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Abstract. We report on the first demonstration of picosecond optical vortex-induced chiral surface relief in an azo-polymer film due to two-photon absorption isomerization. The chiral surface relief exhibits an extremely narrow defocusing tolerance without undesired outer rings due to the Airy pattern of highly focused light. Such chiral surface relief reflects a z-polarized electric field with an azimuthal helical phase caused by spin–orbital angular momentum coupling. © *The Authors. Published by SPIE under a Creative Commons Attribution 4.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI.* [DOI: 10.1117/1.JNP.14.016012]

1 Introduction

Azo polymers enable photoinduced reversible surface relief to be realized;[1] therefore, they will play an important role in the realization of rewritable optical data storage[2–4] and light-driven micro/nanorobots.[5–7] The formation of surface relief in azo polymers generally occurs through several steps: thermodynamically stable trans-form azo polymers are mostly stable at room temperature.[8,9] Irradiation of trans-form azo polymers with nonuniform light leads to nonuniform trans-cis photoisomerization of azo polymers via light absorption and subsequent reversion of the azo polymers to the trans-form by spontaneous thermal reaction and the cis-trans reverse photoisomerization.[10–13] This trans-cis/cis-trans photoisomerization cycle (typical cycle time of 1 to 2 ps) forces a spring-like motion of the azo polymers, which results in spatially anisotropic photofluidity.[14–17] The mass transport of azo polymers thus occurs from a bright region toward a dark region along the polarization direction of the irradiated light by the gradient force based on interaction between photo-oriented azo polymers and the gradient of an optical electric field, i.e., light-induced mass transport, which results in the establishment of surface relief. The structures of the surface relief are thus mostly determined by the spatial intensity profile and polarization of the irradiated light.[18–21] Optical vortices carry an annular intensity profile and orbital angular momentum (OAM), characterized by a quantum number ℓ, which associated with its helical wavefront.[22–26] To date, several researchers have reported that irradiation with a continuous-wave visible optical vortex can force the helical mass transport of irradiated azo polymers to form wavefront-sensitive surface relief, i.e., chiral surface relief, facilitated by the spin angular momentum (SAM) of circularly polarized light with a helical electric field.[27–31]

An ultrafast laser-induced two-photon-absorption (TPA) process offers the trans-cis photoisomerization of azo polymers with high spatial resolution, which could yield further advanced technologies, such as high-density rewritable data storage.[32–34] However, most studies on surface relief formation in azo polymers are still based on single-photon-absorption (SPA).[1,8–21,27–11] Surface relief formation via TPA has not yet been well established. Furthermore, there have been no reports on optical vortex-induced surface relief formation in azo polymers via TPA

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isomerization. Optical vortex-induced TPA will provide not only the helical mass transport of azo polymers for high-density rewritable data storage with a freedom of OAM[35–37] but also entirely new nonlinear and photochemical phenomena, such as an OAM conservation law in TPA, and spin and OAM coupling in TPA.[38–40]

Here we report on TPA-induced chiral surface relief formation by irradiation with a near-infrared picosecond optical vortex.

2 Experiments

2.1 Two-Photon-Absorption Induced Surface Relief

A 1-μm thick azo-polymer (poly-orange tom-1) thin film spin-coated on a slide glass was used in the present experiments, which exhibited strong absorption at 532 nm (no absorption at 1.06 μm), as shown in Fig. 1(a). Therefore, two-photon isomerization should deform the azo-polymer film. A 1.06-μm picosecond laser with a pulse width of 8 ps, a pulse repetition frequency of 35 MHz, and an average power of 40 mW was used as a laser source, and its output was converted into a right-handed circularly polarized optical vortex with a total angular momentum of $J = 2$ by employing a spiral phase plate (OAM: $\ell = 1$) and a quarter wave plate (SAM: $s = 1$). The generated vortex beam was focused to be an annular spot with a diameter of 3.6 μm onto the azo-polymer film surface from the front side, i.e., the atmosphere side, using a high numerical aperture (NA) objective lens (NA = 0.9) [Fig. 1(b)]. The corresponding intensity of the focused vortex beam and the exposure time were then $\sim$1.4 GW/cm^2 and 300 s (dose energy of 12 J), respectively.

