

The ordering alignment of gold nanorods in liquid crystals and its applications to polarization-sensitive SERS

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Abstract. Gold nanorods (GNRs) were synthesized, coated with poly(ethylene glycol) (PEG) chains, and uniformly dispersed into the lyotropic nematic liquid crystal (LC) matrix by our proposed method. The GNRs-LC composites were found to exhibit good stability over days and have high density of GNRs. The extinction spectra of the composites were found to be polarization sensitive when the shearing force were applied, due to the alignment of GNRs driven by the LC molecules, which was also in accordance to the simulation results. A type of Raman reporter, 3,3'-diethylthiatricarbocyanine iodide (DTTC), was co-conjugated onto the GNRs with PEG molecules, and then incorporated into the LC matrix. Thus, its Raman signals could be enhanced by the localized surface plasmon resonance (LSPR) of the GNRs. These surface-enhanced Raman scattering (SERS) signals were found to be polarization sensitive when the shearing force was applied, due to the polarization sensitive enhancement of the local field of GNRs. The nanocomposites with tunable SPR peaks and SERS signals have potential applications in optoelectronic devices.

1. Introduction

Gold nanorods (GNRs), with unique optical properties and good chemical stability, have wide applications in sensing [1-2], imaging [3-4], surface-enhanced Raman scattering (SERS) [5-6], and so on. For a single GNR, its optical properties, like absorption, scattering, and local field, are sensitive to



the polarization direction of the incident light, while the polarization sensitivity is lost for lots of GNRs when they are randomly dispersed. The polarization sensitivity of GNRs would be helpful in their applications in sensing, bioimaging, optoelectronic devices, and so on.

Many efforts have been paid to align GNRs with long-range orientational ordering, including Langmuir-Blodgett technique [7], electric field or magnetic field method [8], droplet evaporation method [9], and so on, while most of them could only align GNRs in a small area. By dispersing GNRs in poly(vinyl alcohol) (PVA) film and stretching them, Perez-Juste et al. obtained large scale of aligned GNRs [10], but the GNRs were fixed in the film and they couldn't be tuned by applied electrical field. Liquid crystal (LC), which could be aligned and tuned by the applied shearing forces, electrical field and magnetic field, is potentially capable to align GNRs with long-range orientational ordering.

In this paper, GNRs were synthesized and poly(ethylene glycol) (PEG) chains were conjugated to improve their stability in LC matrix. The GNRs were dispersed into lyotropic nematic LC matrix, and a much higher density of GNRs were found in the GNRs-LC composites than before. The GNRs-LC composites also had a better long-term stability than reported, and this was very beneficial for their applications in optoelectronic devices. The polarization dependence of the extinction spectra of the GNRs-LC composites were studied by a home-built polarization microscope system, and the results were found to be very different from the behavior of randomly dispersed GNRs. Discrete dipole approximation (DDA) simulation was applied to calculate the extinction spectra of a single GNR with different angles between the polarization direction of the incident light and the long axis of the GNR, and similarities were found between the simulated and experimental results, thus the GNRs should be aligned with long-range orientational ordering in the LC matrix.

Raman scattering has wide applications in sensing and imaging for its capability of providing molecular fingerprints of samples [11]. As the spontaneous Raman scattering is usually too weak to be detected, SERS is commonly used [12]. GNRs, with their novel localized surface plasmon resonance (LSPR) properties, are very effective SERS substrates [13-14], and GNRs-LC composites could be polarization sensitive SERS substrates. In this work, a type of Raman reporter, 3,3'-Diethylthiatricarbocyanine iodide (DTTC) was selected, and DTTC-GNRs-LC composites were prepared. The polarization dependence of SERS signals in DTTC-GNRs-LC composites were studied by a home-built polarization Raman microscope system, and it coincided with the calculated near field of a single GNR in LC matrix with different angles between the polarization direction of the incident light and the long axis of the GNR. Thus the SERS signals would be mainly enhanced by the near field of the GNRs, and they could be modulated by varying the polarization direction of the incident light or the LC director n . The tunability of SERS signals in DTTC-GNRs-LC composites would be meaningful for their applications in sensing, imaging and related fields.

