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Application of microgels for optical tagging

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ABSTRACT

In this paper we present results from our research into the use of microgel-based photonic crystals in an optical tagging application. The basis for this research is the phenomena of self-assembly of hydrogel nano- and microparticles (i.e., microgels) into colloidal crystal Bragg reflectors. Previous research has demonstrated the assembly of Bragg structures that are sensitive in the visible spectral region. This current research focuses on the extension of this process into the infrared regime and the use of these infrared-sensitive structures in the creation of an optical tag. In particular, the research effort emphasizes two primary areas: the development of nanoparticles that are infrared-sensitive and the casting of thin films comprised of these particles. We will also present theoretical data on the optical and physical characteristics of thin films comprised of these particles. This paper will present an overview of the program, outline the processes and issues addressed during our initial efforts in creating these infrared sensitive structures and present a summary of the computational results based on the theoretical analyses.

1. INTRODUCTION

Recent breakthroughs in the chemistry of photonic crystals have led to a potentially new approach for developing an optical tag for military and surveillance applications. Microgels provide an opportunity to synthesize robust optical tags that display unique signatures and performance characteristics in both the visible and infrared portions of the spectrum. In addition, microgels offer the capability to create time-dependent signature tagging through controlled changes in the optical structure. These changes can be tailored to be initiated either by a user-controlled signal or passively through environmental interactions.

Microgel-based infrared reflective films will display their characteristic spectral properties due to Bragg reflection from a periodic dielectric function within the material. To achieve this dielectric periodicity, we are constructing films from colloidal crystals, wherein size monodisperse colloidal particles self-assemble into cubic close packed arrays. In Nature, Bragg reflectors are present in the form of opals, butterfly wings, and Japanese beetle shells, among others[1]. The colloidal crystal represents a synthetic reconstruction of natural opals and represents a simple, yet diverse construct for the creation of non-chromophoric optical materials. We are using this simple construct to create infrared-reflective "bar codes" for optical tagging applications. Hydrogel colloidal crystals developed at Georgia Tech will be cast as thin films, followed by a cross-linking step to render the film dimensionally stable. Spatial patterning of the material will provide a unique optical structure that does not rely on chromophore incorporation and is hence stable with respect to

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photobleaching and other environmental conditions. The inherent advantages of this approach relate to color stability, ease of application, potential reversibility or controlled erosion of the film, and the facile preparation of spatially varying arrays. Figure 1 shows an example of such a film, based on this technology that is active in the visible band. In this case the particle sizes are on the order of a couple of hundred nanometers and show a response in the deep red portion of the spectrum.

2. PARTICLE SYNTHESIS AND ASSEMBLY

Research within the Georgia Tech School of Chemistry has focused on developing Bragg reflective films based on the creation of hydrogel microparticles. This research has focused on developing and refining techniques for creating films of these particles that retain their reflective properties under a variety of external conditions. One consequence of this research is that several approaches to the creation of these particles and films have been identified; these approaches work to create visible-band active structures but no scientific reason exists to prevent their extension to the development of infrared responsive structures. This set of approaches formed the basis for the current work to extend the spectral response into the near- and short-wave infrared. "Soft" hydrogel particles are used to create the Bragg reflective structures; these polymer-based particles are grown to an appropriate size and, then, through one of a variety of chemical or physical processes, the particles "bind" into a coherent planar lattice structure. Typically these particles initially form thin layers that are optically responsive based on short range ordering of the particles; subsequently casting them as thin films results in a stronger optical response through coherent stacking of the planar lattices. To date, the structures developed under these efforts are reflective in the visible band. The goal of the current research is twofold: (1) extend the wavelength response of the structures into the infrared regime, and (2) create an optical tagging (device / structure) based on these new structures. Tag development requires three stages: particle synthesis, crosslinking, and fabrication.

The first stage required the synthesis of larger diameter particles than those created for the visible band. The size of the particles and the lattice spacing in the structure determines the overall optical response of the thin films. The efficiency of the resulting Bragg structure strongly depends on this particle size uniformity; therefore the particle synthesis stage was a critical component in the overall optical performance of the microgel films. Three methods of creating the correct size particles (i.e., with diameters ranging from 1 – 5 microns) are available and will be evaluated: precipitation polymerization, atom transfer radical polymerization, and emulsion polymerization. For these initial trials the precipitation polymerization approach was employed as it provided the most direct extension of existing research.

Hydrogel particles were grown in an aqueous polymer medium through control of the concentration, temperature, etc; during this process, polymer chains in the medium linked up to create particles of increasing diameters. Through control of the macroscopic conditions the growth of the particles could be controlled. As a result, this method created a solution of monosize dispersed particles of the appropriate diameter. For the current work this process produced particles with diameters in the 1 – 3 micron range. Precise determination of the particle diameter required additional diagnostic tests that were not performed at the time of this paper; instead, indirect means were employed to verify the particle diameters. With the particles still in solution a 'soft' linking of the hydrogel particles occurs through the mutual 'hooking' of the polymer chains on the surface of the particles. As a consequence short-range order is imparted to the hydrogel solution resulting in a weak Bragg reflection response, that is, creation of the planar structures of particles.