The optical vortex caused the upward mass transport of azo polymers along the beam propagation axis (z axis). The azo polymers were subsequently directed inward toward the dark core of the optical vortex and revolved along the clockwise direction to establish single-armed chiral surface relief, which reflects the helical wavefront of the optical vortex field within 120 s (4.8 J) [Fig. 2(a)]. The chiral surface relief formed had a diameter of 3.5 μm and a height of $\sim$300 nm. The formation of chiral surface relief on the azo polymers was difficult for an optical vortex with a dose energy of $< \sim$ 3 J, whereas the SPA-induced helical mass transport of azo polymers can
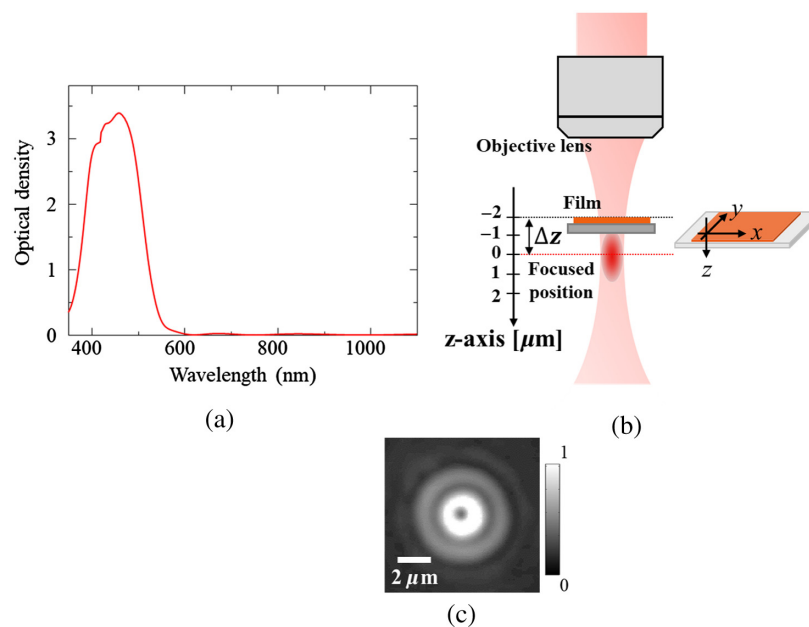

Fig. 1 (a) Absorption spectrum of the azo-polymer film used in the present experiment. (b) Experimental-setup. (c) Experimental spatial profile of the strongly focused optical vortex. The focused optical vortex exhibits multiple rings due to Airy pattern.
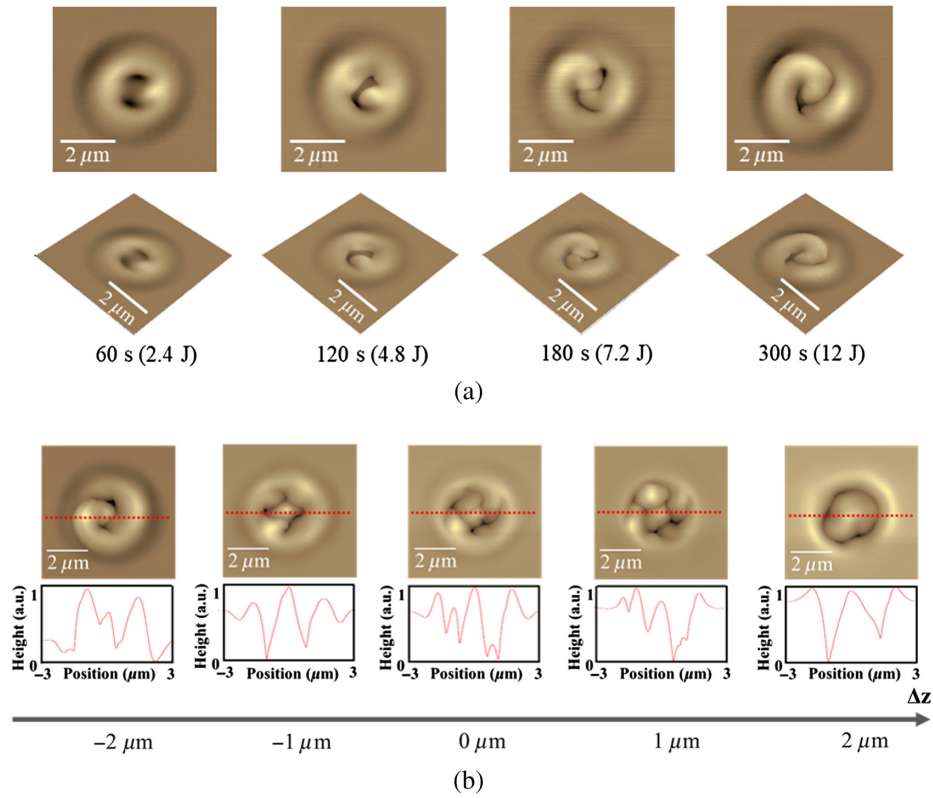
Fig. 2 (a) Temporal evolution of surface relief formation in an azo-polymer film by irradiation with 8 ps optical vortex pulses with $J = 2$. (b) Atomic force microscopy (AFM) images of surface relief produced with various defocusing depths. Chiral relief can be formed only at a defocusing depth Δz of -2 μm. The lower panels show line profiles of surface relief along the red lines in the AFM images.

