

# Biological and Biologically Inspired Photonic Materials and Devices

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## ABSTRACT

We discuss the increasing effort to adopt biological and biologically inspired concepts to solve problems in photonic materials and devices. This effort ranges from exploiting fundamental material properties, as in fluorescent dyes and DNA-derived polymers, to studying structures that interact strongly with photons, exemplified by butterfly wings. An emerging area of interest is the combination of biological or biologically derived materials with organic or inorganic synthetic materials to achieve material systems with unprecedented performance. We discuss several examples from our recent work including erbium-doped sol-gel/DNA-CTMA, diatom photonics, and microring resonator based sensing of biological objects.

**Keywords:** DNA, biophotonics, microrings, biosensing, photonic crystals, microring resonators, optical amplifier

## 1. BACKGROUND

There is a growing interest in photonic materials and devices that derive from biological sources or that are inspired by the elegant engineering that nature provides. It is not difficult to find unique and remarkable photonics in nature, ranging from superfluorescent dyes like green fluorescent protein[1], to the highly ordered photonic crystal structures present in butterfly wings and diatoms[2]. Biopolymer materials have progressed dramatically over the last decade to the point where their functionality has been demonstrated in areas as diverse as sensors, electro-optic modulators[3], organic light emitting diodes[4], and holographic media[5], among other areas. The most successful biopolymer materials have been those derived directly from deoxyribonucleic acid (DNA) biowaste and silk. These materials have a unique blend of optical and electronic properties that have been exploited in optoelectronic applications, while their electronic properties can be exploited for organic electronics. With the increasing acceptance of the utility and need for biologically derived and inspired structures for photonics materials and devices, the question naturally arises as to the best way to take advantage of their unique properties. Emerging work in the field points to the increasing use of hybrid material and device approaches, whereby synthetic organic and inorganic materials systems are combined with biologically derived materials or structures to provide advances in performance or manufacturability, for example. In this paper we will discuss some recent work that we have done to explore this hybrid approach to using biologically inspired materials and structures, with a focus on applications such as optical amplification, optical filtering and biosensing.

## 2. RARE EARTH DOPED DNA/CTMA FOR OPTICAL AMPLIFIERS AND LASERS

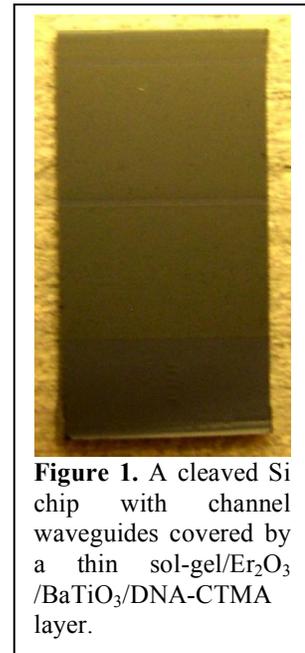
It has been long standing goal of the integrated optic community to develop on-chip erbium ion doped optical amplifiers for loss compensation in in complex photonic integrated circuits. In our previous work [6] we found that inorganic oxide nanoparticles could be uniformly dispersed in DNA-CTMA at high concentrations (> 10wt%). We thus decided to evaluate  $\text{Er}_2\text{O}_3$  nanopowder (> 99.9 wt. % trace metal basis and < 100 nm BET) since  $\text{Er}^{3+}$  has broad applications in the area of optical communications, specifically for optical amplifiers and lasers.  $\text{Er}^{3+}$  can absorb and emit at the telecommunications wavelength of 1.55  $\mu\text{m}$ , and erbium amplifiers and lasers are essential components in optical communication systems. The capability and potential to fabricate  $\text{Er}^{3+}$ -nanoparticle incorporated polymer waveguide amplifiers and lasers via the convenient spin coating process bears investigation. A second candidate material is ytterbium oxide  $\text{Yb}_2\text{O}_3$

nanopowder (<100 nm particle size BET), where  $\text{Yb}^{3+}$  is another very important rare-earth ion for photonics and telecommunications.  $\text{Yb}^{3+}$  ions absorb strongly from 900-1000 nm and emit around 1-1.1  $\mu\text{m}$  under excitation, serving as the workhorse for military and industrial high power solid state and fiber lasers with very broad applications. The capability and potential to disperse  $\text{Yb}^{3+}$  nanoparticles and fabricate  $\text{Yb}^{3+}$ -nanoparticle incorporated waveguide amplifiers and lasers could also carry substantial significance.