Crosslinking of these micro-particles represents the next stage of process; it provides the critical mechanism necessary to strengthen the bonds between the particles and to create and stabilize the long-range order in the polymer assembly. Specifically, this process links up the various planes to create a three dimensional structure. As with the particle synthesis stage several techniques were investigated including the application of an external stimulus such as light or heat, the introduction of an additional molecule into the solution, or drying the solution to force the hydrogel particles into closer proximity. The most successful techniques were found to be those based on light-activated mechanisms. This technique was employed to induce crosslinking of the particles with the corresponding establishment of long-range order in the particle lattice. The net result of this process was a more robust physical structure and a stronger Bragg response from the assembly. In addition, the lattice assembly maintained this order through various carefully imposed physical changes such as temperature variations or drying. Figure 2 shows an example of one such structure constructed from particles of approximately 2 μm diameter developed using these techniques. Two images are shown in this figure

– one is a Scanning Electron Microscope image and the other is a Differential Interference Contrast image. Both show an ordered appearance to the particle assembly.

After the crosslinking stage is finished the solution can be dried to create a thin film of these particles; in this state, the long-range order of the particles, as stated above, will be maintained. The drying step introduces anisotropy to the lattice in the direction normal to the film but the transverse direction maintains the original ordered assembly. Figure 3 shows an example of four such films developed under this program. The particle lattice is oriented to present the <111> direction of a face-centered cubic lattice parallel to the film surface. The right image in the figure shows the normal incidence view of the slide holding the four films; no color is discernible in this view and the underlying logo is discernible. The left image in the figure shows an oblique view of the same slide; in this case, each of the film gels shows a distinctive color – a color based on the particle size and Bragg structure within each of the films. While these films show responsiveness in the visible portion of the spectrum it is expected that they will also show responsiveness in the infrared – these are the next set of tests to be performed on these films. Confirmation of this expectation will allow us to proceed to spatial patterning experiments.

The final stage in the optical tag creation process will involve combining various types of Bragg films in a designated spatial arrangement designed to mimic a specified pattern. Since these films have the capability to be cast in fluid form and dried while still retaining their Bragg reflection characteristics a lithographic approach has been proposed. Figure 4 schematically illustrates this process. It is envisioned that an initial film would be laid down in the desired pattern onto a substrate and covered with an appropriately transparent polymer coating; subsequent patterns could then be laid down using a similar process to build up a three dimensional tag. Each polymer coating can be tailored to 'protect' the underlying layer for a prescribed period of time or external conditions. In this way, a time-varying tag can be created. As the films can be free-standing, the substrate will not be required after the tag has been completed.

3. THEORETICAL ANALYSIS

In conjunction with the experimental work analytical and computer modeling were utilized to provide a more extensive theoretical underpinning for the research and application of the technology to the optical tagging problem. In order to understand the response of a hydrogel-based optical tag to interrogation we began a theoretical analysis into the propagation of electromagnetic waves in periodic dielectric structures. In essence the particle assembly process outlined above creates a structure that has a periodically changing dielectric constant – in this case the dielectric changes are small. Our initial calculations based upon the scalar-wave approximation, ignoring the vector nature of the electro-magnetic field, give incorrect results for these structures.

Consequently, it became necessary to solve Maxwell's equations exactly, taking the vector nature of the electromagnetic field fully into account. We first began an elementary band structure analysis. Using the method of Ho, Chan, and Soukoulis[2], we modeled the band structure of the crystal in the MATLAB programming environment. The resulting equation for the band structure produces an eigenvalue equation, which can be solved using standard matrix-diagonalization methods. Unfortunately, this method proved too cumbersome; for N plane waves the matrices were on the order $2N^3$. Specifically the computational time to solve the eigenvalue problem was excessive (on the order of days) and required a high number of plane waves (i.e., N large) to produce suitable accuracy in the results. In lieu of this technique, we adopted the transfer matrix method introduced by Pendry and MacKinnon[3,4]. The transfer matrix (T-matrix) method is a finite-element method that searches the k-vectors in the first Brillouin zone that correspond to a given energy eigenvalue. This T-matrix technique permits integration of the electric and magnetic fields through the unit cell of a specified complex structure. By transforming the transfer matrix to a plane wave basis the transmission and reflection coefficients may be calculated. Also, this method permits band structure analysis by calculating the eigenvalues of the real space transfer matrix for a simple cell.

