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# Anisotropic Optical Properties of Oriented Silver Nanorice and Nanocarrot in Stretched Polymer Films

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## Abstract

Stretching-induced orientation of both silver nanorice and silver nanocarrots dispersed in or deposited on the surface of poly(vinyl alcohol) (PVA) film was investigated by means of polarized UV-visible-near-infrared (NIR) spectroscopy and atomic force microscopy (AFM). The results show that the film stretching not only aligns the long axis of individual nanorice or nanocarrot preferentially along the stretching direction, but also induces assembly of these nanostructures into oriented arrays of random lengths in the deformation process. Consequently, the longitudinal surface plasmon resonance peaked at 820 nm for nanorice and 1050 nm for nanocarrots before stretching can be replaced by a continuous extinction over the entire 800-1800 nm NIR spectral range after stretching. Stretched PVA films containing either silver nanorice or nanocarrots thus display polarization-dependent transmission of the NIR light.

## 1. Introduction

When gold or silver nanoparticles are embedded in a polymer matrix and the composite is subjected to stretching, their surface plasmon resonance absorption and/or scattering can become incident light polarization-dependent. The reason is that the polymer deformation can induce the alignment or alter the organization of the metallic nanoparticles leading to anisotropic optical properties. Two reported systems illustrate well the interesting possibilities. In the first case, gold nanorods (AuNR) dispersed in polymers like polyethylene (PE) and poly(vinyl alcohol) (PVA) can be completely oriented upon deformation with the long axis of AuNR aligned in the stretching direction.<sup>1-3</sup> When incident light is polarized parallel to the stretching direction, only longitudinal absorption in the near-infrared (NIR) region ( $>700$  nm) is observed, while the transversal absorption in the visible region (around 520 nm) is absent. The opposite is true when the polarization of incident light is set to be perpendicular to the stretching direction. At intermediate polarization angles, both absorptions are present with relative intensities varying with the polarization angle. If the orientation of AuNR induced by polymer stretching is no surprise, especially for nanorods with a relatively high aspect ratio, what happens with spherical silver nanoparticles in stretched polymers is more striking. In highly stretched composite films of PE and silver nanoparticles, the nanoparticles can form pearl-necklace-type arrays along the stretching direction.<sup>4</sup> Consequently, the single absorption maximum at 435 nm in the undrawn film split into two at 420 nm and 480 nm. The relative absorptions at the two maximums depend on the polarization direction of incident light, with the highest absorption at the longer-wavelength when the polarization is parallel to the pearl-necklace arrays of the nanoparticles, and the highest absorption at the shorter-wavelength with perpendicular polarization. Since the two absorption maximums are in the visible region, the composite film displays bright red or yellow

color depending on the polarization of incident light. Application for color filters was demonstrated.<sup>4</sup>

The above findings have motivated us to investigate the orientation behavior of two new types of silver nanostructures of anisotropic form, namely, nanorice and nanocarrots in stretched polymer composites. Of the many nanostructures of metal colloidal particles, reports on recently developed silver nanorice and nanocarrots remain very limited.<sup>5,6,7</sup> In particular, to the best of our knowledge, there is no report so far regarding their optical properties in polymer materials. In contrast to silver nanobars, nanorice has rounded edge and corner,<sup>5,6</sup> while the large “head” and small “tail” of nanocarrots give it an asymmetrical shape.<sup>7</sup> As will be shown in this paper, we found that both silver nanorice and nanocarrot in stretched polymer films can not only have their long axis oriented preferably along the strain direction but also undergo reorganization and assembly during the polymer deformation, which gives rise to polarization-dependent extinction (absorption and scattering) over a broad NIR region from 800-1800 nm, which has been difficult to achieve with AuNR, spherical silver nanoparticles or other plasmonic materials.<sup>1-4,8,9</sup> Our finding suggests that the seemingly chaotic orientation process of silver nanorice or nanocarrots upon stretching of the polymer nanocomposite films could be a simple and effective means for developing new materials potentially useful for applications such as NIR polarizers or beam attenuators.