occur with only a dose energy of $\sim$2 mJ, as previously reported.[28–30] The TPA-induced mass transport of azo polymers[41] is enabled by a longitudinal gradient of light intensity of the focused spot only within a small displacement of focused position from the film along z axis, i.e., defocusing depth Δz, as defined in Fig. 1(b). In fact, the formation of chiral surface relief occurred only at the defocusing depth Δz of -2 μm, which indicates that this is TPA-induced photoisomerization [Fig. 2(b)]. The strongly focused optical vortex, in general, exhibits multiple rings owing to the Airy pattern [Fig. 1(c)]. However, the created surface relief is shaped to be a single-armed ring without outer rings that also manifests strongly TPA photoisomerization with significant optical intensity threshold.

The optical vortex pulse was compressed to $\sim$2 ps without any change of the peak intensity (average power $\sim$10 mW). The optical vortex then typically induced a ring-shaped (not well twisted) surface relief, which mostly reflects the spatial intensity profile of the focused optical vortex field [Fig. 3(a)]. A ring-shaped surface relief (although slightly asymmetric) was produced even with an exposure time of 1200 s.

It is further noteworthy that the optical vortex with an even higher peak intensity induced photon-bleaching of the azo polymer and ablation of the film itself, which resulted in the formation of an abnormal ring-shaped surface relief with two petals [Fig. 3(b)].

These results further indicate that the helical mass transport, i.e., chiral surface relief formation, requires an optical vortex with a pulse duration of at least several photoisomerization cycles. The results of experiments performed by irradiation with optical vortices with various pulse durations are summarized in Fig. 4.

