

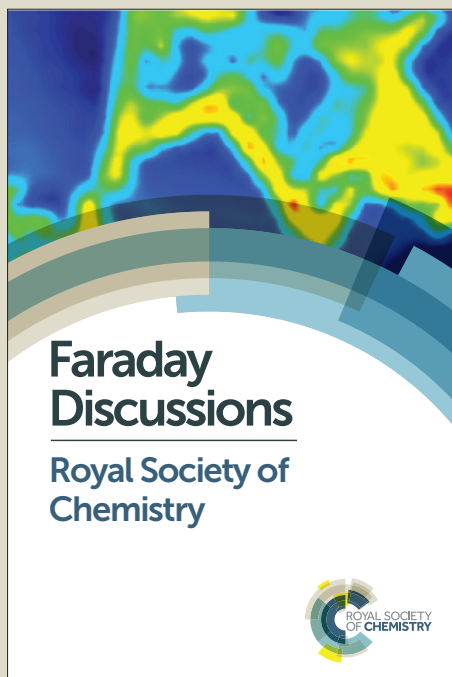
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# Electrical control of Faraday rotation at a liquid/liquid interface<sup>†</sup>

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A theory is developed for the Faraday rotation of light from a monolayer of charged magnetic nanoparticles at an electrified liquid/liquid interface. The polarization fields of neighboring nanoparticles enhance the Faraday rotation. At such interfaces, and for realistic sizes and charges of nanoparticles, their adsorption-desorption can be controlled with a voltage variation  $< 1$  V, providing electrovariable Faraday rotation. A calculation based on Maxwell-Garnett theory predicts that the corresponding redistribution of 40 nm nanoparticles of yttrium iron garnet can switch a cavity with a quality factor larger than  $10^4$  for light of wavelength 500 nm at normal incidence.

## Introduction

Recent theoretical and experimental advances in electrovariable nanooptics have focused attention on the electrically controllable optical response of nanoparticles (NPs) at liquid/liquid interfaces. Many of them are based on the interface between two immiscible electrolyte solutions (ITIES),<sup>1–3</sup> such as that formed between aqueous and organic oil salt solutions. Semiconductor NPs localized at the interface have been predicted to experience large electric fields, which can produce dramatic room-temperature Stark shifts in the optical transmission.<sup>4</sup> The reversible assembly of charged NPs at the ITIES has been predicted to occur as a result of applied potentials as low as  $\sim 1$  V.<sup>4</sup> The reflection and transmission coefficients for light incident on a monolayer of localised metallic NPs were calculated,<sup>5,6</sup> showing a dramatic frequency shift and linewidth broadening of the surface plasmon resonance. The optical properties of gold NPs adsorbed at an ITIES have also been measured.<sup>7</sup> The properties of magnetic NPs at such an interface, however, have not been explored to date, despite the extensive literature on metallic and insulating magnetic NPs in solution, such as iron, cobalt, ferrite, and magnetite ferrofluids,<sup>8</sup> including measurements of Faraday rotation.<sup>9,10</sup>

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Theoretical<sup>11</sup> and experimental<sup>12</sup> studies showed that the Faraday rotation by magnetic NPs in a nonmagnetic matrix depends on the NP density.

Here we predict that an ITIES with a ferrofluid component provides opportunities for electrically tuning the Faraday rotation, using modest ITIES-sustainable voltages, with possible applications in spectroscopy and for electrically switchable Faraday devices such as optical isolators. With a proper balance of forces between the nanoparticles, controlled through the pH of the solution and the Debye screening length of the electrolytes, NPs adsorb at ITIES spontaneously<sup>13,14</sup> to block the energetically unfavorable water/oil interface<sup>5</sup>. When the aqueous phase is sufficiently polarized positive with respect to the oil phase, the NPs are dispersed in the bulk, whereas for negative voltages they are even more strongly embedded into the interfacial region. The applied static magnetic field causes the magnetization of the NPs to orient in the same direction. An increase in Faraday rotation from localized NPs is expected, as a result of the nanoplasmonic interaction between neighboring particles.