## **2. Experimental Section**

### **2.1 Synthesis of Silver Nanorice**

Silver nanorice was synthesized by a polyol method.<sup>6</sup> Briefly, 0.222g poly(vinyl pyrrolidone) (PVP K30, Mw: ~40,000, from Sigma-Aldrich) was dissolved into 20 mL polyethylene glycol 600 (PEG 600, from Xilong Chemical Industry Incorporated Co., Ltd), followed by the addition of 0.5 mL of 2M AgNO<sub>3</sub> aqueous solution. The solution was heated at 70 °C for 2h and then at 100°C for 16 h for the formation of the nanorice structure.

## 2.2 Synthesis of Silver Nanocarrots

Silver nanocarrots were synthesized in a similar way to silver nanorice, following the recipe previously reported by one of our groups.<sup>7</sup> CF<sub>3</sub>COOAg, instead of AgNO<sub>3</sub>, was used as the precursor for the formation of the nanocarrot structure. Briefly, 0.333 g poly(vinyl pyrrolidone) (PVP K30, Mw: ~40,000, from Sigma-Aldrich) was first dissolved into 20 mL polyethylene glycol 600 (PEG 600, from Xilong Chemical Industry Incorporated Co., Ltd). Subsequently, 0.4 mL of 1.5 M CF<sub>3</sub>COOAg aqueous solution was introduced and the reaction was allowed to last 20 h at 90 °C .

## 2.3 Preparation and Stretching of Nanorice- or Nanocarrot-Containing Polymer Films

The PVA sample (Mowiol® 28-99, Mw~145,000, > 99% hydrolysis, from Sigma-Aldrich) was dissolved in deionized water at a concentration of 4 wt% (heating to 80 °C followed by cooling). Likewise, the silver nanorice or nanocarrots were dispersed in deionized water. To prepare the composite film, appropriate amounts of the two solutions were mixed under rigorous stirring. Afterwards, the mixture was cast onto a clean glass slide and dried at room temperature first and then in a vacuum oven at 40 °C for several days. The resulting films had a thickness of about 30

$\mu\text{m}$ . For the film with the silver nanorice or nanocarrots located on surface of PVA, used for the AFM observation, it was prepared by following a reported method.<sup>1</sup>

The stretching of the PVA/nanorice or PVA/nanocarrot films was conducted on a home-made stretching device. The film was heated to 80 °C ( $>T_g$  of PVA) for 5 minutes, and then stretched to the desired strain ratio. After stretching, the film was immediately quenched to the room temperature ( $<T_g$ ) before being used for spectroscopic measurements.

## 2.4 Characterizations

The UV-Vis-NIR spectra were recorded on a Cary 6000i spectrophotometer. Polarized spectra were obtained by mounting a polarizer in front of the sample, with the polarization set to be either parallel or perpendicular to the film stretching direction. Atomic force microscopy (AFM) observations were performed by using a Veeco Dimension Icon equipped with a Nanoscope V controller. Silicon cantilevers with a resonance frequency of 320 KHz and a force constant of 42  $\text{Nm}^{-1}$  were utilized.

## 3. Results and Discussion

### 3.1 PVA/Silver Nanorice

We first wanted to know if the anisotropic shape of silver nanorice allows for effective stretching-induced orientation like in the case of AuNR.<sup>1-3</sup> The results obtained with PVA containing 1 wt% nanorice are given in Figure 1. Shown in Figure 1a are the UV-vis-NIR extinction spectra of an un-stretched film and a stretched film with a draw ratio of 4.5 (the ratio of the film length after stretching over that before stretching). Before stretching, both the