### 2.1. Sol-Gel/DNA-CTMA/ $\text{Er}_2\text{O}_3$ nanocomposite thin films

We dispersed  $\text{Er}_2\text{O}_3$  nanopowder in sol-gels that were previously blended with DNA-CTMA. The surface quality of the nanocomposite films could be significantly improved by mixing  $\text{BaTiO}_3$  together with  $\text{Er}_2\text{O}_3$  nanopowder, resulting in much smoother film surfaces without compromising fluorescence strength; this presumed to be due to the suppression of phase separation through the presence of both species. For any potential practical applications, a waveguiding structure needs to be fabricated for these DNA-CTMA blended,  $\text{Er}^{3+}$  doped nanocomposite materials. The first promising experimental results to create a waveguide using the  $\text{Er}^{3+}$  doped nanocomposites are described here.

Si wafer substrates were used and we etched the Si wafers with a mask to fabricate rectangular trenches that were 10  $\mu\text{m}$  in width and 4  $\mu\text{m}$  in depth. The refractive index of the sol-gel/ $\text{Er}_2\text{O}_3$ / $\text{BaTiO}_3$ /DNA-CTMA is estimated to be around 1.6, while the silicon has a higher refractive index of 3.5, i.e., not suitable as the low-index cladding material. However, all silicon wafers have a thin natural oxide layer,  $\text{SiO}_2$ , of refractive index of 1.45. Therefore, lateral confinement to some extent is expected although a fully functional single-mode waveguide would require a different substrate material. Another reason to select Si as the substrate is the ease with which it may be cleaved to achieve a clean end surface for light coupling, which is critical for these proof-of-concept experimental efforts without extensive surface preparation and processing. Figure 1 shows a cleaved and etched Si chip with a thin layer of sol-gel/ $\text{Er}_2\text{O}_3$ / $\text{BaTiO}_3$ /DNA-CTMA nanocomposite material spin coated on top. The etched channel waveguides that are filled with the nanocomposite material can be visibly observed on the chip running in the horizontal direction.



**Figure 1.** A cleaved Si chip with channel waveguides covered by a thin sol-gel/ $\text{Er}_2\text{O}_3$ / $\text{BaTiO}_3$ /DNA-CTMA layer.

Figure 1 shows a cleaved and etched Si chip with a thin layer of sol-gel/ $\text{Er}_2\text{O}_3$ / $\text{BaTiO}_3$ /DNA-CTMA nanocomposite material spin coated on top. The etched channel waveguides that are filled with the nanocomposite material can be visibly observed on the chip running in the horizontal direction.

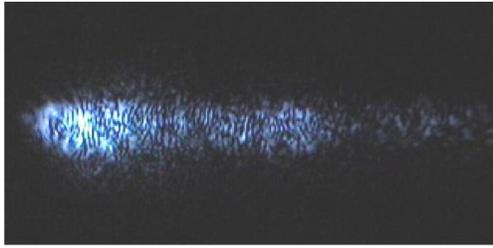
We excited the sol-gel/ $\text{Er}_2\text{O}_3$ / $\text{BaTiO}_3$ /DNA-CTMA thin film covered Si chip with a fiber-coupled 980-nm pump diode and observed the fluorescence emitted. The input pump fiber was butt coupled to a channel waveguide, as shown in Figure 2, left. Green fluorescence was observed to be traveling a much longer distance along the propagation direction (center), in sharp contrast with the fluorescence emission patterns recorded when no waveguiding structures were presented (right); note that this is upconversion fluorescence, which only occurs when erbium is in an environment where nonradiative decay is suppressed. The dramatic improvement of the fluorescence directional propagation is a clear demonstration of the potential for a fully functional waveguide fabricated with sol-gel/ $\text{Er}_2\text{O}_3$ / $\text{BaTiO}_3$ /DNA-CTMA nanocomposite material.