## Theory

We calculate the Faraday rotation angle caused by magnetic NPs assembled at the ITIES according to the Maxwell-Garnett theory<sup>15,16</sup>, and compare it to the rotational angle caused by the same number of NPs dispersed in the bulk. Tuning of the Faraday rotation angle is explored for an optical cavity (Fabry-Perot) geometry, in which light propagation and magnetic field are perpendicular to the interface, and the electrodes would be transparent, shown in Fig. 1. For 40 nm NP's of yttrium iron garnet (YIG), tuning of the Faraday rotation angle by  $\pi/2$  for 500 nm wavelength light is feasible for an optical cavity with a quality factor  $Q$  in excess of  $10^4$ . The principles of calculation and obtained results are presented below.

Faraday rotation can be described with imaginary, anti-symmetric, off-diagonal components of a dielectric permittivity tensor; for a magnetic field  $B_z$ :

$$\tilde{\epsilon} = \begin{pmatrix} \epsilon_x & iA & 0 \\ -iA & \epsilon_y & 0 \\ 0 & 0 & \epsilon_z \end{pmatrix}, \quad (1)$$

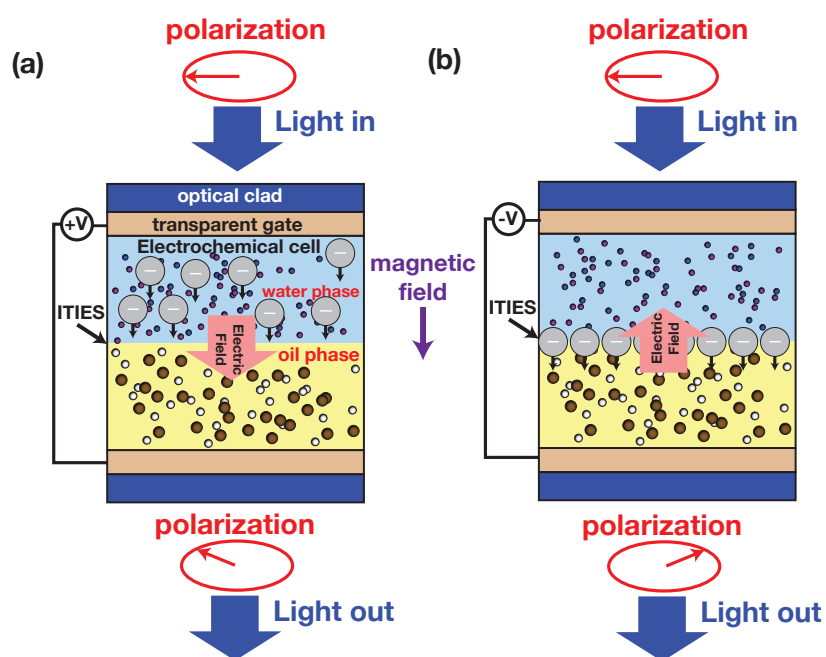
for which  $|\epsilon_x - \epsilon_y| \ll A$ , as is the case in typical magnetic materials. The polarization angle of linearly-polarized light propagating through a medium with the dielectric tensor of Eq. (1) is rotated by an angle per unit length  $\theta = (k_+ - k_-)/2$ , which is proportional to the difference between the wave numbers of the left and right circularly polarized components:  $k_{\pm}^2 = (\omega^2/c^2)(\epsilon \pm A)^{-1}$ . For  $\epsilon_x = \epsilon_y = \epsilon$

$$\theta = \frac{1}{2} \frac{\omega}{c} \frac{A}{\epsilon^{1/2}}. \quad (2)$$

The polarizability of a sphere of radius  $R$  is given by the Clausius-Mossotti expression

$$\tilde{\alpha} = R^3 \tilde{\epsilon}_s \frac{\tilde{\epsilon} - \tilde{\epsilon}_s}{\tilde{\epsilon} + 2\tilde{\epsilon}_s}, \quad (3)$$

where  $\tilde{\alpha}$  is the effective polarizability,  $\tilde{\epsilon}$  is the dielectric permittivity tensor of the sphere material, which has the form of Eq. (1), and  $\tilde{\epsilon}_s = \epsilon_s \mathbb{I}$  is the dielectric



**Fig. 1** When a voltage is applied to the interface of two immiscible electrolytic solutions, two back to back electrical double layers are formed, resulting in an electric field localized at the interface. That electric field interacts with the negatively charged nanoparticles to localize them at the interface or move them to the bulk. a) Potential is such that the NPs remain in the bulk of the liquid, forming a dilute solution. b) Potential is such that the NPs migrate to the liquid-liquid interface, where due to the interaction between polarization fields, they produce larger Faraday rotation. Not drawn to scale.

