Superchiral Surface Waves for All-Optical Enantiomer Separation

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Abstract

We introduce the use of superchiral surface waves for the all-optical separation of chiral compounds. Using a combination of electrodynamics modeling and analytical techniques, we show that the proposed approach provides chiral optical forces two orders of magnitude larger than those obtained with circularly polarized plane waves. Superchiral surface waves allow for enantiomer separation on spatial, temporal and size scales than would not be achievable with alternative techniques, thus representing a viable route towards all-optical enantiomer separation.

Keywords

Optical chirality, Superchirality, Enantiomer Separation, Optical Forces

Chirality is the geometrical property of three-dimensional bodies that are distinct from their mirror image. Enantiomers, i.e. objects that display opposite chirality, have in common
most of their physical and chemical properties, and must interact with a chiral environment to exhibit their chiral attributes. Since chirality is pervasive in nature, and likewise in a large variety of biomolecules, the vast majority of biochemical processes is strongly influenced by the chiral properties of the involved chemical compounds. For these reasons the analysis and separation of chiral molecules has gained traction in the biochemical and pharmaceutical industries. Currently, pharmaceutical manufacturing is moving towards the production of enantiopure chiral molecules, with the expectation that the vast majority of drugs would be chiral by 2020. Circular dichroism (CD) spectroscopy, i.e. the measurement of differential absorption of left and right circularly polarized light, is one of the reference techniques when dealing with enantiomer discrimination. Nevertheless, the differential nature of CD signals typically leads to low signal to noise ratios, thus complicating the measurement of small amount of chiral molecules. In this scenario, new optical characterization techniques have been proposed, which are based on the introduction of superchiral electromagnetic fields, i.e. fields that display an optical chirality \( C = \frac{\epsilon_0 \omega^2}{2} \text{Im}\{E^* \cdot B\} \) larger than that of a circularly polarized plane wave. A variety of solutions, based on plasmonic and photonic nanostructures, have been designed to obtain superchiral light fields exploitable in realistic scenarios, with a particular focus on designing solutions capable of analyzing small amounts of chiral molecules. In parallel with the search for efficient superchiral sensing platforms, the research community devoted significant attention to the study and design of electromagnetic fields for the generation of enantioselective optical forces, i.e. optical forces that can trap, separate, or more in general discriminate between the two different enantiomers of a chiral chemical compound. In this context, several promising approaches have been proposed to tackle the problem. As an example, both evanescent waves (EW) and incoherent combinations of circularly polarized plane waves (PW) are capable of generating purely chiral enantioselective optical forces, whose magnitude and direction depend on the chiral polarizability \( \chi \) of the target chiral compound. On a different note, plasmonic tweezers can serve as chiral optical traps, where the presence of enantioselective forces has
been experimentally verified.\textsuperscript{34,35} Nevertheless, despite the numerous efforts, up to now the magnitude of the generated optical forces only allows to manipulate chiral particles that are significantly larger than typical proteins and pharmaceutically relevant molecules.

Here we show that, by exploiting a 1-dimensional photonic crystal (1DPC) capable of sustaining Superchiral Surface Waves (SSWs)\textsuperscript{42} we can separate chiral particles with radii $r$ and chiral polarizability $\chi$ as small as $r \sim 5$ nm and $c|\chi|/4\pi \sim 10^{-21}$ cm$^3$ on spatial scales of tens of micrometers and temporal scales of tens of seconds, reaching enantionpurity above 99% with the advantage of a platform that is inherently compatible with microfluidics setups and applications.

When working in dipolar approximation, we can express the force exerted by a monochromatic electromagnetic field on a chiral dipole as

$$ F = F_0 + F_{\text{int}} $$

where, in S.I. units, we have\textsuperscript{62}

$$ F_0 = \frac{\text{Re} \{ \alpha_e \}}{\varepsilon_0 \varepsilon} \nabla u_e + \frac{\text{Re} \{ \alpha_m \}}{\mu_0 \mu} \nabla u_m - c \omega \text{Re} \{ \chi \} \nabla h $$

$$ + 2\omega \left( \frac{\mu}{\varepsilon_0} \text{Im} \{ \alpha_e \} p_e + \frac{\varepsilon}{\mu_0} \text{Im} \{ \alpha_m \} p_m^* \right) - c^2 \text{Im} \{ \chi \} [\nabla \times \mathbf{p} - 2k^2 s] $$