transverse resonance peak in the ultraviolet region (380 nm) and the longitudinal peak in the visible and NIR at a maximum wavelength of 820 nm are well visible, indicating quite good dispersion of silver nanorice in the PVA matrix. Significant spectral changes occurred after stretching of the film. While the transverse peak remains similar, an important red shift and broadening of the longitudinal peak were observed. Actually, the NIR extinction peak was broadened so much that it covered a continuous spectral region from 800 to 1800 nm. This result already suggests that silver nanorice in the PVA matrix undergoes a reorganization process induced by the film stretching, and such organizational changes mainly affect the longitudinal resonance of silver nanorice. Polarized extinction spectra of stretched composite films, recorded with the incident light (spectrophotometer's light) polarized parallel and perpendicular to the stretching direction respectively, provide information on the orientation of silver nanorice. As seen in Figure 1b for a film stretched to a draw ratio of 4, greater extinction in the NIR region was observed with parallel polarization, while the opposite is true for the transverse peak in the 380 nm region. These results indicate that the film stretching brings the long axis of silver nanorice to orient preferentially along the stretching direction. We further carried out the experiments with films stretched to different elongations, and determined the order parameter  $S$  from the apparent dichroic ratio  $R = E_{para}/E_{perp}$ , according to  $S = (R - 1)/(R + 2)$ ,  $E_{para}$  and  $E_{perp}$  being the extinction at a given wavelength with parallel and perpendicular polarization, respectively. Figure 2c shows the plots of  $S$  vs. film draw ratio for the transverse peak at 380 nm and two wavelengths in the NIR region, 820 nm (the absorption maximum) and 1800 nm (the longest wavelength investigated). The negative value of the order parameter for the transverse resonance peak indicates that the short axis of silver nanorice is preferentially oriented in the direction normal to the film stretching. The orientation of the long axis of silver nanorice along the

stretching direction is seen from the positive value of the order parameter measured at the two NIR wavelengths. For the two NIR wavelengths, the order parameter increases significantly with increasing the draw ratio up to about 2.3, and the same can be said for the order parameter of the transverse resonance peak. Upon further film elongation to the high draw ratio of 4, the orientation degree seems to vary little within experimental uncertainty. For all the wavelengths, the relatively small values of the order parameter indicate that the orientation degree of silver nanorice remains quite low ( $S=1$  for perfect orientation along the stretching direction and  $S=-0.5$  for perfect transverse orientation). This result is in sharp contrast with the complete orientation of AuNR under similar stretching conditions.<sup>1-3</sup>

The above results paint a picture of strain-induced orientation of silver nanorice in the stretched PVA film. Two features can be noted: 1) stretching induces orientation of the long axis of silver nanorice in the stretching direction, but the orientation is partial; and 2) while the transverse extinction peak remains unaffected, the longitudinal extinction peaked at 820 nm before stretching is replaced by continuous extinction covering the 800-1800 nm NIR region after stretching. A logical explanation for the extinction spectral change is that as the silver nanorice particles orient during the deformation process, they could organize into nanorice arrays by mutual attachment at the ends, which increases the effective aspect ratio and shifts the longitudinal resonance to longer wavelengths. The results in Figure 1 imply that the silver nanorice arrays are oriented along the stretching direction as the individual structures, and that the effective lengths (or extension) of those arrays are highly heterogeneous, which results in the continuous extinction covering the 800-1800 nm NIR region. In other words, film stretching induces not only orientation of individual silver nanorice but also their assembly into oriented



arrays of random lengths. The continuous extinction in the NIR region arising from this heterogeneity is interesting, because it means polarization-dependent transmission of NIR light over a broad spectral region. This can be seen from Figure 2a for a stretched composite film. The transmission in the 800-1800 nm region is much higher for incident light with polarization perpendicular to the stretching direction. Although the contrast is far below what is required for practical application, the finding suggests a way to develop inexpensive materials potentially useful for NIR polarizer or beam attenuator. Obviously, materials for applications need to be optimized by comprehensive studies and many parameters can affect the performance. For instance, Figure 2b shows the results on the effect of the silver nanorice content in the PVA matrix on the polarization-dependent NIR transmission under otherwise the same conditions. Within a low concentration range from 0.2 to 2.5 wt% of silver nanorice, the contrast increases within increasing concentration, mainly due to enhanced extinction with parallel polarization. However, upon further increase of the nanorice content, the NIR transmission with both parallel and perpendicular polarization drops, likely caused by more severe agglomeration of silver nanorice before film deformation. Another parameter affecting the polarization-dependent NIR transmission is the draw ratio of the composite film. Generally, the contrast increases with increasing the film elongation because of enhanced silver nanorice orientation.

For the purpose of imaging the orientation, silver nanorice was also deposited on the surface of a PVA film following a literature method;<sup>1</sup> and the film was stretched under the same conditions. Figure 3a shows that similar polarization-dependent NIR transmission could be obtained with the stretched film. Figures 3b and 3c show AFM topological images of the film before and after stretching. While randomly aligned silver nanorice was observed on the un-stretched film,

aligned stripe-like assembly of nanorice structures of varying lengths were formed on the stretched film. The image shows that the apparent stripe could be formed by attached nanorice along the long axis. The observation is consistent with the above analysis that oriented nanorice could form arrays upon film stretching and the highly heterogeneous lengths of the assembly account for the continuous plasmon resonance covering the wide NIR region from 800 nm to above 1800 nm.

