbed polyimide substrate before applying external voltage. It is found that the transverse mode of gold nanorods shows a blueshift or a redshift when rotating the analyzer parallel or perpendicular to the rubbing direction, respectively, while all longitudinal modes display a redshift behavior. This work offers an easy way to tune the transverse and longitudinal modes of gold nanorods simultaneously, which makes it feasible to establish the color tunable devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335812]

The effect of surface plasmon resonance (SPR) at interfaces has been the focus of intense research due to its specific optical properties and wide applications.^{1,2} The field called plasmonics is of interest in small particles, wires, rods, and thin films, where the major appearance generated by optical excitations is the collective coherent oscillation of electrons locally along the interface.³ Therefore, the absorption peak wavelength caused by the SPR is dependent on the size and the shape of the metallic nanocrystals. Besides, the dielectric environment surrounding the metallic nanostructures plays another important role to affect the absorption peak of SPR, varying the effective dielectric medium surrounding the nanocrystals would shift the SPR modes.^{4,5}

Liquid crystals (LCs) are an outstanding material with easily controllable optical properties via external parameters such as electric field or temperature.^{6,7} Some works have shown the electrically controlled tuning of plasmonic response of a single gold nanoparticle⁸ and gold nanoparticle arrays⁹ by altering the effective dielectric constant environment of LCs.

Gold nanorods possess peculiarly drastic absorption spectra of both transverse and longitudinal plasmon resonances.^{2,3,10–13} However, the effect of SPR of gold nanorods by LCs is not under study until now. In this letter, we report the demonstration to incorporate gold nanorods with LCs for observing the changes of the transverse and longitudinal absorption peak wavelengths by adjusting the external voltage to reorient the LCs.

A schematic of the side-view structure of the LC cell with and without external voltage is shown in Fig. 1. To achieve the purpose of voltage-controlled absorption spectra, LC cells are fabricated, consisting of two counter indium tin oxide (ITO)-coated glass substrates with a PI alignment layer. First, we drop the suspension solution of gold nanorods onto the rubbed PI layer until gold nanorods are dried to settle down in the clearing room. After the combination of top and bottom treated substrates in the same rubbing direction, the nematic LC E7 from Merk is injected into the assembled substrates at the isotropic temperature of the LCs.

The average thickness of the cell gap is about 9 μm . An alternating electric voltage at 1 kHz frequency is applied across the sample (z axis) to avoid the induced separation of charged impurities. A 100 W Xe lamp is focused onto the cell with a condenser, where the illumination light is unpolarized to excite all plasmonic response direction simultaneously. An analyzer in front of the entrance slit of the spectrometer is used to distinguish the direction of the dipole oscillation for advanced analyses. All experiments are performed at room temperature.

Figure 2(a) shows the UV-visible absorption spectra of gold nanorod solution used in this work. The detailed description of the synthesized approach can be found elsewhere.^{14,15} The inset in Fig. 2(a) shows the absorption spectrum results of different gold nanorod doses dried on PI substrate (2, 4, and 12 drops). According to the result, the

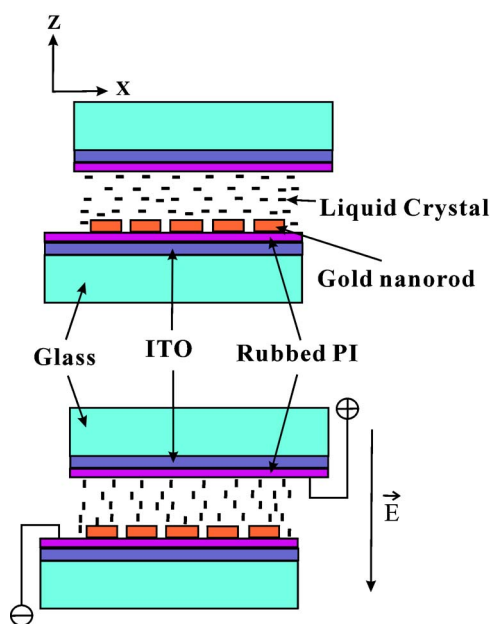


FIG. 1. Schematic showing the structure of fabricated sample with and without an applied electric field. The external electric field aligns the LC perpendicular to the cell plane.