(1)

and

$$ F_{\text{int}} = -\frac{c^3 k^4}{6\pi} \left( \text{Re} \{ \alpha_e \alpha_m^* \} \mathbf{p} - \text{Im} \{ \alpha_e \alpha_m^* \} \mathbf{p}'' + |\chi|^2 \mathbf{p} \right) $$

$$ - \frac{c^2 k^5}{3\pi n} \left( \frac{\varepsilon}{\mu_0} \text{Re} \{ \chi \alpha_m^* \} s_m + \frac{\mu}{\varepsilon_0} \text{Re} \{ \chi \alpha_e^* \} s_e \right). $$

(2)

Here $\omega$ is the light angular frequency, $c$ is the speed of light in vacuum, $\varepsilon_0$ and $\mu_0$ are the vacuum permittivity and permeability, $\varepsilon$ and $\mu = 1$ are the relative permittivity and permeability, $\alpha_e$, $\alpha_m$ and $\chi$ are the electric, magnetic and chiral polarizability, $n = \sqrt{\varepsilon}$ is the refractive index and $k = n\omega/c$ is the light wavevector. The equation terms $u_e = \frac{\varepsilon_0 \varepsilon}{4} |\mathbf{E}|^2$, $u_m = \frac{\mu_0 \mu}{4} |\mathbf{H}|^2$ and $h = \frac{1}{2\varepsilon_0} \text{Im} \{ \mathbf{E} \cdot \mathbf{H}^* \}$ are the electric and magnetic contribution to the energy density and the field helicity. The momentum density $\mathbf{p}$, its imaginary adjoint $\mathbf{p}''$
and its orbital electric and magnetic components $p_e^o$ and $p_m^o$ are defined as:

$$p = \frac{1}{2c} Re\{E \times H^*\}$$

$$p'' = \frac{1}{2c} Im\{E \times H^*\}$$

$$p_e^o = \frac{\varepsilon_0}{4\omega \mu} Im\{E(E \otimes E^*)\}$$

$$p_m^o = \frac{\mu_0}{4\omega \varepsilon} Im\{H(H \otimes H^*)\}.$$  (3)

where the $\otimes$ symbol stands for the tensor product. Finally we have the spin angular momentum $s$ where:

$$s = s_e + s_m = -\frac{\varepsilon_0}{4i\mu\omega} E \times E^* - \frac{\mu_0}{4i\varepsilon\omega} H \times H^*.$$  (4)

In this framework $F_0$ represents the contribution coming from the interaction between the electromagnetic field and the induced dipole moments, while the $F_{\text{int}}$ term arises from the interaction between the induced electric and magnetic dipole moments. When looking at the expression of the optical forces, it is clear that only the terms dependent on the chiral polarizability $\chi$ can be used to obtain enantioselective forces. The adopted mechanism rests on the simple idea that enantiomers of different handedness display chiral polarizabilities of opposite sign, and thus will be subject to optical forces with opposite directions. This leaves us with a limited number of exploitable force terms, and in particular the gradient term $F_g = c\omega Re\{\chi\} \nabla h$, the radiation pressure term $F_p = c^2 Im\{\chi\}\nabla \times p - 2k^2 s$ and the chiral electric interaction term $F_{\text{int}}^e = \frac{c^2 k^5}{3\pi n \varepsilon_0} Re\{\chi \alpha_e^*\} s_e$, where the $\frac{c^2 k^5}{3\pi n \mu_0} Re\{\chi \alpha_m^*\} s_m$ contribution has been discarded because in usual conditions $|\alpha_m|/\mu_0 \ll |\alpha_e|/\varepsilon_0$. Interestingly, each of these force terms has been employed in the literature to devise efficient schemes where pure enantioselective forces are dominant: the gradient terms in the case of plasmonic optical tweezers, the radiation pressure terms with the incoherent sum of circularly polarized plane waves and the electric interaction term with evanescent waves excited at a prism air interface. While extremely promising, each of these approaches comes with the respective drawbacks. The working conditions of the plasmonic tweezers require that
\[ \text{Re}\{\chi\} \geq \text{Re}\{\alpha\}_e/\varepsilon_0, \] demanding the introduction of an index matching approach for the chiral particle and the surrounding medium in order to minimize the magnitude of the electric polarizability.\(^{34}\) The electric interaction term approach (EW scheme), while attractive for its simplicity, is better suited for larger chiral particles, given the functional dependence on the electric polarizability \(\alpha_e.\)\(^{32}\) Finally, the incoherent plane wave approach (PW scheme) allows to operate on large areas, yet the lack of field enhancement mechanisms limits the magnitude of the obtainable chiral forces for reasonable incident powers. It would be ideal to devise a strategy that exploits the features of the PW scheme, and at the same time the field enhancement properties typical of plasmonic and photonic nanostructures. This would allow to obtain large and uniform chiroptical forces over large surface areas. Unfortunately, localized plasmonic and photonic resonances only provide field and chirality enhancements over nanometric hot-spots and work in relatively narrow energy ranges, while traditional surface waves such as Surface Plasmon Polaritons (SPPs) and Bloch Surface Waves (BSWs) provide sizable field enhancements over large areas, but cannot sustain the circular polarization state that is necessary to exploit the chiral radiation pressure term \[ F_p = c^2 \text{Im}\{\chi\}|\nabla \times \mathbf{p} - 2\kappa^2\mathbf{s}|.\]\(^{43,44}\)