2. Methods and experiments

2.1. Materials and instruments

All chemicals in experiments were obtained from commercial suppliers and used without further purification. Thiolated poly(ethylene glycol) (SH-PEG) was purchased from JenKem Technology Co.,

Ltd. Other chemical reagents, which were not specially mentioned, were purchased from Sigma-Aldrich. Deionized (DI) water was used in all the experiments.

2.2. Synthesis of CTAB-GNRs and PEG-GNRs

The GNRs used in our experiments were synthesized according to the classical seed-mediated growth method with small modifications [15]. Firstly, the seed was prepared by pouring 600 μL of ice-cold sodium borohydride (NaBH_4) into the 10 mL of stirring deionized (DI) water solution containing 0.25 mM chloroauric acid (HAuCl_4) and 0.1 M cetyltrimethylammonium bromide (CTAB). It was kept stirring at 28°C for 12 min until the growth of the seed had been completed. Then, the GNR growth solution was prepared by adding 90 μL of ascorbic acid (Vc) into 10 mL of water solution containing 0.5 mM HAuCl_4 , 0.064 mM AgNO_3 and 0.1 M CTAB. After consequent addition of 12 μL seed solution, the GNRs started to grow. After 24h, the growth had been completed and the GNRs were purified by centrifugation and then redispersed in DI water. By adjusting the AgNO_3 concentration in the growth solution, different aspect ratios of GNRs can be obtained.

SH-PEG was used to replace CTAB on the GNRs as reported [4]. Briefly, 250 μL aqueous solution with 2mM 5 kDa SH-PEG was added into 5 ml 3.5 nM CTAB-GNRs solution, and the mixture was dialyzed in a 5 kDa cutoff cellulose membrane to replace the CTAB surfactants on GNRs for 16 h. After the dialysis, samples were purified with centrifugation to remove the excess PEG molecules.

2.3. Preparation and characterization of GNRs-LC composites

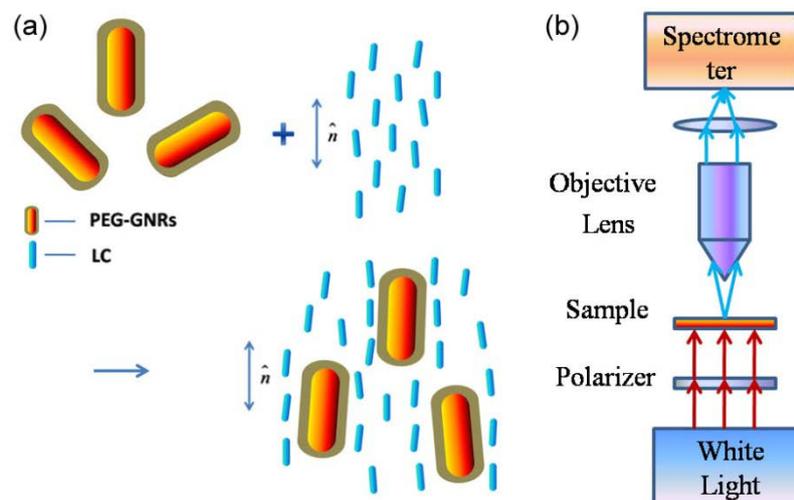


Figure 1. (a) The scheme for preparing GNRs-LC composites. (b) Set up for the polarization dependence measurement of the extinction spectra of GNRs-LC composites.

The surfactant-based lyotropic PEG-GNRs-LC composites in the nematic phase were prepared by mixing 37.5 wt% of sodium decyl sulfate (SDS), 5.5 wt% of 1-decanol and 57 wt% of aqueous suspension of PEG-GNRs from 10^{-8} M to 10^{-6} M together [16], as shown in Figure 1(a). The mixture was then centrifugated at 3000 rpm for 10 min and ultrasonicated for 30 min at room temperature. No visible aggregates were observed, indicating that GNRs were well-dispersed in the nematic phase.