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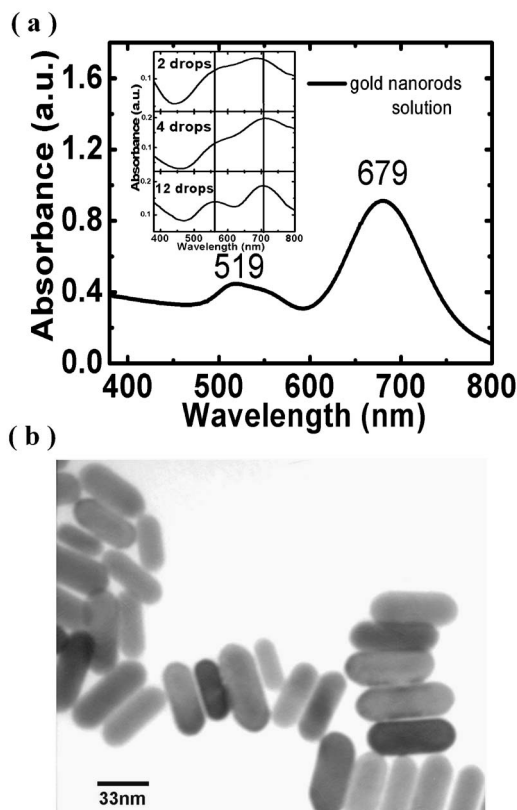


FIG. 2. (a) UV-Visible absorption spectra of gold nanorod solution. (b) TEM image of a dried sample of gold nanorods. The inset in (a) shows the absorption spectrum results of different gold nanorod doses dried on PI substrate (2, 4, and 12 drops).

transverse and longitudinal modes of gold nanorods are not changed while varying the concentration. Hence we can exclude out the possibility that the observed plasmonic peaks are caused by the clustered gold nanorods. As shown by the transmission electron microscopy (TEM) image in Fig. 2(b), the gold nanorods with aspect ratio of 2.72 are obtained, where the length and diameter are 49 nm and 18 nm in average, respectively.

Figures 3(a) and 3(b) show the dependence of absorption spectra of the LCs and gold nanorods as a function of wavelength without external voltage. It is found that the intensity of longitudinal mode is larger than that of the transverse mode in the parallel case. On the contrary, the intensity of transverse mode is larger than that of the longitudinal mode in the perpendicular case. These results indicate that some gold nanorods are arranged along the rubbed PI direction. We think that the gold nanorods aligned to the rubbed PI substrate are caused by the result of LC infiltration. Indeed, some works have observed the similar effect on spherical particles in nematic LCs,^{16–18} which are characterized by preferred alignment of the rodlike LC. Besides, recent works have shown the results of aspherical particles suspended in nematic LCs,^{19–21} indicating that the particle's anisotropic property adds the degrees of freedom that create orientation dependent forces. Therefore, minimizing the elastic energy of nematic LCs leads to sole interactions between gold nanorods, then causes the alignment in our system. Figures 3(c) and 3(d) exhibit the varieties of absorption spectra when the applied electric field is of 10 V/ μ m. Unlike the changes in Figs. 3(a) and 3(b), Figs. 3(c) and 3(d) display the same absorption spectra profile. It revealed that gold nanorods

