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Chiral meta-interface: Polarity reversal of ellipticity through double layers consisting of transparent chiral and absorptive achiral media

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We have studied circular dichroism (CD) in the visible region of composite and double-layer films consisting of a transparent chiral molecule, glucose, and an absorptive achiral dye, rhodamine. Composite and double-layer films show an absorption-induced CD response caused by chirality of glucose at 540 nm, where the rhodamine exhibits absorption. More importantly, in double layers, the polarity of the ellipticity in CD signals is found to be reversed when the incident direction is reversed. We discuss the origin of the polarity reversal, which is very similar to the magneto-optical effect, at the chiral meta-interface without magnetic field.

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Artificial materials consisting of subwavelength-sized units are called metamaterials.[1] Electromagnetic metamaterials manifest several intriguing properties: negative index of refraction,[2,3] cloaking,[4] and narrow-band perfect absorption,[5] which are never observed in nature. A key concept of metamaterials is the assignment of distinct functions to different units, mimicking an intriguing property for light. When realizing negative index of refraction by metamaterials,[6] for example, one may assign magnetic resonance to split-ring resonators[7] and electric response to metallic cut wires;[8] light "regards" the medium consisting of these constituents as an effective medium. This concept is applicable in a broad range of physics in atoms, molecules, and condensed matter.

In this study we focus on the optical activity (OA) of a medium including chiral molecules. OA brings about rotation of a linearly polarized plane of light, i.e., optical rotatory dispersion (ORD), which is caused by a difference in indices of refraction between left-/right-handed circularly polarized light. In absorptive chiral molecules, rotation of the linearly polarized plane is accompanied by circular dichroism (CD), which is due to the absorption difference between left-/right-handed circularly polarized light.[9] Polarity of the ORD and CD angles is independent of the direction of the propagation of light. Let us assume that an angle in CD, ellipticity, is θ after transmitting through a CD medium from the top. When the light transmits from the bottom, the rotation angle is also θ, resulting in the identical polarity of ellipticity in CD spectra. In other words, the transmission of circularly polarized light is symmetric. This is so called reciprocity.

Contrastingly to the OA, the magneto-optical (MO) effect, which is observed for light interacting with a magnetized medium, is well known to be antisymmetric because the rotation angle is determined by the magnetization direction. The ellipticity is rotated to the opposite direction after transmitting through an MO medium from the top and bottom. This results in polarity reversal in ellipticity when light is transmitted from top and bottom. The polarity reversal is never observed in OA without magnetization or magnetic field. In this Rapid Communication, however, we report polarity reversal of ellipticity, which looks similar to the MO effect, through an interface between chiral molecule and achiral dye layers without magnetic field.

In the context of metamaterials, the interface created in this study is a result of assigning chirality and absorption of a natural CD molecule to a chiral molecule and absorptive dye, respectively. The interface can thus be named *a chiral meta-interface*. We discuss the origin of the polarity reversal of ellipticity at the chiral meta-interface without magnetic field. The chiral meta-interface enables us to realize a broadband polarity reversal by using several dyes with different absorption wavelengths.

We first study a composite of chiral molecules and absorptive dye as shown in Fig. 1(a). 3.2 mg of achiral absorptive dye, called rhodamine, was mixed with 200 mg of ultraviolet (UV) curable resin, called PAK01. 20 mg of glucose as a chiral molecule is added to the mixture. The resin with both rhodamine and glucose was dropped onto a quartz, and sandwiched with another quartz substrate. By irradiating UV light for 5 min, the resin was cured and composite film was prepared. CD of the samples was measured using JASCO J-820. In the measurements, a CD peak (dip) is defined as rotation of the polarization plane to the right (left) when the light propagation is observed from the detector.

Figure 2(a) shows CD spectra of a composite film including glucose and rhodamine. Figure 2(b) shows absorption spectra simultaneously measured; a strong absorption peak is observed at about 540 nm. Glucose is transparent in this wavelength. The absorption is thus caused by rhodamine. In Fig. 2(a), vertical and horizontal axes correspond to ellipticity and wavelength in vacuum, respectively. A composite including D-glucose and rhodamine (solid red line) shows a CD dip at about 540 nm, where an absorption peak due to rhodamine is observed in Fig. 2(b). A solid blue line in Fig. 2(a) corresponds to CD spectra when light is transmitted from the bottom. The CD spectra after transmission from the bottom exhibits a CD dip very similar to that from the top.