### 3.2 PVA/Silver Nanocarrot

By stretching silver nanocarrot-containing PVA films, we basically performed the same experiments as described above for the nanorice. Shown in Figure 4 are the results of stretching induced orientation of 0.9 wt% nanocarrots in the polymer. Figure 4a compares the unpolarized absorption spectra of the PVA/nanocarrot film before and after stretching to draw ratio of 4. Before stretching, the transverse peak of silver nanocarrots is observable at 374 nm, while the longitudinal extinction band appears at much longer wavelengths than the nanorice, peaked at about 1050 nm. After stretching, the spectral changes are similar to nanorice in PVA. That is, the position of the transverse peak remains the same, but the longitudinal peak is broadened with the peak maximum shifted to 1200 nm. The apparent increase in the absorption around 374 nm is likely due to increased scattering in the UV region. This result suggests that the film stretching could also lead to agglomeration of nanocarrots in the strain direction, resulting in longer effective aspect ratio than well-dispersed nanocarrots. Figure 4b shows the polarized absorption spectra recorded with the stretched film. Very large parallel and perpendicular dichroism for the longitudinal and transverse peak, respectively, are visible, which indicates a high degree of stretching induced orientation of silver nanocarrots with the long axis along and the transverse

axis normal to the stretching direction. Given in Figure 4c are the plots of order parameters vs. film draw ratio, measured at two NIR wavelengths, 1200 nm (peak maximum) and 1800 nm, and at the transverse resonance 374 nm. Indeed, the data confirm that stretching of the PVA/nanocarrot film can effectively induce orientation of the nanocarrots, and that the orientation degree increases with increasing the draw ratio up to 4. The stretching induced orientation of nanocarrots is significantly higher than that of nanorice. This can be seen from  $S > 0.5$  for the long axis of nanocarrot at draw ratio of 4, as compared to  $S < 0.3$  for nanorice.

Likewise, the orientation of silver nanocarrots in the stretched film can be used to generate polarization-dependent transmission of NIR light. Figure 5 shows the polarized transmission spectra, over the 300-1800 nm region, recorded with two stretched films (draw ratio=4) loaded with 0.3 and 0.9 wt% nanocarrots, respectively. As compared to PVA/nanorice (Fig.2), two main differences can be noticed. First, the transmission contrast between perpendicular and parallel polarization is much higher, which is a direct consequence of the higher orientation of silver nanocarrots in the stretched film. Secondly, at a low content of nanocarrots (0.3 wt%), the film stretching orients the nanocarrots, but good dispersion of the silver nanostructure remains. This can be seen from the longitudinal peak still centered near 1050 nm and the absence of polarization-dependent transmission for wavelengths above 1500 nm. Only at the relatively high concentration of nanocarrots (0.9 wt%), the stretching results in not only orientation of the nanocarrots but also their agglomeration along the longitudinal direction, which leads to the polarization-dependent transmission over the wider NIR spectral region.

Again, by stretching a film of silver nanocarrots deposited on the surface of PVA, AFM can be used to image the stretching induced orientation of nanocarrots. Figure 6 shows a film before and after stretching to draw ratio of 4. Prior to stretching, there is no preferential orientation of nanocarrots and some agglomeration exists. By contrast, after stretching, nanocarrots are aligned with their long axes along the strain direction. In addition to dispersed nanocarrots, very heterogeneous agglomeration, involving varying number of nanocarrots and different aspect ratios, can be seen in the image, which explains the broadening of the longitudinal band over the NIR region. Moreover, there is no indication of any preferential mode of agglomeration, as both “head-to-head” and “head-to-tail” alignment can be observed. The whole of the results indicates that silver nanocarrots in a stretched PVA film behave in a similar way to the nanorice, orienting the long axes in the stretching direction and undergoing heterogeneous agglomeration. Under the applied sample preparation conditions, the nanocarrot appears to be better dispersed in the PVA matrix, which may contribute to the higher stretching induced orientation, but also to the absence of agglomeration at relatively low nanocarrot content in the film.