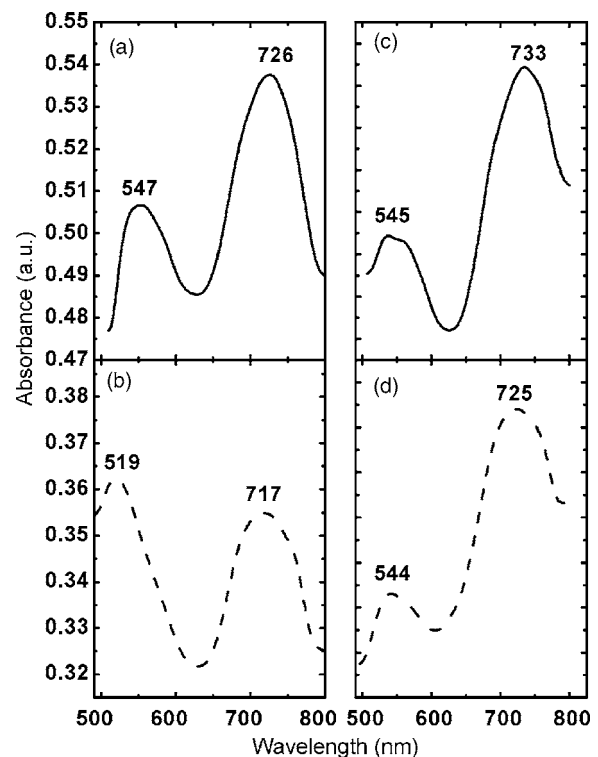


FIG. 3. Dependence of absorption spectra of the LCs-gold nanorod nano-composite as a function of wavelength. (a) and (b) show the results without external voltage. (c) and (d) display the results upon applying an electric field of 10 V/ μ m. The solid line or dashed line represent that the analyzer is oriented parallel or perpendicular to the PI orientation, respectively.

have been driven from the original location to other random direction resulted from reorienting the LCs with an external voltage. Indeed, applying an external field can alter the distortions of the LC alignment around the particles,²² especially be more complicated on nanorods due to their anisotropic property.^{19–21} Therefore, these complex distortions induce elaborate interactions between the nanorods such as the elastic torque, the viscous drag, and so on,^{20,21} thus lead to macroscopically random behavior, which will reduce the anisotropy of gold nanorods.

As shown in Fig. 3(a), the initial values of transverse and longitudinal modes are 547 and 726 nm when the analyzer is parallel to the PI direction, while they display initial values of 519 and 717 nm in perpendicular situation in Fig. 3(b). Moreover, the peak wavelengths of transverse and longitudinal modes become 545 and 733 nm in parallel condition in Fig. 3(c) and 544 and 725 nm in perpendicular condition in Fig. 3(d), respectively. The transverse mode in parallel situation displays a blueshift, and a redshift in perpendicular situation. The blueshift can be easily understood according to the changes of the refractive index of the LC. Before the applied electric field is turned on, the transverse mode in parallel condition only feels the high refractive index value ($n_e=1.74$) of the LC. After the field is applied, the resulting refractive index value is a combination of n_e and $n_o=1.52$. Therefore, the observed blueshift is a consequence of the reduction in the effective refractive index.

The pronounced redshift observed for the transverse mode in perpendicular condition can not be explained similar to the discussion of blueshift. It should only feel the low refractive index value n_o of the LC. The reorientation of LC molecules on the surface of nanoparticles is a very compli-

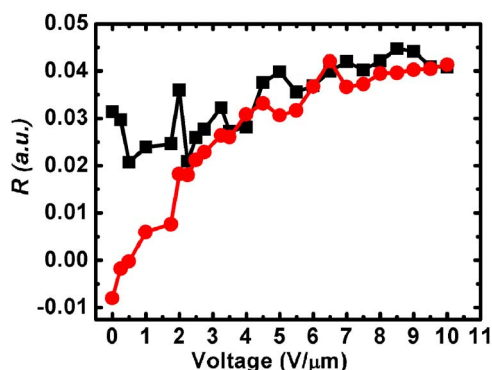


FIG. 4. (Color online) Diagram of R vs external electric field. Squares (■) or circles (●) display results when the analyzer is parallel or perpendicular to the PI direction, respectively. R is defined as the intensity of longitudinal mode minus the intensity of transverse mode.

cated problem. For instance, the local density of the LC molecules near the surface of nanoparticles can be changed due to the applied electric field.^{8,23,24} Here, we will adapt the result of the field-induced local density enhancement to describe the observed redshift.

