C DNA-

-

Qingkun Liu,[1] Anton Kuzyk,[2] Masayuki Endo,[3] and Ivan I. Smalyukh[1,4,5,*]

[1]Department of Physics, University of Colorado, Boulder, Colorado 80309, USA
[2]Department of Neuroscience and Biomedical Engineering, Aalto University School of Science, P.O. Box 12200, FI-00076 Aalto, Finland
[3]Department of Chemistry, Graduate School of Science, Kyoto University, Yoshida-ushinomiyacho, Sakyo-ku, Kyoto 606-8501, Japan
[4]Department of Electrical, Computer, and Energy Engineering, Materials Science and Engineering Program and Soft Materials Research Center, University of Colorado, Boulder, Colorado 80309, USA
[5]Renewable and Sustainable Energy Institute, National Renewable Energy Laboratory and University of Colorado, Boulder, Colorado 80309, USA
*Corresponding author: ivan.smalyukh@colorado.edu

Received 12 March 2019; revised 6 May 2019; accepted 7 May 2019; posted 7 May 2019 (Doc. ID 362122); published 28 May 2019

Photo-responsive nanomaterials hold great promise for realizing information processing devices, micro-machines, and biosensors. Scalable assembly of such materials using mesostructured liquids, such as liquid crystals, remains a challenge due to the poor compatibility of nanostructures and the host medium. Here we demonstrate a new type of colloidal dispersion of plasmonic DNA-origami with photo-switchable chirality in cellulose nanofiber-based liquid crystals. The composite material inherits properties of DNA-origami plasmonic nanostructures, so that the composite's chirality can be erased by ultraviolet light and recovered by visible light. The cellulose nanofibers provide a liquid crystalline host with weak optical birefringence, which barely affects the polarization of the incident light, so that the response is dominated by circular dichroism of uniformly dispersed plasmonic nanostructures. Our approach may serve as a new platform for scalable assembling DNA origami-templated nanomaterials.

https://doi.org/10.1364/OL.44.002831

Photo active materials exhibit remarkable functional properties for information storage, nano-machines, and biological applications [1–3]. Several techniques have been developed to fabricate, such photo-responsive materials, including molecular motors [4,5] and light-driven colloids [6–8]. Photo-responsive materials with dimensions of structural units at several tens of nanometers are particularly important because of the variety of new properties arising from the ensuing mesoscale structure and composition. For example, recently, researchers developed plasmonic nanostructures assembled on DNA origami templates in a powerful way that tethers the exotic optical properties of the nanoparticles to the programmability of DNA strands [9–15]. However, assembling these DNA-templated nanostructures into scalable ordered phases and mesostructured materials has proven to be challenging. Liquid crystals (LCs) have been used to assemble the nanostructures into long-range ordered composites [16,17], but conventional LCs have poor compatibility with DNA, which is very sensitive to the pH, ionic strength, and organic chemical species. On the other hand, a cellulose nanofiber (CNF) colloidal dispersion, a biomaterial compatible with DNA, could be a suitable host medium capable of forming a lyotropic LC phase at a vanishing low concentration due to the large aspect ratio of CNFs. However, the utility of using such CNF-based lyotropic LCs for mesoscale colloidal organization has not be demonstrated so far.

Here we demonstrate a new composite material which comprises photo-responsive plasmonic nanomaterials templated by DNA origami colloidally dispersed in a nematic lyotropic LC. Gold nanorods (GNRs) assemble into chiral structures on DNA-origami templates, whose chirality can be reversibly switched by light. LC is readily formed by CNF at a low concentration in a nearly neutral aqueous solution. When dispersed in CNF-based lyotropic nematic LC host, the composites exhibit excellent stability and show photo-switchable chirality. Since the CNF-based LC shows very low linear birefringence, it does not significantly change the polarization of the incident light used to control the nanostructures, as well as does not alter the switchable circular dichroism of the composite. This is the first demonstration, to the best of our knowledge, of switching between chiral and non-chiral LC medium with plasmonic optical response and circular dichroism. In more common types of chiral additives, like chiral molecules, chirality leads to helicoidal structures of director, but we achieve a completely new type of behavior, where medium is switched between chiral and non-chiral states while structure of director never becomes helicoidal but rather retains a unidirectional alignment of director [18]. This new composite may open the door for scalable fabrication of optically active material from the DNA-templated nano-scale building blocks.