permittivity of the surrounding fluid, with  $\mathbb{I}$  the unit matrix. We assume  $\epsilon_s$  is the same for both liquids. For a suspension of small particles dispersed in the *bulk* of a liquid, the diagonal and off-diagonal elements of the effective permittivity tensor are<sup>17</sup>

$$\epsilon_b = \epsilon_s + \frac{3f\epsilon_s(\epsilon - \epsilon_s)}{3\epsilon_s + (1-f)(\epsilon - \epsilon_s)}, \quad (4a)$$

$$A_b = \frac{3f\epsilon_s A}{3\epsilon_s + (1-f)(\epsilon - \epsilon_s)}, \quad (4b)$$

where the volume fraction of NPs is denoted by  $f$  and  $\gamma = (\epsilon + 2\epsilon_s)/(\epsilon - \epsilon_s)$ . In the limit of  $f \ll 1$  the expressions coincide to those found for highly dilute solutions,<sup>11</sup> and Eq. (4a) becomes the standard Maxwell-Garnett expression.<sup>15,18</sup> For a system with just enough NPs to cover the interface in a monolayer,  $f = 4/3\pi R^3 n_s/l$ , where  $l$  is the depth of the bulk region and  $n_s$  the number of particles per unit area of the interface. The corresponding Faraday rotation per unit length for a bulk region with dispersed nanoparticles ( $\theta_b$ ) is then calculated from Eq. (2) with  $\epsilon \rightarrow \epsilon_b$  and  $A \rightarrow A_b$ .

The dielectric permittivity of a  $2R$ -thick monolayer (or submonolayer) of NPs at the liquid/liquid interface where the Faraday rotation occurs is given by

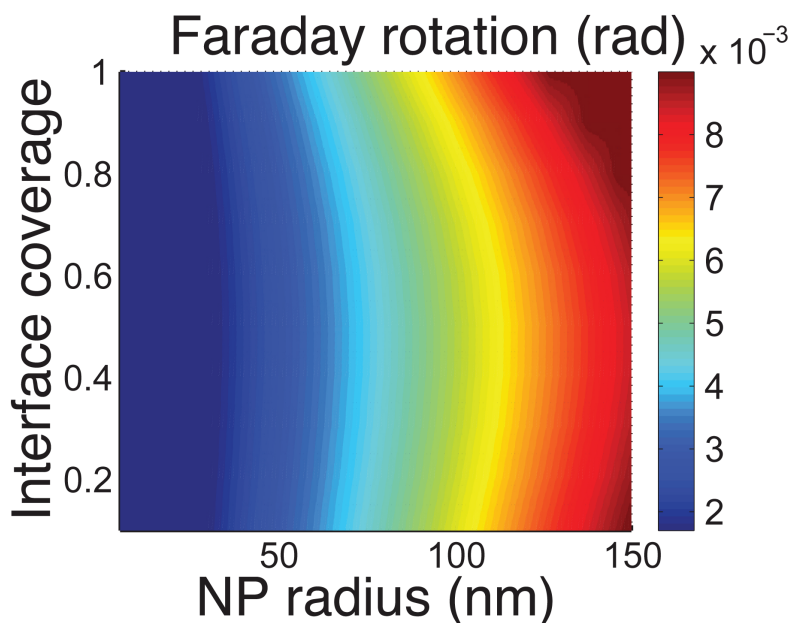
$$\tilde{\epsilon}_m = (1 - n_s\pi R^2)\epsilon_s\mathbb{I} + \frac{4\pi n_s}{2R}\tilde{\alpha}_m. \quad (5)$$

The first term in Eq. (5) accounts for the unoccupied interface between the two liquids, while the second term provides the contribution of the NPs present at the interface. In the case where the two liquids on either side of the ITIES have significantly different permittivities, the expression in Eq. (5) needs to be adjusted; here for simplicity we neglect the usual minor difference in the refractive indices of the two phases (this difference can be accounted for using the method of Ref.<sup>6</sup>). For a hexagonal lattice of NPs at the interface,  $n_s = \Theta/(2\sqrt{3}R^2)$ , where  $\Theta = N/N_{\max}$  is the coverage of the monolayer: the number  $N$  of NPs present at the interface relative to the maximum occupation number  $N_{\max}$ . The polarizability of the monolayer can be calculated as in Eq. (8) of Ref.<sup>16</sup>

$$\tilde{\alpha}_m = \tilde{\alpha}(\mathbb{I} + \tilde{\alpha}\tilde{U})^{-1}, \quad (6a)$$

$$\tilde{U} = \frac{U_0\Theta^{3/2}}{a^3\epsilon_s} \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (6b)$$