Different amounts of GNRs were added to measure their solubility in LC matrix. The GNRs-LC composites were sandwiched between two glass slices separated by 0.02 mm gap using Mylar film spacers and uniformly aligned by shearing for further characterization. The CTAB-based lyotropic CTAB-GNRs-LC composites in the nematic phase was also prepared following the same procedures except that they were consisted of 25% CTAB and 75% of aqueous GNRs dispersion of 10^{-8} M.

The extinction spectra of these composites were measured by spectrometer (Ocean Optics, USB2000). The solubility of GNRs in LC matrix was obtained by recording the extinction spectra of GNRs-LC composites with varies GNRs concentrations. The long-term stability of GNRs-LC composites was characterized by measuring the extinction spectra at different time intervals.

The alignment of GNRs in LC matrix was verified by studying the polarization dependence of the extinction spectra of GNRs-LC composites with a home-built polarization microscope system, as shown in Figure 1(b). The white light from the halogen lamp was converted to be linearly polarized by a polarizer, while the polarization direction was modulated by its rotation angle. The sample was shined by the linearly polarized white light. The signal from the sample was collected by an objective lens (40 \times) and then to be directed into the spectrometer (Ocean Optics, USB2000).

DDA simulation was applied to calculated the extinction spectra of a single GNR with different angles between the polarization direction of the incident light and the long axis of the GNR [17]. The GNR was assumed to be a cylinder with hemispherical caps, with an effective radius of 20.3 nm and an aspect ratio of 1.25. The GNR was composed of gold and the surrounding media was LC with the refractive index of 1.39 [18]. The angle between the polarization direction of the incident light and the long axis of the GNR was set to be 0-90 degrees, with an interval of 10 degrees, and the corresponding extinction spectra of GNR were calculated.

2.4. Preparation and characterization of DTTC-GNRs-LC composites

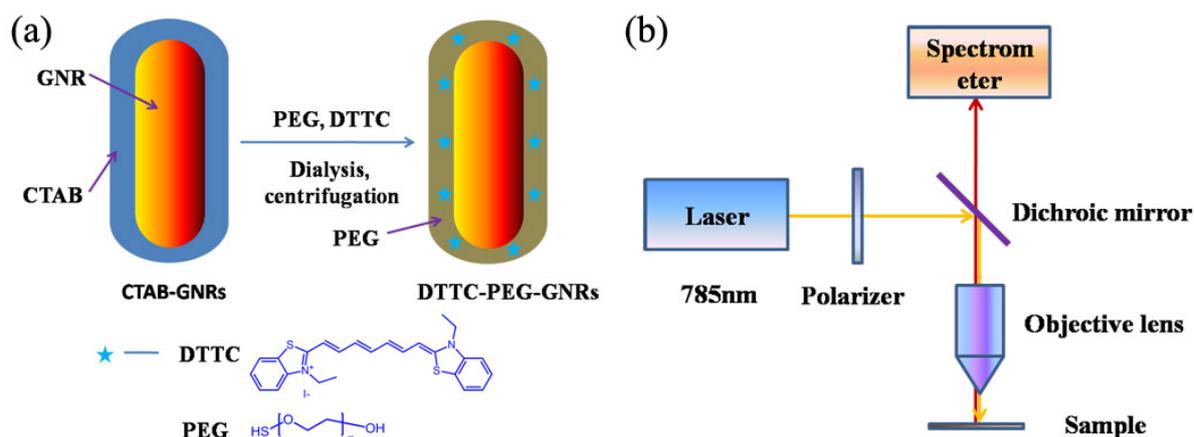


Figure 2. (a) The scheme for preparing DTTC-PEG-GNRs. (b) Set up for the polarization sensitive SERS detection.

DTTC was selected as the Raman reporter, and it was conjugated onto the GNRs as reported, as shown in Figure 2(a) [4]. Briefly, 100 μ L ethanol solution with 1 mM DTTC and 250 μ L aqueous solution with 2 mM 5 kDa SH-PEG were added into 5 mL 3.5 nM GNRs solution, and the mixture was

dialyzed in a 5 kDa cutoff cellulose membrane for 16 h. After the dialysis, samples were purified with centrifugation to remove the excess reactants, and DTTC-PEG-GNRs were obtained. Then DTTC-GNRs-LC composites were prepared via the same routine as before, with DTTC-PEG-GNRs being added instead of PEG-GNRs.