In Fig. 2(a), a composite film including rhodamine and L-glucose, which is the enantiomer of D-glucose, shows a CD peak at 540 nm (dotted yellow line). The polarity of CD response is reversed by switching the chirality of glucose. When light is transmitted from the bottom, we still observed a CD peak (dotted green line). These results indicate that the chirality of the glucose in the composite is responsible for the CD feature at 540 nm. We note that glucose alone does not

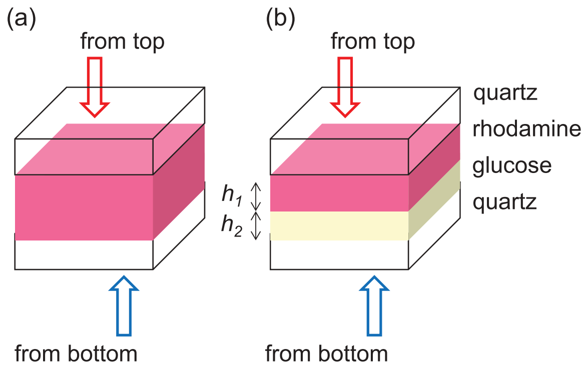

FIG. 1. (Color online) Schematic illustrations of (a) a composite film and (b) double-layer film of chiral molecule, glucose, and absorptive dye, rhodamine. Red and blue arrows correspond respectively to the direction of light transmission from the top and bottom. h_1 and h_2 correspond to thickness of rhodamine layer and glucose layer, respectively.

show any CD responses at this wavelength due to a very small absorption. The CD response is thus induced by the absorptive molecule even though the chiral molecule originally shows no CD response at this wavelength—an absorption-induced CD signal. A similar phenomenon is known as plasmon-induced CD,[10–14] in which an oscillating dipole of a chiral molecule induces dissipative chiral currents in achiral plasmonic metal nanoparticles due to Coulomb interaction. We should notice here that the polarity of CD responses in the composite film is independent of the incident direction of the light. In other words, the transmission of the circularly polarized light is symmetric as we predict. We, however, show in the following that the symmetry can be broken by making an interface between transparent glucose and absorptive rhodamine layers.

For preparing double-layer films, D/L glucose (100 mg) is dissolved into ethanol (1 ml). 20 μl of the solution is dropped onto a quartz substrate and is dried up. The mixture of rhodamine and PAK01 was then dropped and covered by another quartz substrate. By irradiating UV light for 5 min, the resin was cured. This experimental procedure results in double layers of D/L glucose and rhodamine sandwiched by quartz substrates [Fig. 1(b)].

Figures 3(a) and 3(b) show ellipticity and absorption spectra of double-layer films consisting of a glucose layer and a rhodamine layer. Absorption spectra exhibit again an absorption peak at about 540 nm, which originates from the rhodamine. In Fig. 3(a), we first focus on a double-layer film consisting of D-glucose and rhodamine layers (red and blue lines). An ellipticity spectrum after transmission from the top, i.e., from rhodamine to D-glucose, indicated by a solid red line shows a dip at about 540 nm, where the rhodamine shows an absorption maximum. Interestingly, when the sample is irradiated from the bottom (solid blue line), i.e., from

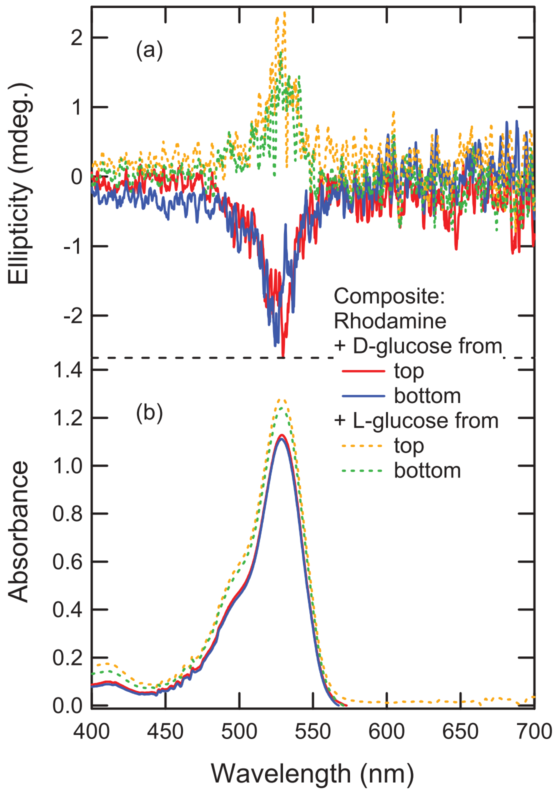

FIG. 2. (Color online) (a) Ellipticity and (b) absorbance of composite films containing glucose and rhodamine as a function of wavelength in vacuum. Solid red and blue lines correspond to the film using D-glucose. Dotted yellow and green lines correspond to the film using L-glucose.