On the basis of the results obtained with both PVA/nanorice and PVA/nanocarrot, it appears that there is an optimal concentration of the nanoparticles in PVA for achieving high contrast of the polarization-dependent NIR transmission. The concentration should be high enough to induce the desired end-by-end lining up of the nanorice or nanocarrots upon film stretching, but still sufficiently low to avoid side-by-side agglomeration. A design rule for maximizing the contrast over a large NIR spectral range (800-1800 nm) can be established as follows. 1) Either silver nanorice or nanocarrots at an appropriate concentration should be well dispersed in a transparent polymer film without any agglomeration. 2) Stretching of the composite film should induce

complete orientation of the long axes of the nanostructures and, in the process, assemble the individual nanorice or nanocarrots into arrays of different lengths, while side-by-side agglomeration should be avoided. 3) The agglomerated arrays should contain only a few nanorice or nanocarrots, so that the small aggregates in the stretched film remain well dispersed and, consequently, the film retains a high transparency. If these conditions are met, NIR light polarized parallel or perpendicular to the stretching direction could be totally extinguished or transmitted through, respectively.

This study reveals that the main problem is the limited degree of orientation for either silver nanorice or nanocarrots in stretched PVA films. If their long axes are perfectly (or almost perfectly) aligned along the stretching direction, the transversal extinction over the NIR spectral region will be minimized as a consequence. To improve the degree of orientation, future studies might envisage the use of liquid crystalline polymers (LCPs) as the matrix of the silver nanostructures. If the polymer film can be stretched with either the nanorice or nanocarrots embedded in an ordered but fluid liquid crystalline phase, the orientation degree could be significantly enhanced due to lower viscosity of the orienting medium. In case freestanding LCP films are difficult to prepare, PVA can still be employed. Indeed, the use of this polymer to align either LCPs<sup>10-12</sup> or low molar mass liquid crystals<sup>13</sup> have been previously demonstrated.

#### **4. Conclusions**

We have reported the finding that by embedding silver nanorice or nanocarrots in polymers (or depositing them on polymer surface), stretching of the composite film can align the long axes of silver nanorice or nanocarrots along the stretching direction. Moreover, oriented nanorice or

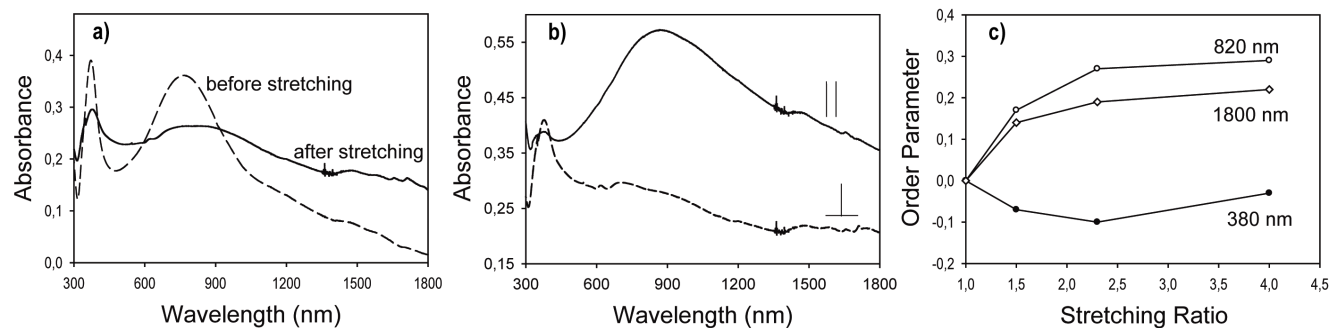
nanocarrot structures assemble into arrays of varying lengths that are also aligned in the film stretching direction. As a result of this orientation and organization of these anisotropic silver nanostructures upon deformation, the longitudinal plasmon resonance, peaked at 820 nm for PVA/nanorice and 1050 nm for PVA/nanocarrot in the un-stretched film, can be replaced by a continuous extinction covering a wide NIR spectral region of 800-1800 nm. The oriented PVA/nanorice or PVA/nanocarrot film can thus exhibit polarization-dependent transmission of NIR light.