An optical vortex with $J = 0$ was also generated by inversion of the quarter wave plate, which produced only a nonhelical single damp-shaped surface relief, regardless of the pulse duration and exposure time (Fig. 5).
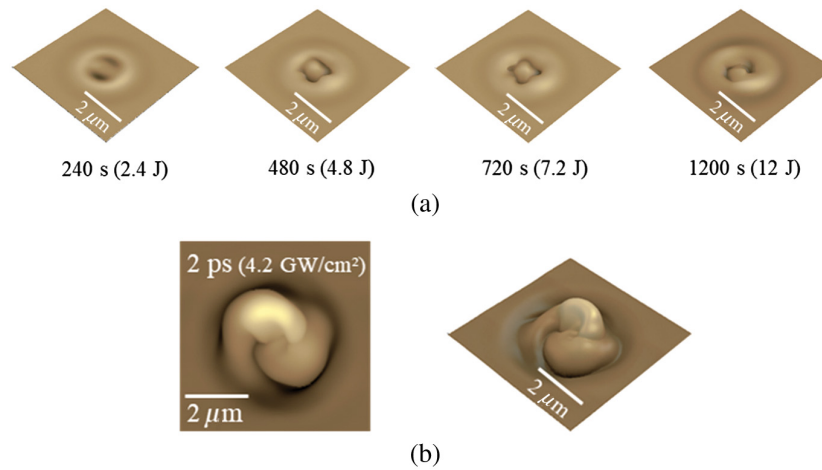
Fig. 3 (a) Surface relief formation in azo-polymer film by irradiation with a 2-ps optical vortex with $J = 2$. The surface relief formed was mostly ring-shaped (not well twisted). (b) Surface relief with two petals was formed by a 2-ps optical vortex. The intensity of the focused optical vortex was measured to be 4.2 GW/cm^2.
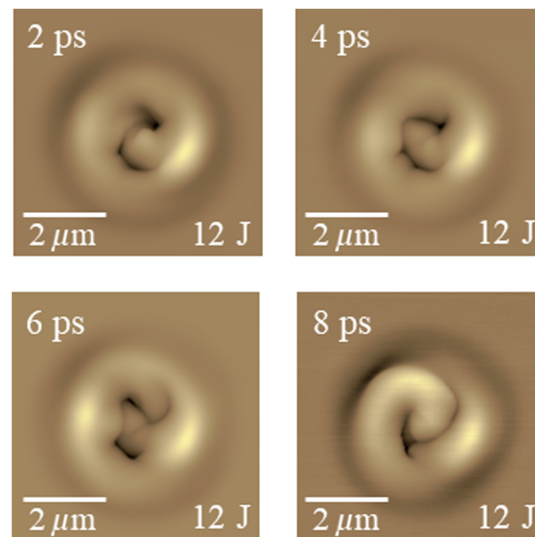

Fig. 4 TPA-induced surface relief formed by optical vortices with various pulse durations (2, 4, 6, and 8 ps).

2.2 Single-Photon-Absorption Induced Surface Relief

We also investigated SPA-induced surface relief formation by employing a 532-nm optical vortex with a pulse width of 8 ps, a pulse repetition frequency of 35 MHz, and an average power of 3 μW. The optical vortex was focused to be an annular spot with a diameter of 3.6 μm at the focal plane; the corresponding intensity was estimated to be 105 kW/cm^2 and the exposure time was 300 s (dose energy: 0.9 mJ). The irradiated azo polymers also exhibited surface relief that was directed in a clockwise direction [Fig. 6(a)]. However, the resultant chiral surface relief had outer rings due to the Airy pattern of the strongly focused optical vortex. The height of the surface relief was typically measured to be 100 nm. Chiral surface relief was further formed at any defocusing depth Δz within the range of -2 to $+2$ μm [Fig. 6(b)]. These results indicate that TPA-induced photoisomerization enables the formation of chiral surface relief in azo polymers with high longitudinal and transverse spatial resolution [Fig. 6(c)].
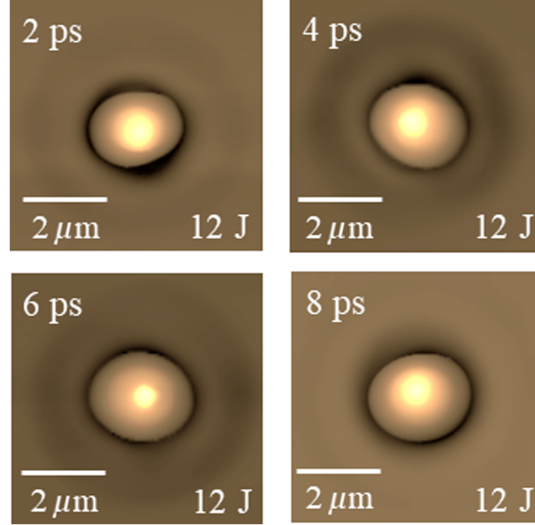
Fig. 5 TPA-induced surface relief formed by optical vortices ($J = 0$) with various pulse durations.

It should be noted that a 2-ps optical vortex did not induce efficient helical mass transport of the azo polymer [Fig. 6(d)]. Therefore, the helical mass transport of the azo polymer, even via SPA, requires an optical vortex with a pulse duration of at least several photoisomerization cycles.

3 Discussion

The experiments on TPA and SPA suggest that TPA contributes primarily to photoisomerization rather than mass transport of azo polymers. Here we discuss the surface relief formation based on classical optical radiation force based on time-averaged Poynting vector.