Here we propose a solution that simultaneously exploits the field enhancement properties of photonic nanostructures and the large active areas typical of the PW solution. We employ a radically different paradigm, which uses the optical properties of 1DPCs to generate superchiral electromagnetic fields. The whole approach rests on the idea that 1DPCs support both transverse-electric (TE) and transverse-magnetic (TM) Bloch surface waves (BSWs).\(^{45}\) An appropriate engineering of the multilayer structure, specifically the introduction of an additional 1DPC termination with a much shorter lattice parameter, allows for the superposition of the TE and TM dispersion relations. This solution admits the simultaneous excitation of TE and TM surface waves, and therefore the excitation of superchiral surface waves at the 1DPC surface, much like the combination of two orthogonal linear polarization states with the appropriate \(\pi/2\) phase shift would result in a circular polarization state in free space (Figure 2). This configuration leads to superchiral surface waves that provide...
Figure 1: A schematic representation of different setups for the generation of optical enantiomselective forces. (a) 1DPC SSW platform, with the incoming incoherent elliptically polarized waves represented at the bottom, and the corresponding enantiomeric separation happening at the top. The 1DPC and termination periods are defined as \(d_{1DPC}\) and \(d_{\text{def}}\), respectively, while \(d_{H,L}\) stands for the thickness of the high and low refractive index materials in the 1DPC. (b) Incoherent counter-propagating plane wave setup (PW). (c) Evanescent wave setup (EW).

homogeneous, enhanced superchiral fields over arbitrarily large surfaces and a wide spectral range,\(^ {42}\) with optical chirality enhancements as large as two orders of magnitude if compared with circularly polarized plane waves, as already discussed in a previous publication. The same mechanism provides a comparable intensification of the enantioselective forces, thus paving the road towards all-optical enantiomer separation. For the following, we model the 1DPC already described in Ref.\(^ {42}\) The 1DPC consists of alternating high (H) and low (L)
Figure 2: Local field and optical chirality plots along the $z$-axis, across the 1DPC platform, for TE and TM incident plane waves, with a $\lambda_c = 380$ nm wavelength and a $\theta_c \sim 66^\circ$ incident angle. Plane waves are incident from the left. (a) $E_x$ and $H_x$ components. (b) $H_y$ and $E_y$ components. (c) $H_z$ and $E_z$ components. (d) Optical chirality enhancement for an elliptically polarized incident plane wave. The light gray field profiles are calculated for an evanescent wave traveling at a prism-water interface ($n_{\text{inc}} = 1.53$, $n_{\text{water}} = 1.33$), where the prism and 1DPC top interfaces have been aligned for a straightforward profile comparison.