**Figure 2.** (Left) Pump fiber butt to a channel waveguide; (center) green fluorescence propagating in a channel waveguide; (right) fluorescence emitted in a uniform thin film.

## 2.2 Sol-Gel/DNA-CTMA/Yb<sub>2</sub>O<sub>3</sub> nanocomposite thin films

In addition to Er<sub>2</sub>O<sub>3</sub> nanopowder, we have extended our effort to another rare-earth ion, ytterbium (Yb<sup>3+</sup>) to study how Yb<sup>3+</sup> nanoparticles can be dispersed into the sol-gel system with DNA-CTMA serving as the capping agent. We utilized Yb<sub>2</sub>O<sub>3</sub> nanopowder, < 100 nm particle size, from Sigma-Aldrich. To fabricate sol-gel/Yb<sub>2</sub>O<sub>3</sub>/DNA-CTMA nanocomposite films, first, 2.0 g Yb<sub>2</sub>O<sub>3</sub> was dissolved in 1.9 g 1-methoxy-2-propanol (MOP), and the solution was heated and sonicated for about one hour. Then, 0.2 g of methacryloxypropyltrimethoxysilane (MAPTMS) was added, and the blend was heated and sonicated for about four hours. Afterwards, 1.0 g DNA-CTMA/MOP solution (12 wt.%) was added, and the mixed solution was heated and sonicated for about one hour. The final nanocomposite solution could be passed through a 0.45 μm filter and was directly applied for the spin coating process on Si wafer substrates.



**Figure 3.** Blue fluorescence observed in sol-gel/Yb<sub>2</sub>O<sub>3</sub>/DNA-CTMA nanocomposite films.

We again excited the sol-gel/Yb<sub>2</sub>O<sub>3</sub>/DNA-CTMA thin film coated Si chip with a fiber-coupled 980-nm pump diode and observed the fluorescence emitted. This time, characteristic blue upconversion fluorescence was observed, as shown in Figure 3. The strong blue luminescence of ytterbium originates from the cooperative upconversion of Yb<sup>3+</sup>-Yb<sup>3+</sup> clusters in the Yb<sup>3+</sup>-doped nanocomposites. It is a unique fluorescence that is only attributed to the presence of Yb<sup>3+</sup> ions with long radiative lifetimes.

In the foregoing we have established DNA-CTMA as an effective capping agent for dispersing metal oxide nanoparticles in sol-gel systems, which will undoubtedly lead to numerous applications in photonics and electronics.