The polarization dependence of the SERS signals from the DTTC-GNRs-LC composites was characterized by a home-built polarization Raman microscope system, as shown in Figure 2(b). The 785 nm laser beam from the source was converted to be linearly polarized by a polarizer. It was reflected by a Raman dichroic mirror (transmission: 802-900 nm, reflectance: 400-800 nm) and then focused onto the sample by an objective lens (40×). The Raman signal from the sample were collected with the same objective lens, filtered by the Raman dichroic mirror, and then directed into the Raman spectrometer (BWTEK). The output laser power in our experiments was 300 mW, and the Raman signal integration time was 10 s.

DDA simulation was applied for the near field calculations of a single GNR in LC matrix with different angles between the polarization direction of the incident light and the long axis of the GNR [19]. The structure of the GNR was as above, and the surrounding media was LC, with refractive index of 1.39. The incident light was 785 nm, propagating in the z direction, with electrical amplitude $|E|$ of 1. The angle between the polarization direction of the incident light and the long axis of the GNR was set to be 0, 30, 60, and 90 degrees. The near field electrical intensity $|E|^2$ of GNR at the plane $z = 0$ was calculated.

3. Results and discussion

3.1 The solubility of GNRs in LC matrix

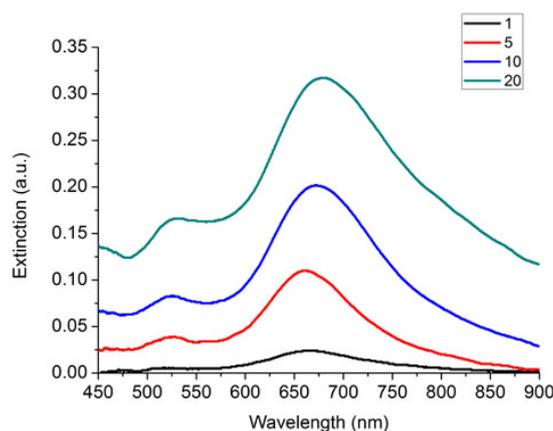


Figure 3. The solubility of PEG-GNRs-LC composites.

The maximum concentration of GNRs in our previous reported CTAB-GNRs-LC composites was about 10^{-8} M [20], and it was denoted as 1. Different amounts of PEG-GNRs were added into the LC matrix, and the extinction spectrums were shown in Figure 3. It was found that as many as 20 times of GNRs were found to be soluble in PEG-GNRs-LC composites, which was about 2×10^{-7} M. From the

increasing extinction peak and fine spectrum shapes, the GNRs in LC matrix would have good dispersibility and stability. The high concentration of GNRs in PEG-GNRs-LC composites is very meaningful in manufacturing optical devices.

3.2 The long-term stability of GNRs in LC matrix

The long-term stability of the GNRs-LC composites was characterized by measuring the extinction spectra at different time intervals, as shown in Figure 4. For PEG-GNRs-LC composites, as shown in Figure 4(a), the extinction spectra kept stable until 108 h, with little decrease in the LSPR peak, indicating the good stability of PEG-GNRs in surfactant-based LC matrix. For CTAB-GNRs-LC composites, as shown in Figure 4(b), there was a sharp decrease in the LSPR peak at 52 h. At 110 h, the extinction spectrum had nearly been flat, which was an indication of the aggregation of GNRs in the composites. The improvement in long-term stability of PEG-GNRs-LC composites may come from the strong bond of thiol group with gold surface and the compact covering of polymer. The superiority in long-term stability of PEG-GNRs-LC composites makes them more appropriate in fabrication of nanoscale devices.