refractive index materials, and in particular we choose Ta$_2$O$_5$ ($n_H = 2.06 + 0.001i$) and SiO$_2$ ($n_L = 1.454 + 0.0001i$), while the upper semi-infinite space is water ($n_{\text{water}} = 1.33$) and the incident medium is a BK7 glass ($n_{\text{inc}} = 1.53$). The crystal periodicity is $d_{1\text{DPC}} = 333$ nm, and the respective layer thicknesses are $d_H = f_H d_{1\text{DPC}}$ and $d_L = (1 - f_H) d_{1\text{DPC}}$, where $f_H = 0.26$ is the filling factor. The 1DPC termination is an additional multilayer characterized by a period $d_{\text{def}}$ much smaller than $d_{1\text{DPC}}$. It consists of $N_{\text{def}} = 5$ periods of alternating Ta$_2$O$_5$ and SiO$_2$ layers. The total thickness is expressed as a function of the 1DPC parameters as $t_{\text{def}} = d_L c_{\text{def}}$, with $c_{\text{def}} = 1.1$. The termination period then becomes $d_{\text{def}} = t_{\text{def}}/N_{\text{def}},$
Figure 3: Electric, magnetic and chiral polarizability plot for a chiral sphere with optical constant $\epsilon_p = 2.0(1 + i)$, chirality parameter $\kappa = 0.2$ and radii varying from $r = 2 \text{ nm}$ to $r = 30 \text{ nm}$.

and accordingly the layer thicknesses are $d_{H,\text{def}} = f_{H,\text{def}} d_{\text{def}}$ and $d_{L,\text{def}} = (1 - f_{H,\text{def}}) d_{\text{def}}$, where $f_{H,\text{def}} = 0.03$ is the termination filling factor. We finally note that the termination ends with a low refractive index layer. We model the target chiral compound as a spherical nanoparticle with optical constant $\epsilon_p = 2.0(1 + i)$, chirality parameter $\kappa = 0.2$ and radii varying from $r = 2 \text{ nm}$ to $r = 30 \text{ nm}$.\cite{32,33} Figure 3 reports the chiral target polarizabilities as a function of the size parameter $kr$ where $k = 2\pi n_{\text{water}}/\lambda_c$, $\lambda_c = 380 \text{ nm}$ is the illumination wavelength and $n_{\text{water}} = 1.33$ is the environment refractive index. It is clear how the choice of these parameters preserves the typical magnitude hierarchy between electric, chiral and magnetic polarizability, where we have $|\alpha_e|/\epsilon_0 \gg c|\chi| \gg |\alpha_m|/\mu_0$.\cite{33} The chiral polarizability values range from $\frac{c|\chi|}{4\pi} \sim 10^{-21} \text{ cm}^3$ for $r = 2 \text{ nm}$ to $\frac{c|\chi|}{4\pi} \sim 10^{-18} \text{ cm}^3$ for $r = 30 \text{ nm}$ particles, roughly keeping an order of magnitude gap with the electric and magnetic polarizability terms within the whole size range.

To analyze and put into context the chiroptical forces associated with SSWs, it is useful to study them as a function of the chiral particle size, and compare them to those obtainable with the already employed PW and EW schemes.\cite{32,33} In the case of SSWs, we employ the already described 1DPC structure illuminated at the coupling wavelength and angle $\lambda_c = 380 \text{ nm}$ and $\theta_c \sim 66^\circ$, and position the target $30 \text{ nm}$ above the 1DPC surface. For simplicity, in the following we model a structure illuminated with a single incident beam,
Figure 4: Chiral optical forces, normalized to the incident power, vs size parameter for the superchiral surface wave, plane wave and evanescent wave configurations.