The electromagnetic fields of the circularly polarized optical vortex strongly focused by a lens with a high NA ($= \sin \theta_{max}$) > 0.8 can be analyzed using the theoretical formula as the Debye vector integral:[42]

$$\mathbf{E}(r, \varphi, z) = \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = -\frac{ikf}{2\pi} \int_0^{\theta_{max}} \int_0^{2\pi} \left(\frac{\sqrt{2}f \sin\theta}{w}\right)^{|\ell|} \exp\left(-\frac{f^2 \sin^2\theta}{w^2}\right) \sin\theta\sqrt{\cos\theta} \exp(i\ell\phi)$$

$$\times \begin{bmatrix} (\cos^2\phi \cos\theta + \sin^2\phi) \pm i \cos\phi \sin\phi(\cos\theta - 1) \\ \cos\phi \sin\phi(\cos\theta - 1) \pm i(\cos^2\phi + \sin^2\phi \cos\theta) \\ \sin\theta \exp(\pm i\phi) \end{bmatrix} e^{ik[z\cos\theta + r\sin\theta\cos(\phi-\varphi)]} \mathrm{d}\phi \, \mathrm{d}\theta,$$

$$(1)$$

where E_x, E_y, and E_z are the x-, y-, and z-polarized electric fields in the focused plane; f is the focal distance; w is the beam waist; k is the wave vector; and r, φ, θ, and ϕ are shown in Fig. 7(a). The circularly polarized optical vortex with $J = 2$ produces an annular amplitude profile and a 4π azimuthal phase shift due to constructive spin–orbital coupling effects in an isotropic and homogeneous material, thereby yielding an annular focused spot, which is defined as the sum of the transverse and z-polarized electric fields[43–46] [Figs. 7(b)–7(d)]. The resulting scattering force on the azo-polymer film, given as[29]