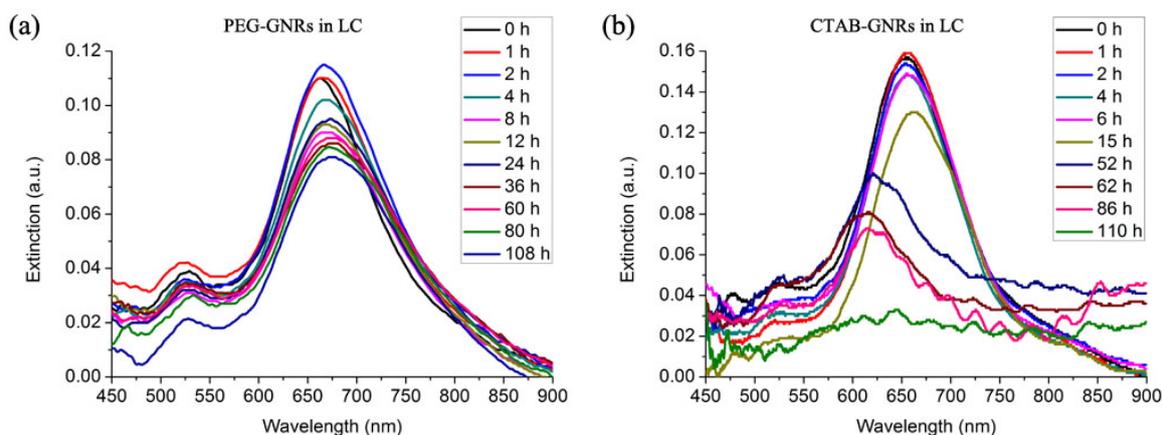


Figure 4. The long-term stability of PEG-GNRs-LC composites (a) and CTAB-GNRs-LC composites (b).

3.3 The polarization dependence of GNRs in LC matrix

The experimental extinction spectra of PEG-GNRs in LC matrix with different angles between the polarization direction of the incident light and the LC director n were shown in Figure 5(a). When the polarization direction of the incident light was parallel to LC director n , there was only one LSPR peak near 670 nm appeared. With increasing the angle between the polarization direction of the incident light and LC director n by rotating the polarizer, a new LSPR peak near 520 nm came up, while the LSPR peak near 670 nm fell down. When the polarization direction of the incident light was perpendicular to LC director n , the LSPR peak near 520 nm reached its maximum, while the LSPR peak near 670 nm vanished. This was quite different from the randomly dispersed GNRs in aqueous solutions, and it was very similar to the aligned GNRs, thus it would be an indication of the long-range orientational ordering alignment of GNRs in LC matrix.

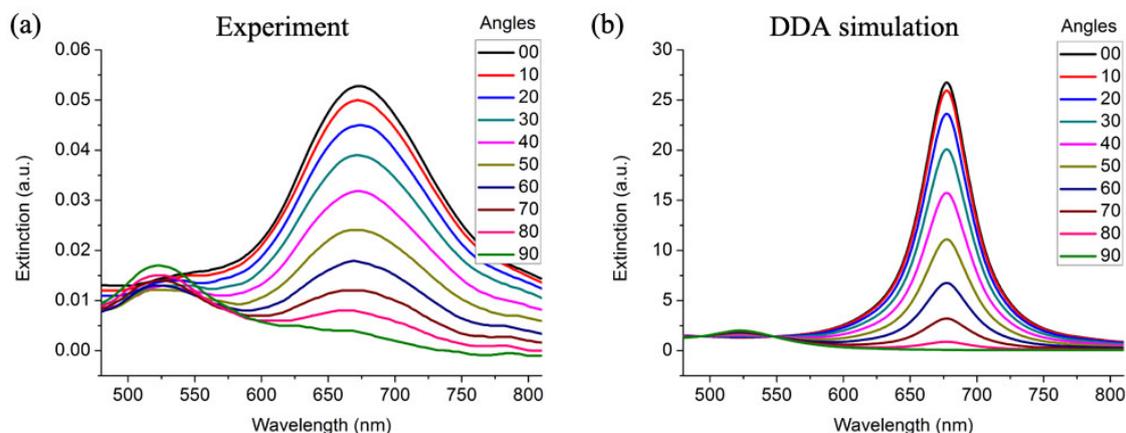


Figure 5. (a) The experimental extinction spectra of GNRs in LC matrix with different angles between the polarization direction of the incident light and the LC director n . (b) The calculated extinction spectra of GNRs in LC matrix with different angles between the polarization direction of the incident light and the long axis of the GNRs via DDA simulation.