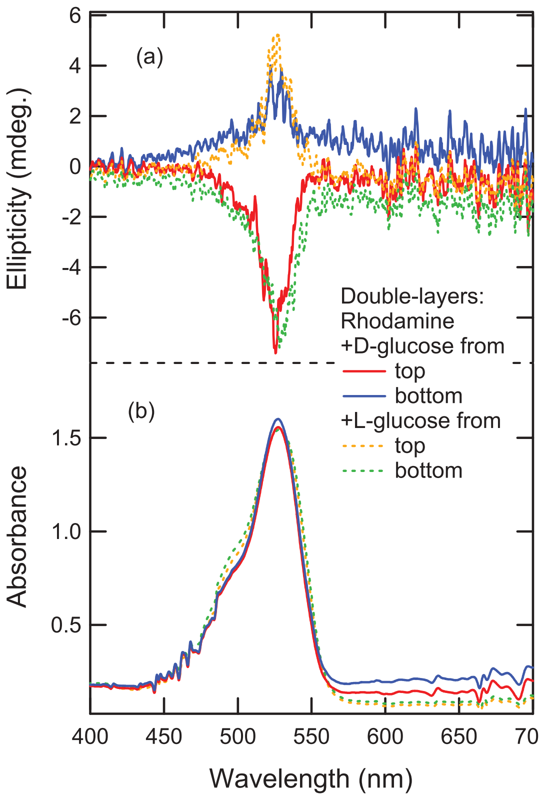

FIG. 3. (Color online) (a) Ellipticity and (b) absorbance of double-layer films consisting of a glucose layer and a rhodamine layer as a function of wavelength in vacuum. Solid red and blue lines correspond to the film using D-glucose. Dotted yellow and green lines correspond to the film using L-glucose. Top (bottom) corresponds to incident direction from rhodamine to glucose (from glucose to rhodamine).

D-glucose to rhodamine, we observe a peak in the ellipticity spectrum. The polarity of ellipticity is reversed by reversing the incident direction. The polarity reversal is accompanied with an antisymmetric transmission of the circularly polarized light, which is similar to the MO effect, due to the breaking of the symmetry.

We move on to ellipticity spectra of a double-layer film with rhodamine and L-glucose, the enantiomer of the D-glucose, shown by dotted yellow and green lines in Fig. 3(a). The polarity of ellipticity must be changed by switching the chirality of glucose. Indeed in an ellipticity spectrum of the sample after transmission from the top (dotted yellow line), a peak is observed. When the sample is irradiated from the bottom (dotted green line) a dip is seen in the ellipticity spectrum; the polarity reversal with incident direction is observed again. These results indicate that the polarity reversal is associated with the chirality of the molecules at the interfaces. We should stress here that in the interface there is no magnetic field. By attaching a chiral transparent medium to an achiral absorptive medium, in other words, splitting a CD medium into a transparent chiral medium and an absorptive achiral medium, we can make an interface for realizing the polarity reversal—a chiral meta-interface as illustrated in Fig. 1(b).

We calculated the ellipticity by the transfer matrix method to address the origin of the polarity reversal observed in the experiments of the chiral meta-interface. In a chiral medium, the constitutive equations are written to be $\vec{D} = \varepsilon_0 \varepsilon \vec{E} - i\xi\sqrt{\varepsilon_0/\mu_0}\vec{B}$, $\vec{H} = (\mu_0\mu)^{-1}\vec{B} - i\xi\sqrt{\varepsilon_0/\mu_0}\vec{E}$, where $\vec{E}$, $\vec{B}$, $\vec{D}$, and $\vec{H}$ are the electric field, the magnetic field, the electric flux density, and the magnetic field strength. ε, μ, and ξ are the electric permittivity, the magnetic permeability, and the chiral parameter. ε_0 and μ_0 are the permittivity and permeability of vacuum. If these equations are coupled with Maxwell equations, $\vec{k} \times \vec{E} = \omega\vec{B}$ and $\vec{k} \times \vec{H} = -\omega\vec{D}$, we obtain the index of refraction to be

$$n_{\mathrm{L,R}} = n_0 \pm n_1 \hat{k}, \tag{1}$$

where L and R represent left- and right-handed polarizations, respectively. ω is angular frequency, $\vec{k}$ is a wave vector, and $\hat{k} = \vec{k}/|\vec{k}|$ is a propagating direction of light. n_1 is proportional to ξ that is related to the amount of the OA. The refractive index of the achiral layer is n_{achiral}.

In calculation, we assumed $n_0 = 1.50 - 0.02i$, $n_1 = 0.010 - 0.001i$, and thicknesses $h_2 = h_1 = 1\ \mu\mathrm{m}$. Figure 4 shows calculated ellipticity as a function of the wavelength in vacuum, λ. The black solid line corresponds to a result of an interface with air as a control. The calculation result of the control shows small ellipticity because of the small absorption. The ellipticity is always positive and the absolute value increases monotonically as λ decreases. This is reasonable because the optical path length of the chiral medium becomes long and the ellipticity should increase with decreasing wavelength.