Here  $U_0 = 11.03$  defines the dipole-dipole interaction within the lattice and is constant for a given lattice type, here chosen as hexagonal<sup>19</sup>;  $a$  is the minimum lattice constant, corresponding to  $N = N_{\max}$ . Eq. (6) is valid for an average distance between neighboring particles of a few radii, as no multipole interactions are considered, and in the limit of long wavelengths compared to the lattice constant.



**Fig. 2** Faraday rotation caused by NPs in the bulk and at the interface depends on the interfacial coverage and the NP size. The total number of NPs in the system is that necessary for a monolayer coverage. Parameter values:  $\epsilon_s = 1.78$ ,  $\epsilon = 4.84$ ,<sup>20</sup>  $\lambda = 500$  nm,  $\theta \leq 5 \times 10^4$  rad/m.<sup>21</sup>

From Eqs. (1), (3), and (6),  $\tilde{\alpha}_m$  can be calculated:

$$\tilde{\alpha}_m = \frac{\epsilon_s R^3}{\gamma} \begin{pmatrix} \frac{2}{2-C} & \frac{4iB}{(C-2)^2} & 0 \\ -\frac{4iB}{(C-2)^2} & \frac{2}{2-C} & 0 \\ 0 & 0 & \frac{1}{C+1} \end{pmatrix}, \gamma = \frac{\epsilon + 2\epsilon_s}{\epsilon - \epsilon_s} \quad (7a)$$

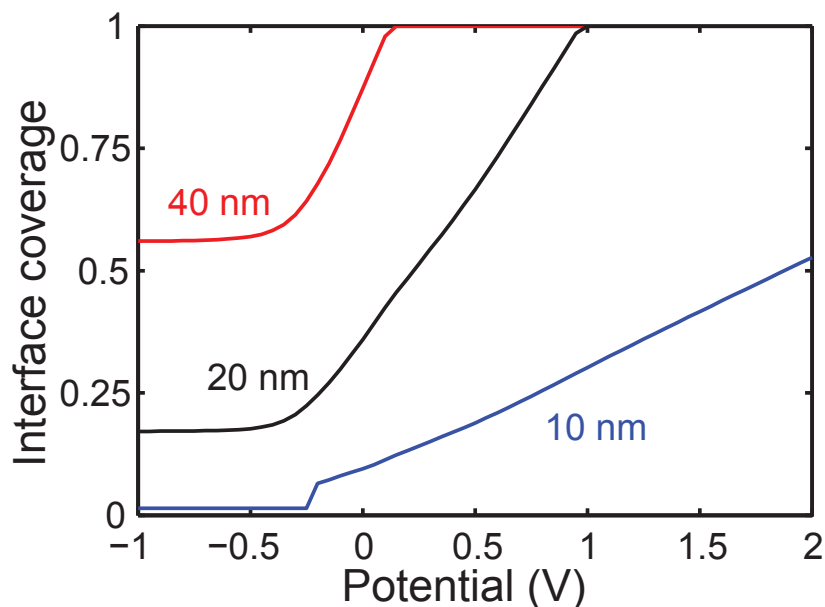
$$B = \frac{3\epsilon_s A}{(\epsilon - \epsilon_s)(\epsilon + 2\epsilon_s)}, C = \frac{R^3 U_0 \Theta^{3/2}}{\gamma a^3}. \quad (7b)$$

From Eqs. (5) and (7),  $\epsilon_m$  can be calculated, and thus the corresponding Faraday rotation. In the limit of vanishing dipole-dipole interaction, identifying  $2\pi n_s R^2 \rightarrow 3f$ , and taking the limit of a dilute solution ( $1 - n_s \pi R^2 \rightarrow 1$ ), the results for bulk, Eq. (4), are retrieved.

## Results

Figure 2 displays the net rotation in radians caused by NPs dispersed in the system for a transparent magnetic material commonly used in Faraday isolators, yttrium iron garnet (YIG). Full coverage of the interface is not crucial in obtaining a sizeable rotation difference between the nanoparticle-covered and free interface.