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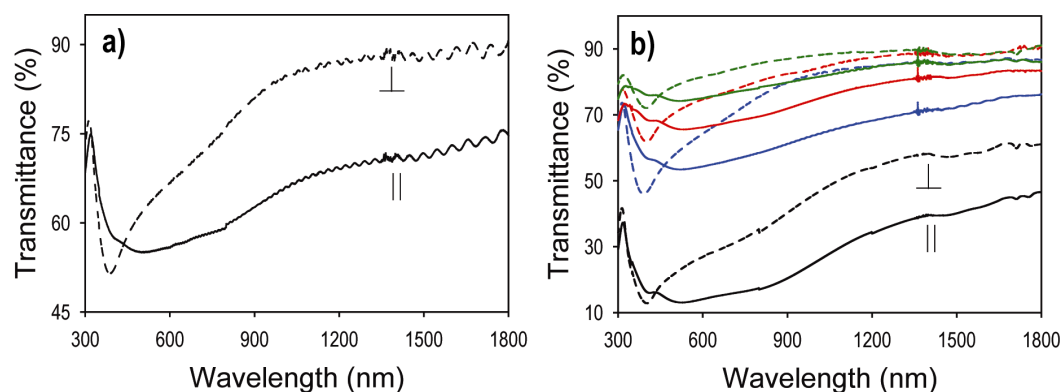
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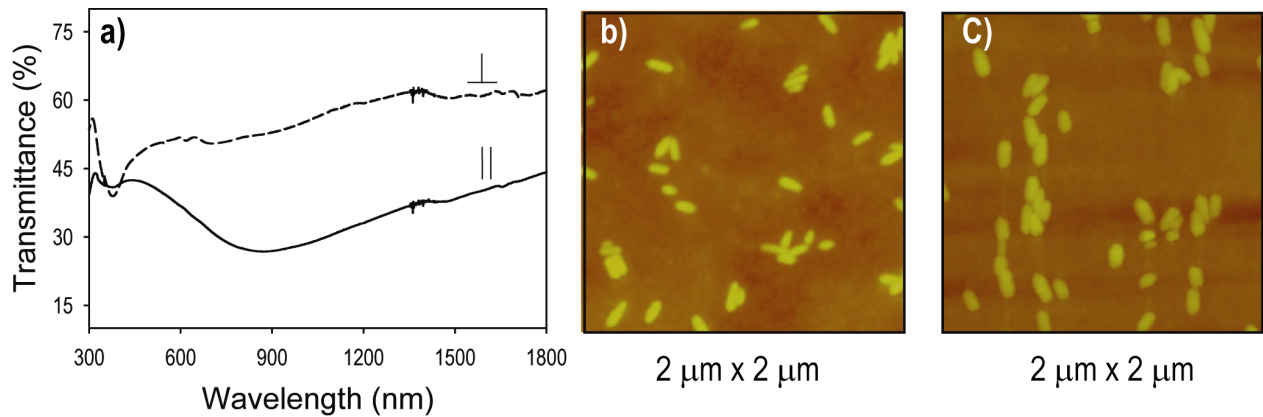


**Figure 1.** a) UV-vis-NIR absorption (extinction) spectra of a PVA/silver nanorice (1 wt%) film before and after stretching to draw ratio of 4.5. b) Polarized absorption spectra for a composite film stretched to draw ratio of 4.5, with the incident beam polarized parallel and perpendicular to the film stretching direction, respectively. c) Order parameter of silver nanorice measured at three wavelengths corresponding to the transverse (380 nm) and longitudinal surface plasmon resonance (820 and 1800 nm).