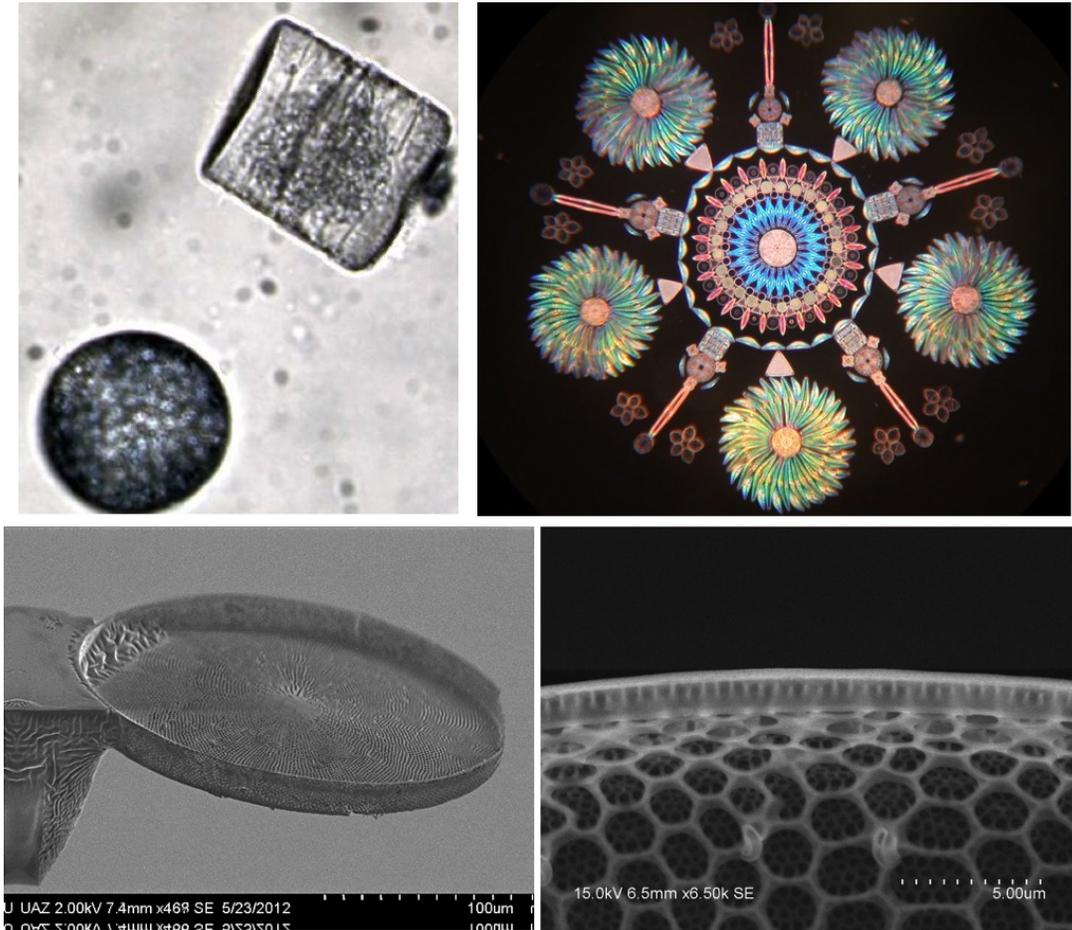
## 3. DIATOM PHOTONICS

Diatoms, a widespread type of natural phytoplankton, have attracted considerable attention from generations of researchers. They are interesting for many reasons including their photosynthetic processes, relevant to renewable energy, their relevance to water quality management and environmental protection; their beautiful siliceous outer shell (or frustule), the intriguing symmetries present in the frustules [7-9]; and their viability as a template to create devices/units with desired optical properties for remote detection which would then allow for the creation of multifunctional particles with significantly-enhanced tagging capabilities.

We are now investigating the optical properties of diatom siliceous shells for various applications including microresonators, photonic crystal filters, and surface enhanced Raman devices for ultrasensitive detection and sensing. The primary diatom species we have worked with is *Coscinodiscus wailesii*, which we can now grow thanks to training by colleagues at the Scripps Institute in San Diego. Figure 4 shows several images of diatoms; all except Figure 4(b) are from our lab. Figure 4(c) shows a diatom attached to an optical fiber, and we have used this capability to fine position diatoms for optical interrogation.