The voltage-dependent coverage of an ITIES with functionalized NPs as a function of the applied electrical potential has been calculated based on the free

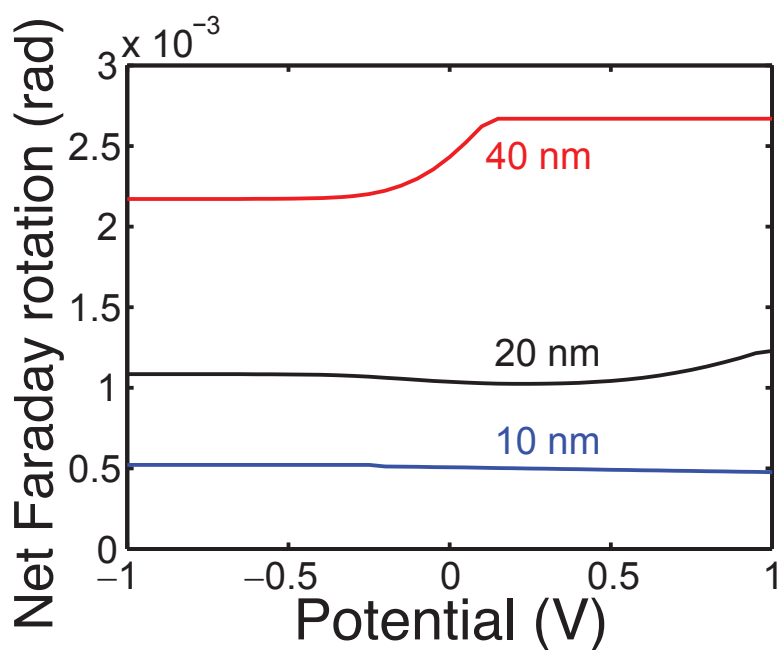


**Fig. 3** A small variation in the applied potential changes the interfacial coverage  $\Gamma$  dramatically. This is the combined result of the energy profile of a single NP and the electrostatic interaction between two NPs at the interface. Curves were calculated following Refs.<sup>5,22</sup>, as described in Supplementary materials. Parameter values:  $\epsilon_1 = 78.8$  (water),  $\epsilon_2 = 10.7$  (1,2 dichloroethane),  $z = -4000$ ,  $\kappa_1 = 5 \times 10^7 \text{ m}^{-1}$  (0.2 mM),  $\kappa_2 = 6 \times 10^8 \text{ m}^{-1}$  (5 mM),  $\sigma_{12} = 0.03 \text{ N/m}$ ,  $\mu = 10^{-11}$ ,  $\theta_{\text{contact}} = 0.55\pi$ .

energy profile of a single NP at the ITIES.<sup>4,5</sup> Localised NPs were allowed to interact pairwise via screened electrostatic forces. Depending on system parameters such as the NP size and charge, the contact angle with the two liquids, and the magnitude and polarity of the applied field, a stable or metastable bound state of the NP arises at the interface. The same parameters for the free energy used in Ref.<sup>5</sup> have been assumed here.<sup>†</sup> The gradual population of the ITIES with NPs as the voltage is changed is depicted in Fig. 3 for three NP sizes.

For a system with  $R = 40 \text{ nm}$  and  $\epsilon = 4.84$  the rotation per unit length in the bulk,  $\theta_b$ , and in the monolayer,  $\theta_m$ , are  $4 \times 10^{-2} \text{ rad/m}$  and  $10^4 \text{ rad/m}$  respectively. The net rotation when all particles are dispersed in the bulk liquid is  $l \cdot \theta_b = 2.1 \times 10^{-3} \text{ rad}$ , while from the monolayer  $2R \cdot \theta_m = 2.7 \times 10^{-3} \text{ rad}$ , leading to a difference in polarization angle of  $6 \times 10^{-4} \text{ rad}$  for a single pass, Fig. 4. The change in the Faraday rotation upon accumulation of the NP at the interface originates from the enhancement of the off-diagonal dielectric polarizability of a single NP due to the polarization fields of neighboring NPs. As those neighboring NPs approach, the enhancement increases up to the point where one achieves a full monolayer coverage of the interface.