undergoing trans-cis photoisomerization in response to ultraviolet (UV) and visible (VIS) light were incorporated into DNA strands for reversible control of DNA hybridization and manipulation of spatial configuration of DNA origami templates. [Figs. 1(a)–1(c)]. DNA origami structures consisted of two 14-helix bundles with dimensions of 80 nm × 16 nm × 8 nm linked in the center by two flexible single-stranded segments (Fig. 1). The two linked origami bundles form a chiral object with a tunable angle. GNRs were attached to each origami bundle to form a chiral plasmonic nanostructure [Fig. 1(c)]. Figures 1(c) and 1(e) shows schematics and TEM images of the plasmonic dimers. The dimers exhibit binding preference to the TEM grid, and the GNRs appear side by side in the TEM images [Fig. 1(e)].

To ensure an excellent dispersion of plasmonic DNA-origami in LCs, an aqueous nematic LC consisting of biocompatible cellulose nanofibers was chosen. CNFs were produced through the oxidation of bleached wood pulp catalyzed by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical under mild pH aqueous conditions by following the modified procedures described in literature [19

positive birefringence, the blue interference color of the second order indicates the optical axis (long axis) of the CNF is parallel to the slow axis (γ) of the waveplate, while the orange interference color of the first order shows the optical axis of the CNF is perpendicular to γ from the Michel-Levy chart. The birefringence of the dilute colloidal dispersion of CNFs is calculated to be on the order of 10^{-5} based on the interference color and the length of the optical path. The good dispersion of GNRs nanostructures in CNF LC is also confirmed by the scattering from individual particle under dark-field microscope [Fig. 2(d)]. Importantly, the composite was designed in such a way that GNRs within the origami do not experience a strong aligning potential from the LC host medium, as was the case in previous works [14–16]. Unlike in the case of individual GNRs, the dimensions of overall plasmonic DNA-origami are relatively isotropic [Figs. 2(a) and 2(b)], which allows them to be randomly oriented within the anisotropic host medium. This random orientation is confirmed by lack of correlated polarization dependencies of polarization-dependent scattering from nanostructures in dark field images like the ones shown in Fig. 2(d). In turn, as we show below, this lack of orientational ordering of GNRs and switching of their relative orientations within the origami-based nanostructures allows us to obtain CD spectra, differently from the case of switchable linear dichroism presented in the past studies [16,17].

The GNR assembly shows photo-switchable chirality of individual nanostructures within the nematic LC host. On visible light illumination, the azobenzene molecules are converted to trans-form and the photo-responsive DNA origami is locked into a chiral structure [Fig. 1(a)]. When light interacts with the chiral plasmonic nanostructure, plasmons are excited in the two GNRs, leading to a characteristic extinction spectrum [Fig. 3(a)]. Furthermore, because of the proximity of GNRs within the same DNA-origami nanostructure, the surface plasmons from the two nearby GNRs are coupled, resulting in plasmonic CD. This is revealed through characterization of CD spectra when DNA origamis are in a chiral conformation [Fig. 3(b)]. In contrast, on ultraviolet light illumination, the azobenzene molecules on DNA-origami are converted to the cis-form, resulting in dehybridization of the DNA-origami duplex [Fig. 1(a)]. The photo-responsive segment is opened, and the conformation of the origami nanostructure is therefore relaxed into an achiral form. Consequently, the CD response after

Two-photon-absorption based fluorescence signal from the GNRs excited by circularly polarized light at 870 nm confirms the good dispersion of the chiral plasmonic nanostructures in