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Article

Preparation of Nanocomposite Plasmonic Films Made from Cellulose Nanocrystals or Mesoporous Silica Decorated with Unidirectionally Aligned Gold Nanorods

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Abstract: Using liquid crystalline selforientationally ordered anisotropic plasmonic nanoinclusions.

Keywords: gold nanorods; cellulose nanocrystals; liquid crystal; plasmonics; mesoporous silica

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1. Introduction

Nanostructured materials are poised to revolutionize scientific instruments, technologies, and consumer devices. Liquid crystalline intermediate phases confer long-range orientational order that has been previously used to improve the properties of fibers and deposited films for biomedical [1], optical [2], and electronic [3,4] applications. Liquid crystals (LCs) can act as smart hosts that align anisotropic nanoparticle inclusions and leverage nanoscale anisotropy into device scale polarization sensitivity [5]. Self-assembly of plasmonic nanoparticles in LCs has been extensively studied recently [6–8]. Gold nanorods (GNRs) have two surface

Figure 3. SEM imaging of thin films of CNCs with embedded GNRs (with a thin carbon coat to improve conductivity). (**a,b**) Co-located images obtained with (**a**) in-lens (

polarization-dependent SPR effect, indicating that silica capped GNRs maintained their rod-like structure. Using low-voltage SEM, we observed that the films had a mesoporous structure, which was consistent with what was previously observed for such films without GNRs [21]. GNRs tended to be evenly dispersed throughout the film, with a lower degree of alignment than in the cellulose films. The estimated scalar order parameter of GNRs that we could achieve by polarization-dependent extinction spectra in this case was . The reduced value of the orientational order parameter may be partially due to the high-temperature treatment known to affect gold nanoparticles [22]. The longitudinal plasmonic peak shifted from 680 nm (Figure 1d, 2h) to 630 nm (Figure 3c) due to a combination of two effects, the nanorods being deformed by heating and the silica having different dielectric properties than the cellulose. However, it is interesting that the alignment persisted upon removal of CNCs, providing a potentially useful approach for scalable fabrication of composite mesostructured films with orientationally ordered plasmonic nanoparticles in a silica matrix. These obtained hybrid thin films can be practically useful. The mesoporous silica surface, which encloses the GNRs, can be functionalized with various chemicals, and the unique absorption properties of the film could be used to study chemical reactions, or to create a catalyst for chemical reactions. The presence of orientationally-ordered plasmonic nanostructures in such films may provide the means of efficient use of light for controlling and guiding reactions and processes in various applications.

Figure 4. Mesoporous silica films containing aligned GNRs. (**a,b**) Bright field polarizing microscopy images with the polarization parallel (**a**) and perpendicular (**b**) to the director. (**c**) Absorption spectra of the film as measured with polarization parallel (red) and perpendicular (blue) to the director. (**d,e**) TPL images of GNRs taken with polarization parallel (**d**) and perpendicular (**e**) to the director, confirming alignment of the gold nanoparticles with their long axes on-average parallel to the director. The homogeneous TPL signal in the images confirms uniform distribution of GNRs. (**f,g**) SEM images of the mesoporous film showing (**f**) alignment of GNRs and (**g**

2.3. Discussion

Unlike their dichroic dye based counterparts, plasmonic polarizers allow for very precise control over the operational spectrum of a polarizer as well as the ability to polarize light of different wavelengths, including the ultraviolet and infrared parts of an optical spectrum [23]. The transverse plasmonic absorption is generally a function of the material used for the rod-like nanoparticles, with nickel having an absorption peak at 380 nm, silver absorbing at 420 nm, gold at 525 nm and copper at ~580 nm [23]. The longitudinal SPR

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