keeping in mind that in practical applications a second incoherent beam with $\theta'_c = -\theta_c$ is needed in order to cancel the in-plane contribution of the non-chiral forces. We follow a similar approach when calculating the comparison force terms for the PW setup, i.e. we employ a single circularly polarized plane wave at $\lambda = \lambda_c$ in a $n_{\text{water}} = 1.33$ medium, and remember that we need a second incoherent contribution for any practical application. Finally, for the comparison with the EW force term, we illuminate a glass $n_{\text{inc}} = 1.53$ prism at $\lambda = \lambda_c$ and $\theta = \theta_c$ with a TM polarized plane wave and monitor the induced chiral force 30 nm above the prism water interface. Figure 4 compares the $|F_{\text{ssw}}|_{p,x}$ and $|F_{\text{pw}}|_{p,x}$ radiation pressure force terms for SSW and PW setups against the EW $|F_{\text{int,y}}^{\text{ew}}|$ force term, as depicted in Figure 1. The enantioselective force generated by the SSW configuration is between one and two orders of magnitude larger than that obtained with the plane wave configuration with the same incident power. The gap becomes larger if the comparison is made with the transverse interaction terms, reaching a ratio as large as 5 orders of magnitude towards smaller particle sizes. It is nevertheless interesting to note that the EW force term display a stronger size dependency through the $\text{Re}\{\chi_{\alpha}^c\}$ factor. It thus becomes a viable alternative towards the larger side of the size spectrum, taking also in account the fact that the EW approach requires a single incident beam setup. Overall, the forces per unit of incident power achievable with the SSW approach range from $|F_{\text{ssw}}|_{p,x} \sim 10^{-17} \text{ N/(1 mW/1}\mu\text{m}^2)$ for
Figure 5: Optical force map, normalized to the incident power, for the superchiral surface wave configuration, calculated for a 5 nm chiral sphere 30 nm above the 1DPC surface. The thin dashed line indicates an angular slice taken at constant wavelength $\lambda_c = 380$ nm.

$r = 2$ nm to $|F_{p,x}^{\text{ssw}}| \sim 10^{-13}$ N/(1 mW/1 $\mu$m$^2$) for $r = 30$ nm particles, making it a viable solution for all-optical enantiomer separation.

To further investigate the properties of SSW based enantioselective forces, we examine the 1DPC platform performance for different illumination conditions. To do so we choose an $r = 5$ nm chiral sphere and, as before, we position it 30 nm above the 1DPC surface. Figure 5 reports the map for the $|F_{p,x}^{\text{ssw}}|$ force term for wavelengths in the $\lambda \sim 300 - 550$ nm range and incident angles in the $\theta \sim 58 - 70^\circ$ range. The density plot reveals that the maximum chiral force is obtained along a diagonal line cutting the map from the top-left to the bottom-right corner. This maximum force line corresponds to the superposition of the TE and TM Bloch surface waves dispersion relations or, in other words, the line follows the dispersion relation of the SSW. This approach therefore provides large chiral forces on a wide energy spectrum, ranging from the UV to the visible range, at the only expense of tuning the incident illumination angle to match the SSW excitation conditions. Outside the dispersion relation region, the obtained forces are on average one to two orders of magnitude smaller, becoming comparable to those obtained with the simpler plane wave setup.

We can obtain further insight in the $|F_{p,x}^{\text{ssw}}|$ term behavior by slicing the force map at
the $\lambda_c = 380$ nm wavelength. Figure 6 reports the obtained force angular spectrum, and compares it with the force resulting from the alternative PW and EW approaches. Figure 6 clearly shows that, at the coupling angle around $\theta_c \sim 66^\circ$, SSWs provide chiral force enhancements of about two orders of magnitude. It is also apparent that, in this size range ($r = 5$ nm), evanescent wave forces do not represent a valid alternative for all-optical enantioseparation, and even more so when dealing with small chiral molecules. We finally note that the SSW angular force spectrum displays a less evident feature around $\theta \sim 60.3^\circ$, i.e. in correspondence of the critical angle. The feature indicates that evanescent waves excited with circularly polarized light can generate radiation pressure chiral forces ($|F_{p,x}^{\text{eva}}|$, along the $x$-axis) that, while being more than one order of magnitude smaller than the SSW counterpart, are still larger than those obtained with simple plane waves.