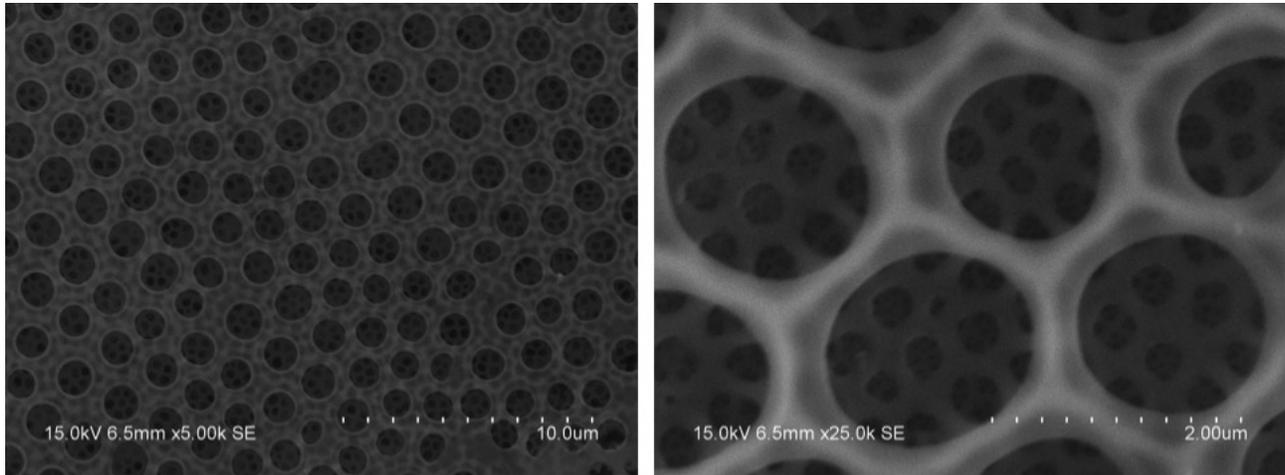
Photonic crystals are periodic micro/nanostructures that are designed to effect the propagation of electromagnetic waves in unusual and controllable ways. 1-D photonic crystals are already widespread in the form of optical thin-film coatings on lenses and mirrors. Higher dimensional photonic crystals are of great interest for both fundamental and applied research. Photonic crystal fiber, a two dimensional photonic crystal, is important for applications in nonlinear optical devices and dispersion control. Three-dimensional photonic crystals offer even more functionalities but they are still in the development phase due to the numerous challenges in their manufacture.

It has been very difficult to efficiently create three-dimensional photonic crystals working in the visible wavelength range by conventional lithographic techniques due to small feature sizes required. Nature, however, has been very successful in this endeavor with many examples of complicated three-dimensional photonic crystals, e.g. butterfly, bees, beetle, etc. Diatoms are also good creator of photonic crystals that are special since their photonic crystal shells are made of glass. This material can be preserved in nature for millions of years in form of diatomite. It is also ideal for optics since there is no problem with material absorption that would normally be a concern with other types of materials. Diatoms as living photonic



**Figure 4.** a) Optical image of living diatoms (*Coscinodiscus wailesii*). b) Microscope slide of arranged diatoms by K. D. Kemp. c) SEM image of a diatom frustule attached to an optical fiber. d) High magnification SEM image of a diatom frustule showing the intricate periodic nano-scale silica structure.

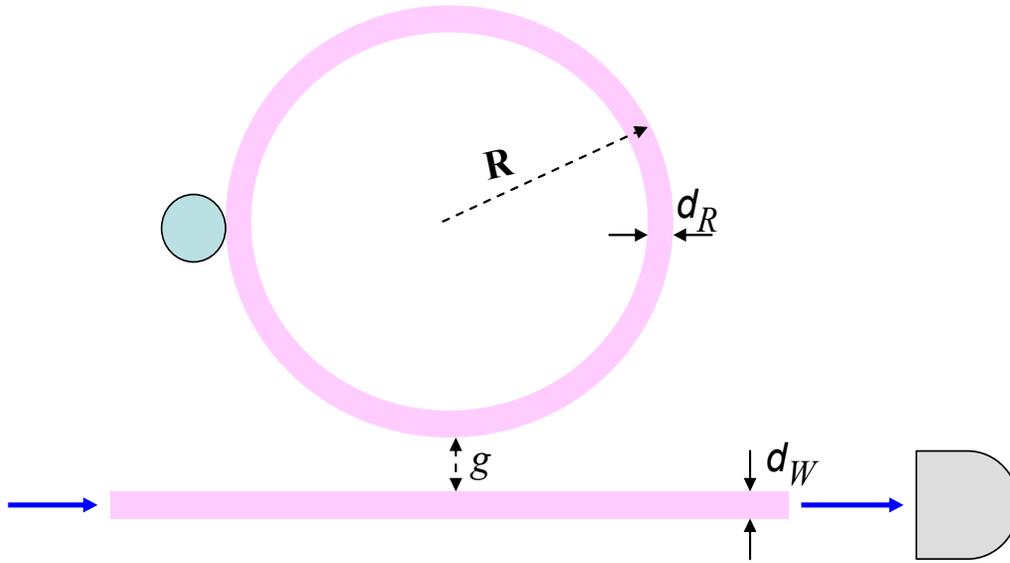
crystals have been investigated theoretically by Fuhrmann *et. al* [7]. We have now been able to establish experimentally the presence of a strong diffraction behavior in diatoms and have used bright supercontinuum sources together with optical fiber techniques to show that the diffracted spectrum changes with position of the interrogating beam on the diatom surface, providing the potential for sophisticated tagging schemes [10]. Figure 5 shows SEMs of diatoms we have grown that clearly evidence the quasiperiodic structure that diatoms adopt, a structure that clearly has favorable nanostructure for exhibiting photonic crystal effects.