<sup>†</sup> Electronic Supplementary Information (ESI) available: Further information on the calculational procedure. See DOI: 10.1039/c000000x/



**Fig. 4** The net Faraday rotation for light passing one time perpendicular to the interface varies with the applied potential. A change in the coverage as a function of potential was assumed as in Fig. 3. Significant effects appear only when a large enough potential is applied to lead to monolayer coverage. Parameter values:  $\epsilon_s = 1.78$ ,  $\epsilon = 4.84$ ,<sup>20</sup>  $\lambda = 500$  nm,  $\theta \leq 5 \times 10^4$  rad/m.



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## Discussion

Although the rotation of the polarization angle upon one pass through the interface is modest, the effect is amplified in a high quality factor cavity. The criteria for switching the cavity from completely transmissive to reflective is that the shift in resonant frequency due to the altered Faraday rotation would exceed the cavity linewidth ( $\approx \omega/Q$ , where  $\omega$  is the resonant frequency of the cavity). This would occur for a cavity with a quality factor  $Q > 10^4$ .

## Conclusion

We have presented a geometry for electrically-controllable Faraday rotation due to nanoparticle accumulation at a liquid-liquid interface. The enhanced polarization of the nanoparticles due to their accumulation at the interface leads to an enhancement of the normal-incidence Faraday rotation. This effect should be visible in a high quality factor ( $Q > 10^4$ ) optical cavity. For a small electrochemical cell and voltages less than 1 V, electrical switching of a Faraday isolator can be achieved in this geometry.

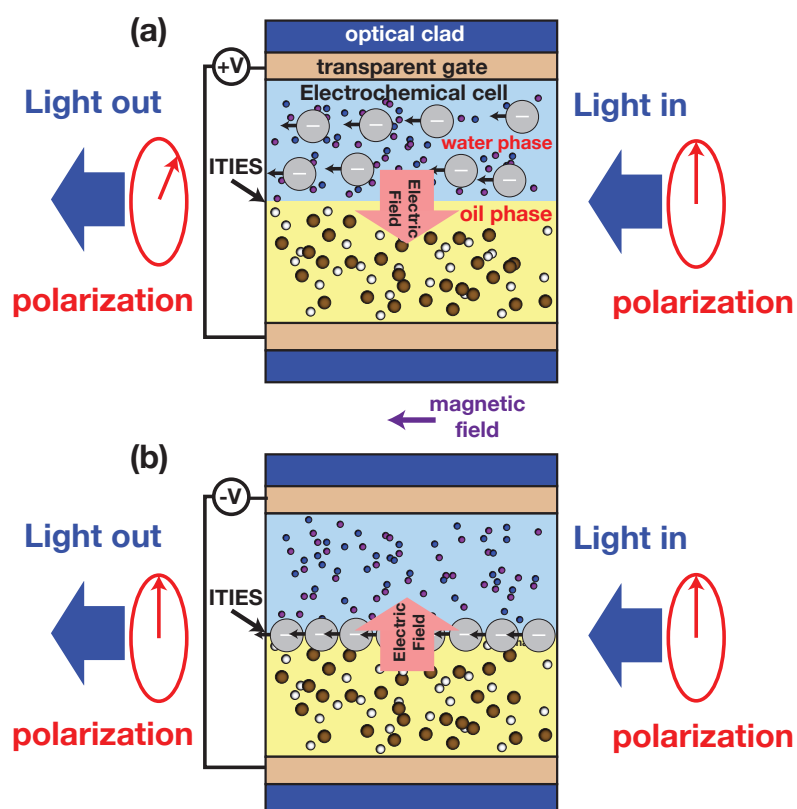
As a concluding note we emphasize that other nonlinear optical effects are possible that involve switching the Faraday rotation due to NP accumulation at the interface. As an example, in Fig. 5 we show a waveguide geometry. Here the highly anisotropic linear polarization of the nanoparticles when accumulated at the interface, seen from Eq. (6), leads to an efficient quenching of the Faraday rotation for light propagating parallel to the interface. The linear birefringence that causes the quenching of the Faraday rotation can be compensated for with other linear birefringent elements in an optical device.

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**Fig. 5** Schematic of a waveguide version of Fig 1. a) Potential is such that the NPs remain in the bulk of the liquid, forming a dilute solution, and Faraday rotation occurs. b) Potential is such that the NPs migrate to the liquid-liquid interface, where due to an interface-induced birefringence the Faraday rotation is quenched. Not drawn to scale.

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