The calculated extinction spectra of GNR in LC matrix with different angles between the polarization direction of the incident light and the long axis of the GNR via DDA simulation were shown in Figure 5(b). Compared with the experimental results on Figure 5(a), the same trend on the extinction spectra of GNR could be observed when varying the polarization angles. When the angle was 0 degree, the longitudinal LSPR peak reached its maximum. With increasing the angles, the longitudinal LSPR peak decreased and the transverse LSPR peak increased. When the angle was 90 degrees, the transverse LSPR peak reached its maximum. These changes would be another sign that the GNRs in LC matrix had been aligned with long-range orientational ordering.

3.4 The polarization dependence of SERS signals in DTTC-GNRs-LC composites

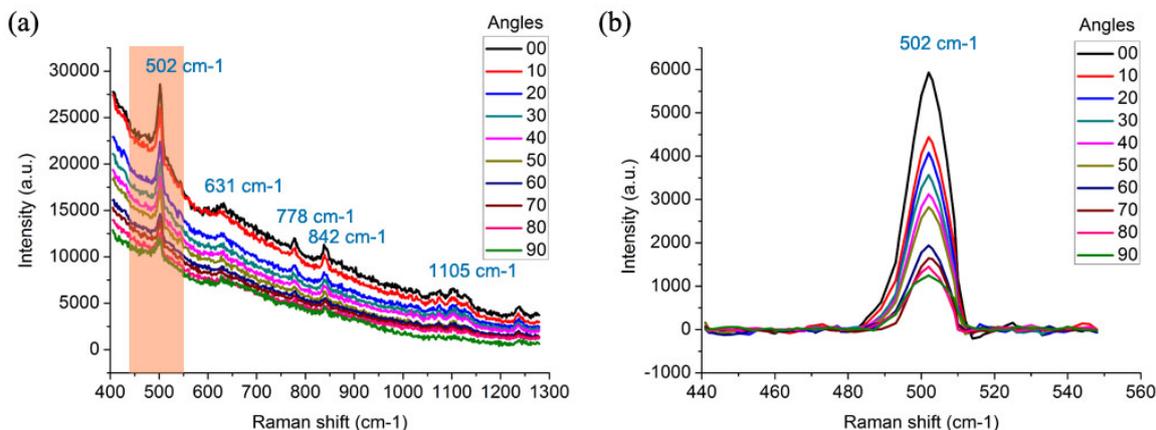


Figure 6. The SERS signals from DTTC-GNRs-LC composites with different angles between the polarization direction of the incident light and the LC director n . (a) with background, (b) background subtracted.

The SERS signals from DTTC-GNRs-LC composites with different angles between the polarization direction of the incident light and the LC director \mathbf{n} was shown in Figure 6(a). The composites had several specific Raman bands such as 502, 631, 778, 842 and 1105 cm^{-1} , which coincided with those of DTTC molecules [21]. For clarity, the strongest Raman band at 502 cm^{-1} was picked out, and the background was subtracted, as shown in Figure 6 (b). When the polarization direction of the incident light was parallel to the LC director \mathbf{n} , the Raman band at 502 cm^{-1} got its maximum value of 6000, indicating strong enhancement of Raman signals. When the angle between the polarization direction of the incident light and the LC director \mathbf{n} increased, the Raman band at 502 cm^{-1} decreased. When the polarization direction of the incident light was orthogonal to the LC director \mathbf{n} , the Raman band at 502 cm^{-1} got its minimum value of 1000. Thus the SERS signals from the DTTC-GNRs-LC composites were sensitive to the polarization direction of the incident light.