**Figure 5.** SEM images of the siliceous frustule of a diatom (*Coscinodiscus wailesii*). The images reveal the periodic structure that is typical for a photonic crystal.

#### 4. FDTD MODELING OF MICRORING PHOTONIC SENSING OF PARTICLES

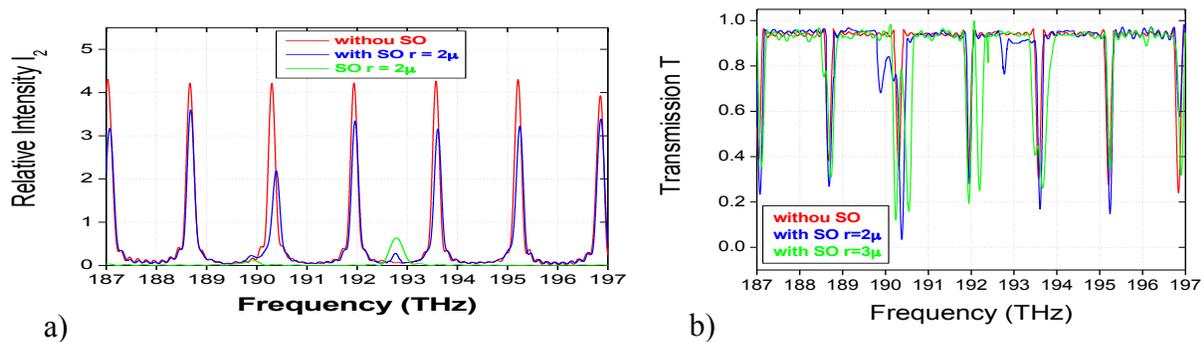
There is strong interest in the use of microphotonic devices for biological sensing, where the sensing of cells and proteins is primarily targeted. We have focused our initial efforts on the modeling of microring-based sensors using finite difference time domain (FDTD) methods to enable the modeling of light propagation through the microresonator structures and perturbed versions of microresonators such as we see in Figure 6 below[11]. Due to the enormous computation time required for even simple structures, we have limited our work to 2-D microresonators, such as the microring shown in pink. The blue disk adjacent to the microring represents a different material that could be attached to the microring, the object to be sensed. Let us consider a typical microring resonator in which a waveguide (tapered fiber) couples to a resonant microring adjacent to a scattering object (SO) as shown in Fig. 6. A light beam is launched into the fiber from the left. The light beam propagates in the waveguide and then couples to the microring, where whispering gallery mode (WGM) resonances enable multiple recirculation of the light, resulting in multiple interactions between the light and the SO. Note that, once the light beam is coupled to the microring, frequency components that are close to WGM resonances of the cavity will be re-circulated multiple times depending on the quality of the cavity  $Q$ . For example, in a planar microcavity with quality  $Q$  factor of  $10^8$  the resonant light can interact with the particle about 100,000 times. By monitoring the WGM optical resonances excited in the microcavity and/or the eigenmodes of the particle, the unique optical signature of the composite system can be elucidated. We have developed a framework to numerically investigate the general problem of microring resonators in the presence of scattering objects using the finite-difference time-domain (FDTD) method. The FDTD method can completely describe light recirculation in the WGM cavity and the multiple interactions between the light and the object. This feature is very unique to WGM sensing, and is almost impossible to describe accurately by other simplified modeling methods such as coupled mode theory. It is worth noting that FDTD method has been extensively applied to simulate and analyze WGM of isolated microdisks [12, 13], microdisks and microrings [14]. The accuracy of the FDTD method for problems in linear optics was first demonstrated for the directional coupler [15]. Since then, the perfectly matched layer (PML) absorbing boundary condition (ABC) was introduced [16], providing the means to terminate the calculated grid space with extremely low reflection.