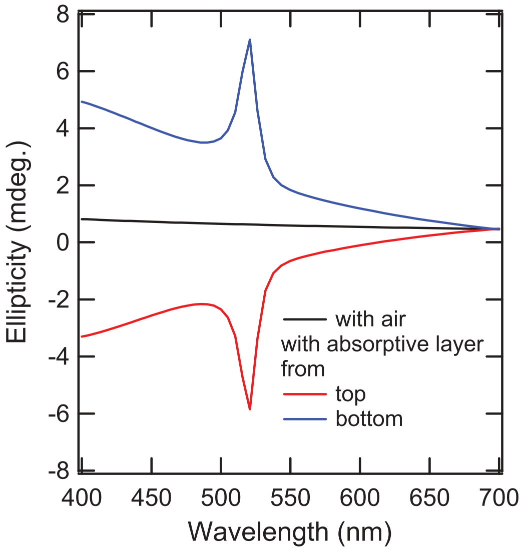

FIG. 4. (Color online) Calculated ellipticity of chiral medium alone (black line), chiral meta-interface between chiral medium and absorptive achiral medium (red and blue lines). Red (blue) line is ellipticity after transmission from the achiral (chiral) medium, which corresponds to the spectrum after transmission from the top (bottom) in the experiments.

Red and blue lines correspond to calculation results of a chiral meta-interface. Because experimental absorption spectra show a peak at about 540 nm, an absorption, i.e., the imaginary part of n_{achiral}, was introduced in the following:

$$n_{\mathrm{achiral}}^2(\omega) = 4.0 + \frac{\omega_0^2}{\omega^2 - \omega_0^2 - i\gamma\omega}, \tag{2}$$

where $\omega = 2\pi c/\lambda$, $\omega_0 = 3.4 \times 10^{15}\ \mathrm{s}^{-1}$, and $\gamma = 1.9 \times 10^{16}\ \mathrm{s}^{-1}$. The red (blue) line is a result of transmission from the achiral (chiral) medium, which is similar to the experimentally measured spectrum after transmission from the top (bottom). We see that, by attaching an absorptive nonchiral medium to chiral medium, the ellipticity shows a peak or dip. The peak and dip are enhanced at the absorption. Surprisingly, the peak in the red line is reversed in comparison with the blue line—polarity reversal is reproduced. This numerical calculation demonstrates that attaching an absorptive achiral medium to a chiral medium leads to the enhancement of the ellipticity and an interface can realize the polarity reversal of ellipticity.

What is important in the polarity reversal at the chiral meta-interface is a directional difference of refractive indices at an interface between chiral and achiral media as well as a polarization difference. From Eq. (1), a left-handed polarized wave, for example, "feels" the refractive index $n_0 + n_1$ ($n_0 - n_1$) when it transmits from an achiral (chiral) medium to a chiral (achiral) medium. Due to multiple reflections at the interface with this directional difference, ellipticity is enhanced even though intrinsic ellipticity is very small. This mechanism of an enhancement is a characteristic property of our model and physically distinct from the planar-chirality mechanism.[15,16] In such planar-chirality systems, the constitutive materials have no OA but the artificial structure produces. Thus if the incident direction of light is reversed in such systems, CD signals can never be reversed. On the other hand, our system has the intrinsic OA that is enhanced by the structure. It may happen in a certain condition as ours that CD signals can be reversed by reversing incident direction.

The polarity reversal observed at the chiral meta-interface seems to be similar to that observed in an MO effect when we consider only transmission of circularly polarized light. The physics must be, however, very different from the MO effect because of an absence of a magnetic field and magnetized medium at the chiral meta-interface. Nevertheless, if we focus on transmission of circularly polarized light, it is reasonable to assume a virtual "magnetic field" at the interface in order to explain the polarity reversal of ellipticity. In photonic systems, circularly polarized lights correspond to spins of photons. The spin polarization of photons can thus be achieved in a photonic system using a chiral medium with breaking space-inversion symmetry. The present study demonstrates that the connection of a chiral medium with an achiral medium results in an enhancement of spin polarization for light, leading to a virtual "magnetic field" for light at the interface and mimicking an MO effect without a magnetic field.

In conclusion, we have studied ellipticity of composite and double-layer films consisting of transparent chiral glucose and absorptive achiral rhodamine. Both composites and double layers consisting of glucose and rhodamine show an absorption-induced ellipticity signal at 540 nm, where the rhodamine exhibits absorption. More importantly, when we create a chiral meta-interface by double-layers consisting of chiral and absorptive layers, we realize polarization reversal of ellipticity, which is very similar to an MO effect, even though there is no magnetic field. The chiral meta-interface connecting an achiral medium and a chiral medium with breaking space-inversion symmetry results in a virtual "magnetic field" for light, mimicking an MO effect without a magnetic field.

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