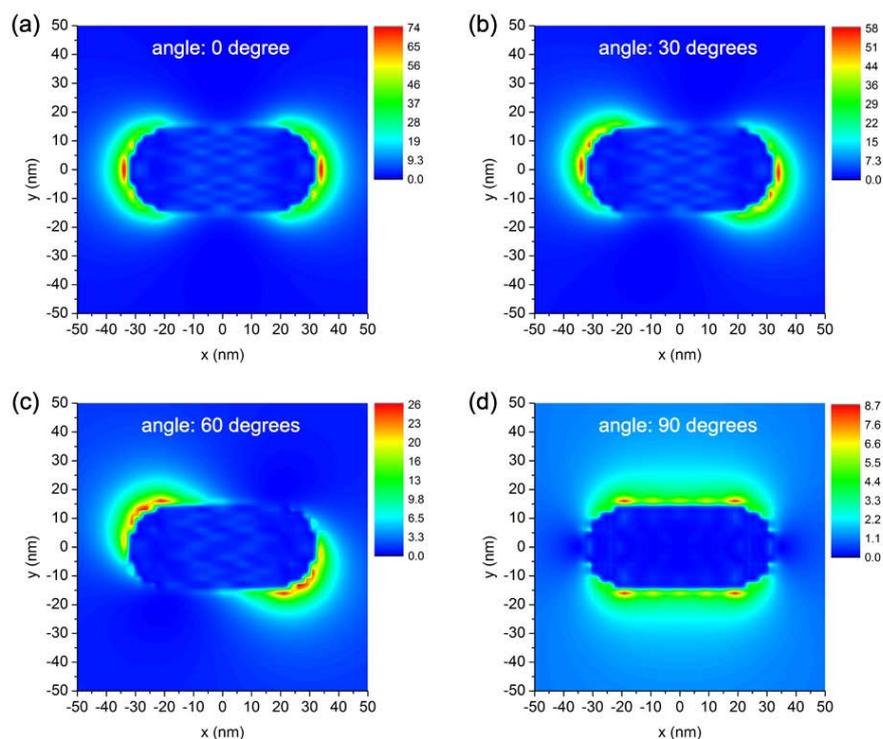


Figure 7. The calculated near field electrical intensity $|E|^2$ of a single GNR in LC matrix with different angles between the polarization direction of the incident light and the long axis of the GNR. (a) The angle was 0 degree. (b) The angle was 30 degrees. (c) The angle was 60 degrees. (d) The angle was 90 degrees.

The calculated near field electrical intensity $|E|^2$ of a single GNR in LC matrix with different angles between the polarization direction of the incident light and the long axis of the GNR was shown in Figure 7. When the angle was 0 degree, the near field electrical intensity of GNR reached its maximum. With increasing the angles, the enhancement of the near field electrical intensity of GNR decreased. When the angle was 90 degrees, the enhancement of the near field electrical intensity of

GNR reached its minimum. These coincided with the variations of the SERS signals from DTTC-GNRs-LC composites. Thus the polarization sensitivity of SERS signals of DTTC-GNRs-LC composites would be from the polarization sensitivity of the near field enhancement of aligned GNRs in LC matrix, and the SERS signals could be tuned by varying the polarization direction of the incident light.

4. Conclusions

In summary, GNRs were synthesized via the seed-mediated growth method, and they were conjugated with PEG chains to improve the stability. The PEG-GNRs were dispersed into lyotropic nematic LC matrix, with good solubility and long-term stability. The experimental extinction spectra of the GNRs-LC composites obtained from a home-built measuring system were found to be polarization sensitive, and the relationship was in accordance to the calculated results of a single GNR in LC matrix via DDA simulation, indicating that the GNRs had been ordering aligned. DTTC was selected as the Raman reporter, and DTTC-GNRs-LC composites were prepared. The SERS signals from DTTC-GNRs-LC composites were found to be polarization sensitive, and they were from the polarization sensitivity of the near field of GNRs. The alignment of GNRs and polarization sensitivity of SERS signals in GNRs-LC composites would be meaningful in their application in sensing, imaging, optoelectronic devices, and so on.

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