**Figure 6.** Schematic of a microring with a perturbing particle: a ring resonator (radius  $R$ , width  $d_R$  and index  $n_R$ ) coupled to a waveguide (width  $d_W$ , index  $n_W$ ). The gap between the ring and the waveguide is  $g$ . A particle (radius  $r_{SO}$  and index  $n_{SO}$ ) is adjacent to the ring.

Let us generally describe the FDTD simulation method for a typical single-SO microring system. We consider a two-dimensional (2D) problem where the  $z$ -directed electric field is normal to the  $x$ - $y$  plane of the grid. We employ the PML ABC in our simulation of the light propagation in the waveguide-microring-SO system. It is worthwhile to stress here that accurate FDTD simulations in resonant cavities in general, and especially in WGM cavities have several challenges: (i) the computation time required for accurate simulation of the light recirculation in WGM cavities is much longer than that required for typical scattering or propagation problems, and (ii) even if the reflection due to the numerical boundary conditions is very small within PML ABC, its effects can adversely affect the simulation results. This is especially the case when the light is reflected at the end of the waveguide, counter-propagates and couples back to the microring, where it undergoes recirculation in the cavity. To avoid boundary reflection during light recirculation in the microring, we introduced a long waveguide around the sensing area, which includes the microring and the SO. The goal is to make light keep propagating or get trapped after it passes the microring so as to avoiding reflection in the waveguide. The optimization challenge in this simulation is to design an extended waveguide that can keep light propagating or get trapped as long as possible, while at the same time minimizing the computational space and time needed.

We performed FDTD simulations for the system without the SO, and for SOs having different sizes and indices as shown in Fig. 7 in which the spectrum of a microring with  $R = 20\mu\text{m}$  without an SO is compared with the spectrum of the same microring with adjacent SO with radii of  $r = 2,3\ \mu\text{m}$  ( $n_{SO} = 3.6$ ). Let us first discuss some main features of the results shown in Fig. 7. The frequency 192 THz is one of the resonant modes of the ring as shown by the red curves in Fig. 7a and 7b for the relative intensity inside the microring and the transmission, respectively, for the ring without an SO. When a scattering object is included, a disk with diameter  $r$  and index  $n_{SO}$ , interesting effects occur including scattering by the SO, shifts of the resonant modes, and new modes appearing in the spectrum that depend on the physical properties of the SO, such as size and refractive index. With this framework firmly established, it is possible now to model a variety of complex microresonator particles both to determine the effect of adding adhesive features and to design objects with unique spectral signatures.



**Figure 7.** (a) Relative intensity inside microring ( $R = 20\mu\text{m}$ ,  $d_R = 1\mu\text{m}$ ,  $n_R = 1.46$ ), (e) transmission (red); with SO  $r = 2\mu\text{m}$  (blue) and with SO  $r = 3\mu\text{m}$  (green),  $n_{SO} = 3.6$ .

## 5. CONCLUSION

In summary we have reviewed several recent examples of the development and investigation of photonic biological and biologically inspired materials and devices. Hybrid systems, whereby biological elements are combined with inorganic materials and devices to achieve advanced functionality, have been principally highlighted. We see that DNA-CTMA makes an excellent capping agent that enables a broad range of high performance optical composites, demonstrated here for rare earth doped oxide nanoparticles. The siliceous skeletons or frustules of diatoms are seen to having intriguing structures that could lead to dramatic optical effects. Finally, we apply FDTD techniques to simulate the interaction of microring resonator modes with small objects that represent individual cells and macromolecules, evidencing a new modality of biosensing. Clearly, there is an exciting road ahead at the interface between photonics and biological materials and structures.

## 6. ACKNOWLEDGEMENTS

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