As a last investigation, we want to study the lateral diffusion of the $r = 5$ nm chiral target, assuming that it is suspended in water, inside a microfluidic channel, under the influence of the purely chiral forces described above. The diffusion of the pure, non-interacting enantiomers is described by the Fokker-Plank equation:

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} - v \frac{\partial \rho}{\partial x}, \quad (5)$$
Figure 7: (a) Enantiomer ($r = 5$ nm sphere) concentration profiles at the time $t = 90$ s for the superchiral surface wave, plane wave, and evanescent wave configurations, where the $\delta_{1/2}$ symbols stands for the amount of enantiomer contained to the right hand side ($x > 100 \mu$m) of the microfluidic channel. (b) Temporal evolution of the enantiomer concentration for the superchiral surface wave configuration.

with vanishing flux boundary conditions at the channel walls

$$x_0 \frac{\partial \rho}{\partial x} \bigg|_{x=0} = \rho(0, t), \quad x_0 \frac{\partial \rho}{\partial x} \bigg|_{x=L} = \rho(L, t) \quad (6)$$

and uniform enantiomer distribution $\rho(x, 0) = \rho_0$ at the time $t = 0$. In the equations, $\rho(x, t)$ is the enantiomer concentration, $D = \frac{k_B T}{6 \pi \eta r}$ the diffusion coefficient, $v = \frac{F D}{k_B T}$ the drift velocity under a force $F$, $k_B$ the Boltzmann’s constant, $T$ the solution temperature, $\eta$ the fluid viscosity and $L$ the microfluidic channel width. It is interesting to note that an intrinsic spatio-temporal scale emerges from the Fokker-Plank equation, where the spatial evolution happens on a natural length scale defined as $x_0 = D/v$, while for the temporal evolution we can define $t_0 = D/v^2$. Starting from $t_0$ we can finally obtain an effective time constant for the enantiomer diffusion process with $\tau_{\text{eff}} \sim \tau = 4t_0$ if $L \gg 2\pi x_0$ and $\tau_{\text{eff}} \sim \tau_1 = L^2/(\pi^2 D)$ if $L \ll 2\pi x_0$. To calculate the diffusion profiles, we choose a room temperature condition of $T = 293.15$ K, the corresponding water viscosity $\eta = 10^{-3}$ Pl, and an incident power
of 1 mW/1µm², which is a fairly typical value for optical tweezers setups. Consequently, for the constant force term, we choose the maximum values reported in Fig. 6, obtaining $|F_{p,x}^{sw}| \sim 2 \cdot 10^{-16}$ N, $|F_{p,x}^{pw}| \sim 4 \cdot 10^{-18}$ N and $|F_{int,y}^{e,ew}| \sim 3 \cdot 10^{-22}$ N, where in any case we consider the force applied along the $x$-axis to comply with the notation of Eq. 5. Figure 7 reports the enantiomer concentration profiles for an $L = 200$ µm microfluidic channel after a time $t = 90$ s, where the adopted channel width and diffusion time are chosen as a function of the natural spatial and temporal scales emerging when using the $|F_{p,x}^{sw}|$ force term, with $L \sim 10 x_{0,sw}$ and $t \sim 10 t_{0,sw}$. The concentration profiles of Fig. 7(a) reveal that only the SSW approach can produce a sizable enantioseparation, with 97.4% of the enantiomer displaced in the right hand side of the microfluidic channel ($x > 100$ µm). In this case, the separation process is further facilitated by the presence of strong gradient forces along the $z$ direction, pushing the chiral compounds towards the 1DPC surface, where the $|F_{p,x}^{sw}|$ term is larger. On the other hand, the concentration profiles associated to the PW and EW schemes are virtually unchanged compared to the initial conditions, since the magnitude of the associated force terms does not grant a substantial profile change on these spatio-temporal scales. The temporal evolution of the SSW concentration profiles, displayed in Fig. 7(b), further reveal that sizable deviations form the uniform distribution $\rho_0$ can be obtained on the time scale of a few seconds, to finally reach a 99.3% separation for the stationary solution. It is also clear that, for many practical purposes, the $t = 90$ s concentration profile can be considered virtually identical to the stationary one.

In conclusion, we have proposed the use of superchiral surface waves for all-optical enantiomeric separation. Our solution provides forces up to two orders of magnitude larger than those obtained with alternative approaches, allowing for the all-optical separation of chiral targets on otherwise unachievable spatial, temporal and size scales. The suggested 1DPC platform can operate in a wide energy range and is inherently compatible with standard microfluidic setups, thus representing a substantial step towards the all-optical separation and manipulation of chiral molecules and nanoparticles.
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