$$\mathbf{F}_{\text{scattering}} = \langle -i\omega\varepsilon_0\chi\mathbf{E} \times \mathbf{B} \rangle = \frac{\omega\varepsilon_0}{2}[\chi_r \, \mathrm{Im}(\mathbf{E} \times \mathbf{B}^*) + \chi_i \, \mathrm{Re}(\mathbf{E} \times \mathbf{B}^*)] \qquad (2)$$
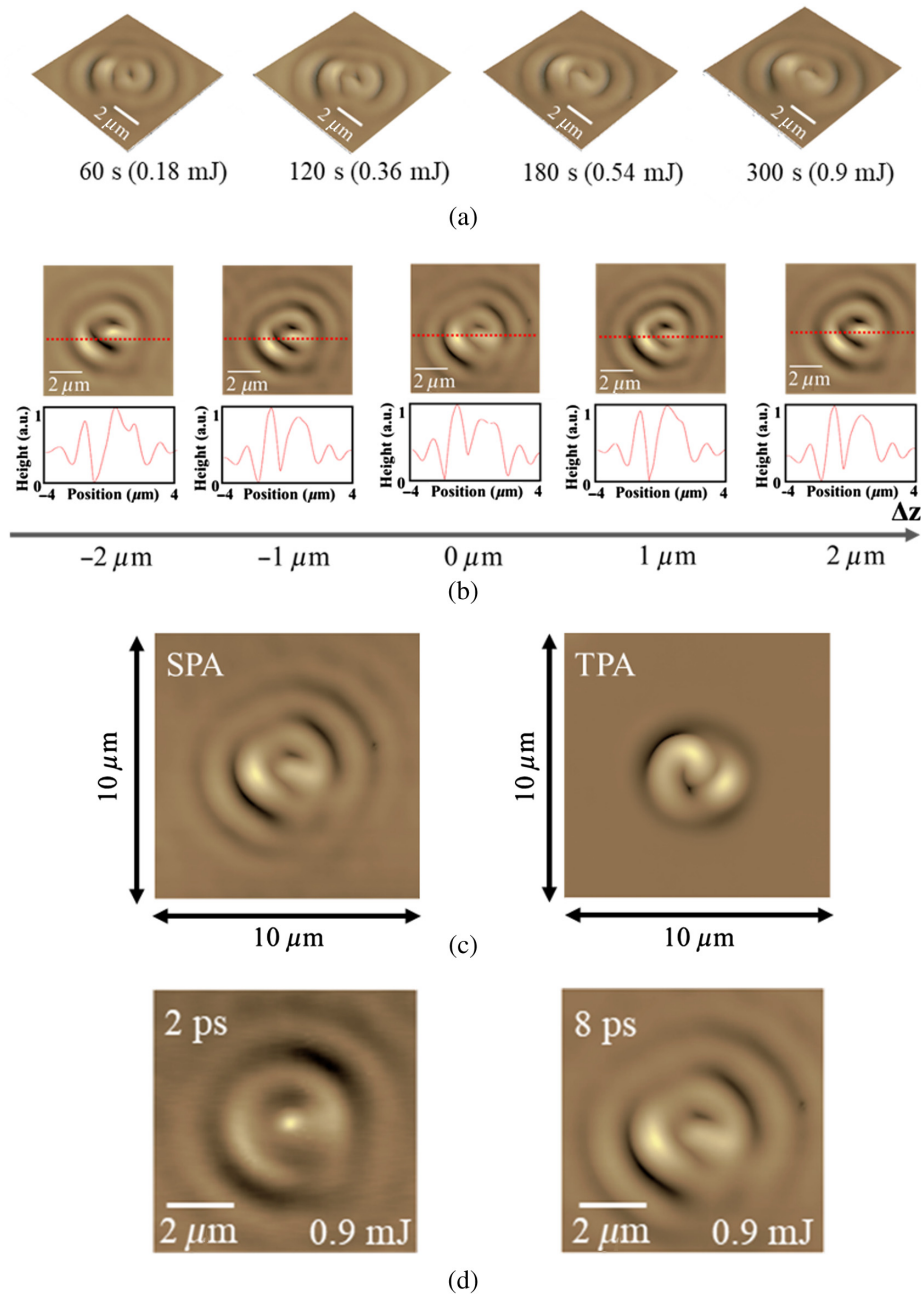
Fig. 6 (a) Temporal evolution of surface relief formation in an azo-polymer film by irradiation with 532 nm 8 ps optical vortex pulses with $J = 2$. (b) AFM images of surface relief formed with various defocusing depths. Chiral relief is formed at any defocusing depth Δz within the range of −2 to +2 μm. (c) SPA or TPA induced chiral surface relief. TPA produces chiral relief without any undesired outer rings due to the Airy pattern. (d) Surface relief formed by 532 nm optical vortices with pulse durations of 2 and 8 ps.

twists and directs the azo polymer toward the dark core with the assistance of the gradient force ($F_{\text{gradient}} = -\text{d}I/\text{d}r$), so as to form a ring-shaped helical surface relief [Fig. 7(h)].