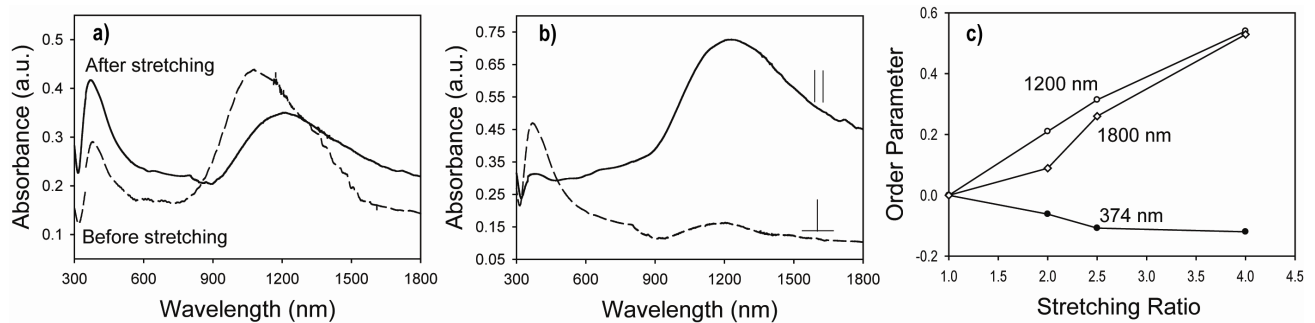


**Figure 2.** a) Polarization-dependent transmission spectra of a stretched PVA/silver nanorice (0.8 wt%) film (draw ratio=4) with the polarization of the incident beam polarized parallel and perpendicular to the film stretching direction. b) Polarized transmission spectra of composite films containing different concentrations of silver nanorice: 0.2 wt% (green), 0.4 wt% (red), 0.8 wt% (blue) and 2.4 wt% (black).

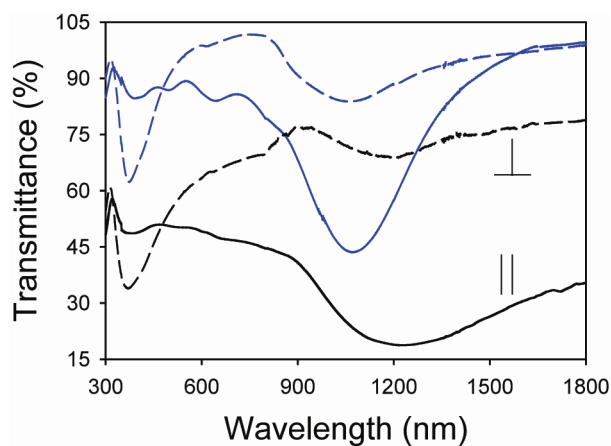




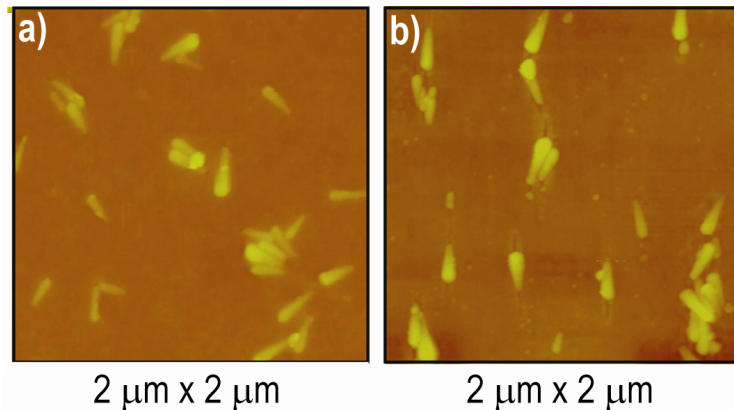
**Figure 3.** a) Polarized transmission spectra of silver nanorice deposited on the surface of a PVA film before being stretched to draw ratio of 4. b) and c) AFM topological images of the film in a) before and after stretching, respectively.



**Figure 4.** a) UV-vis-NIR absorption (extinction) spectra of a PVA/silver nanocarrot (0.9 wt%) film before and after stretching to draw ratio of 4. b) Polarized absorption spectra for a composite film stretched to draw ratio of 4, with the incident beam polarized parallel and perpendicular to the film stretching direction, respectively. c) Order parameter of silver nanocarrot measured at three wavelengths corresponding to the transverse (374 nm) and longitudinal surface plasmon resonance (1200 and 1800 nm).



**Figure 5.** Polarization-dependent transmission spectra of stretched PVA/silver nanocarrot films (draw ratio=4) containing two different concentrations of nanocarrots: 0.3 wt% (blue) and 0.9 wt% (black), the polarization of the incident beam being polarized parallel and perpendicular to the film stretching direction.



**Figure 6.** AFM topological images of a PVA film with silver nanocarrot deposited on the surface before (a) and after stretching (b) to draw ratio of 4.