Unlike the varieties of the transverse mode, the longitudinal mode exhibits a different process. It is observed that a redshift occurs when applying an electric field to align the LCs perpendicular to the cell plane, regardless of whether the analyzer is parallel or perpendicular to the PI orientation. We can interpret the redshift in the following way. First, according to the nature of nanorods, the long axis senses the field-induced local density effect more than the short axis because of the corresponding increased length contribution. Second, we find that the gold nanorods in our device can form an alignment along the rubbed PI substrate, which also enhances the field-induced local density effect in the long axis direction. Therefore, according to the intrinsic characteristic and directionality from the macroscopic viewpoint, the redshift effect will significantly dominate over the blueshift and then result in our observed phenomenon.

To understand the varieties of gold nanorods through external voltage further, we analyze all the experimental data and define a value R = the intensity of longitudinal mode minus the intensity of transverse mode. A diagram of R as a function of external electric field is shown in Fig. 4. The result indicates that the directionality on gold nanorods is destroyed by applying the external voltage. A plot of detailed varieties of plasmon peak position versus external electric field is shown in Fig. 5.

In summary, this letter reports on electrically controlled shifts of the plasmonic response of gold nanorods embedding in liquid crystals. We have observed that gold nanorods can be aligned along the rubbed PI substrate before applying external voltage. The observed results are interpreted in terms of both effects of the changes of refractive index as well as local density of the LC molecules.

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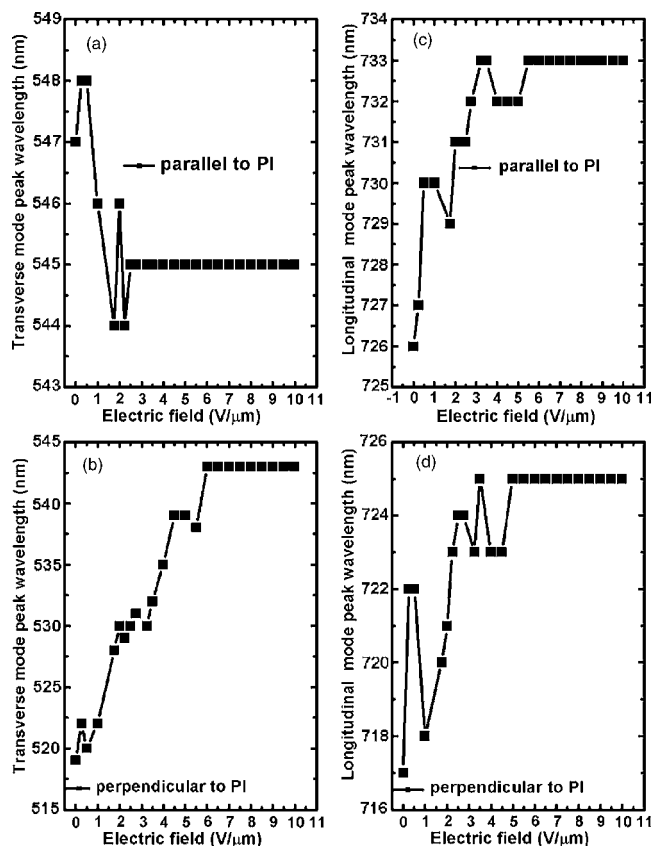


FIG. 5. Plot of varieties of plasmon peak position vs external electric field. (a) and (b) exhibit the changes of the transverse mode when the analyzer is parallel or perpendicular to the PI direction. (c) and (d) show the changes of the longitudinal mode for parallel or perpendicular analyzer direction.

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