In contrast, an optical vortex with $J = 0$ creates a theoretically focused spot with a central bright spot due to destructive spin–orbital coupling effects [Figs. 7(e)–7(g)], thereby yielding a damp-shaped relief via TPA induced photoisomerization [Fig. 7(i)]. These analyses support the observed experimental surface relief. Though it is beyond the scope of this paper, further modeling of optical radiation force, including TPA effects, should be investigated as a future work.
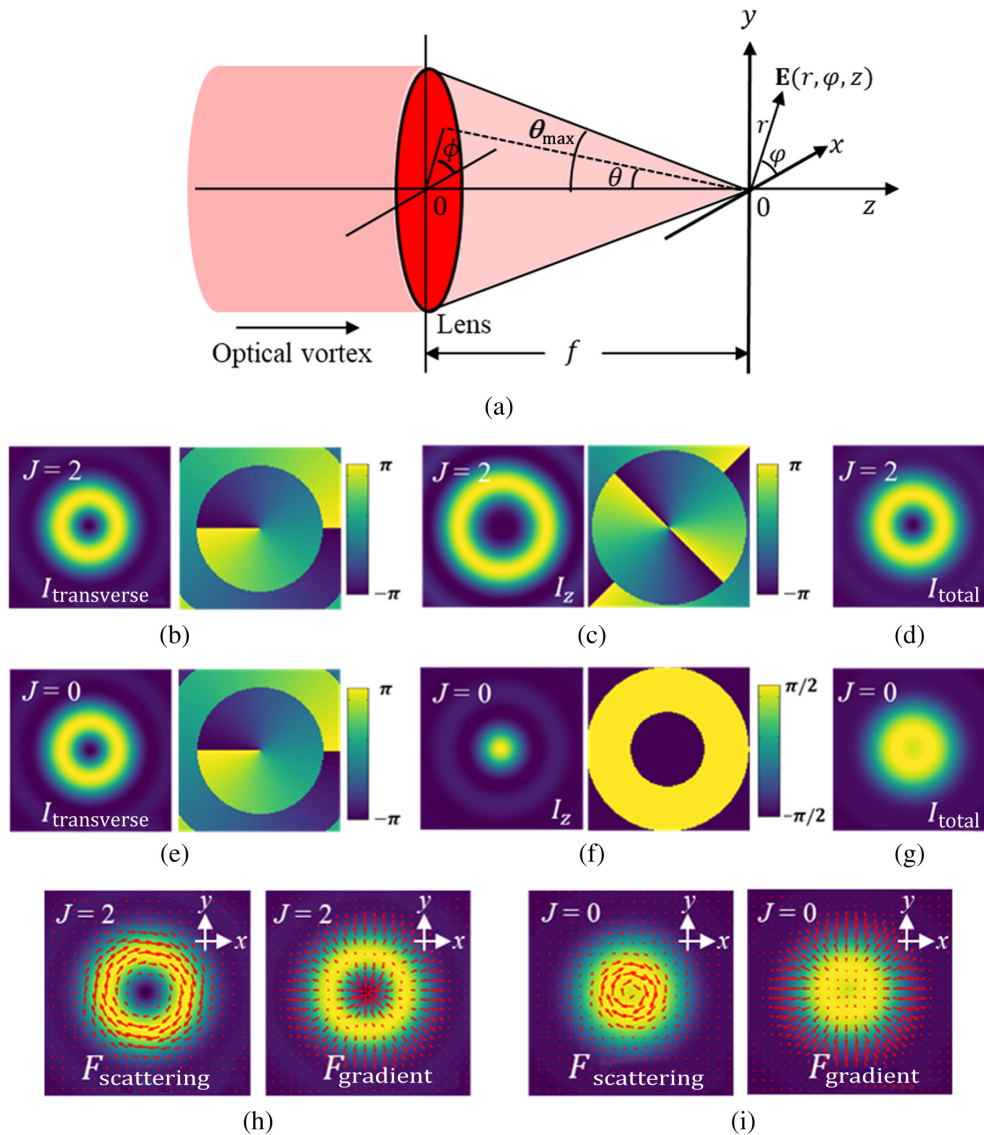
Fig. 7 (a) The coordinate system for strongly focused optical vortex. Theoretical spatial intensity profiles and phases of (b), (e) transverse (in the focused plane) and (c), (f) z-polarized electric fields of strongly focused circularly polarized optical vortices with $J = 2$ and $J = 0$. (d), (g) Spatial intensity profiles of strongly focused circularly polarized optical vortices with $J = 2$ and $J = 0$. Optical scattering and gradient forces created by strongly focused optical vortices with (h) $J = 2$ and (i) $J = 0$.

4 Conclusion

We have successfully demonstrated the formation of TPA-induced chiral surface relief in an azo-polymer film for the first time by employing a picosecond optical vortex source. The TPA-induced photoisomerization allows the formation of chiral surface relief with high longitudinal and transverse spatial resolution, i.e., without undesired outer rings due to Airy patterns and only within an extremely narrow defocusing tolerance. The formation of such surface relief also requires an optical vortex with a pulse duration of at least several trans-cis/cis-trans photoisomerization cycles. An optical vortex with a pulse duration of <6 ps impacted the formation of chiral surface relief with the use of any focusing region and exposure time. The SAM-OAM coupling effects create a strong z-polarized electric field with an azimuthal phase, which contributes significantly to the helical mass transport of the azo polymer.

Such TPA-induced helical mass transport is expected to lead to the realization of high-density optical data storage with the freedom of OAM and offer entirely new physical insights for the interplay between structured light fields and materials.

Acknowledgments

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