We adopted the code developed by A. J. Reynolds[5] at the University of Glasgow for our numerical calculations. We calculated the reflectance spectra for radiation impinging on the <111> face of both isotropic and anisotropic fcc close-packed crystals (74% filling fraction) in the dried and the swollen states. For the dried state we used: $\varepsilon1 = 2.22$ and $\varepsilon2 = 1.00$, where $\varepsilon1$ is the dielectric constant of the spheres and $\varepsilon2$ is the dielectric constant of the background. For the swollen state we used: $\varepsilon1 = 1.780$ and $\varepsilon2 = 1.769$.

The following graphs show the reflectance spectra for selected cases. The calculations were performed using a normalized frequency parameter defined in the equation below; the normalized frequency is related to the wavelength of the radiation by the relation:

$$\lambda = \frac{D\sqrt{2}}{\nu_N},$$

where D is the diameter of the spheres. For the graphs in this paper this normalized frequency has been converted to wavelength by assuming the particle diameter equals 0.5 μ and 1.0μ, for the dehydrated and hydrated cases respectively. Both TM and TE reflectances as well as the total reflectance are plotted as a function of wavelength. First we consider an fcc isotropic crystal. Figures 5 and 6 show the reflectance spectra for the dehydrated state at normal incidence and at 10 degrees from the normal. The normal incidence case shows a peak around 9 μ and no dependence on the polarization of the radiation. This peak provides the primary response of the film; the spectral "sidelobes" are suppressed significantly in this view. Figures 7 and 8 show similar views of a hydrogel film in the hydrated state. In this case the particle size and the lattice are slightly expanded. For normal incidence these curves show a dual wavelength response at wavelengths of approximately 1.05 μ and 2.05 μ. No polarization dependency is observed in these data. The nature of this response provides an intriguing potential for a dual wavelength approach to the tag development or a mechanism for determining the hydration state of the tag. For the 10 degree incidence (Figure 8) the two original peaks are still present but an additional strong reflectance response is produced at approximately 1.1 μ. The origin of this added structure requires additional study.

Future work will focus on refining these calculations for different viewing geometries and various particle sizes as well as examining the impact of disorder in the planar structures on the spectral response. A key issue to address is producing a detailed understanding of the change in the spectral response of both film types arising from different observation directions. The impact of the spectral sidelobes on the film signature is an important aspect to developing an operational tag. In addition, the response of the films under both ambient lighting conditions and active illumination will be studied. Finally, measurements are scheduled to confirm the theoretical calculations presented here.

4. SUMMARY

The Georgia Tech group is extending microgel photonic crystal technology to the infrared region of the spectrum. We have developed precipitation polymerization methods that allow for reproducible synthesis of highly monodisperse particles in the 1-3 micron range. In addition, theoretical modeling of the microgel photonic crystals has been implemented to supplement the tag development experiments to aid in understanding the overall process.

ACKNOWLEDGMENTS

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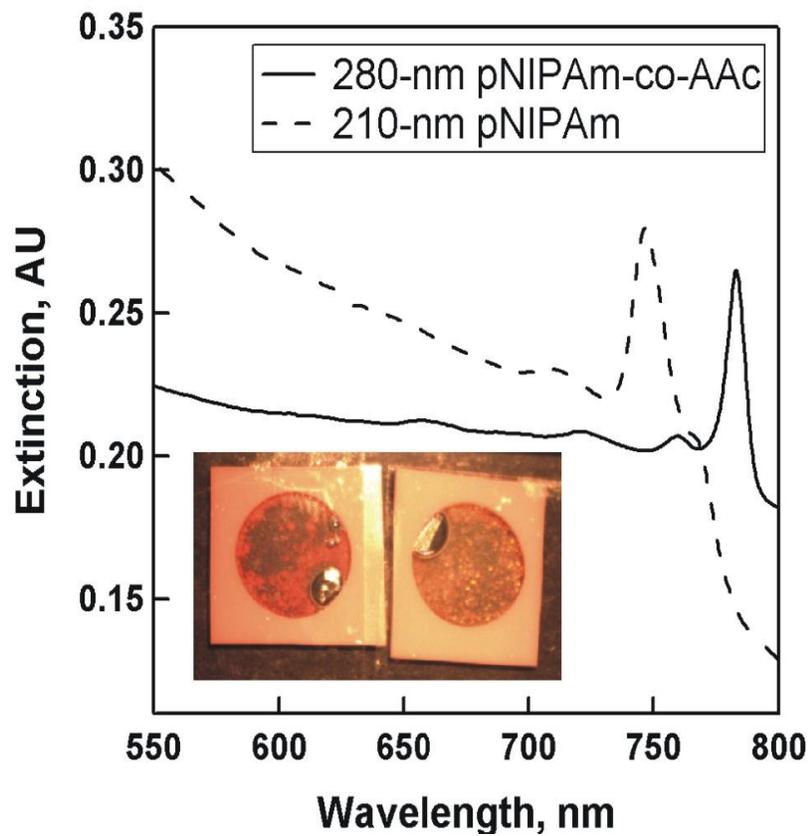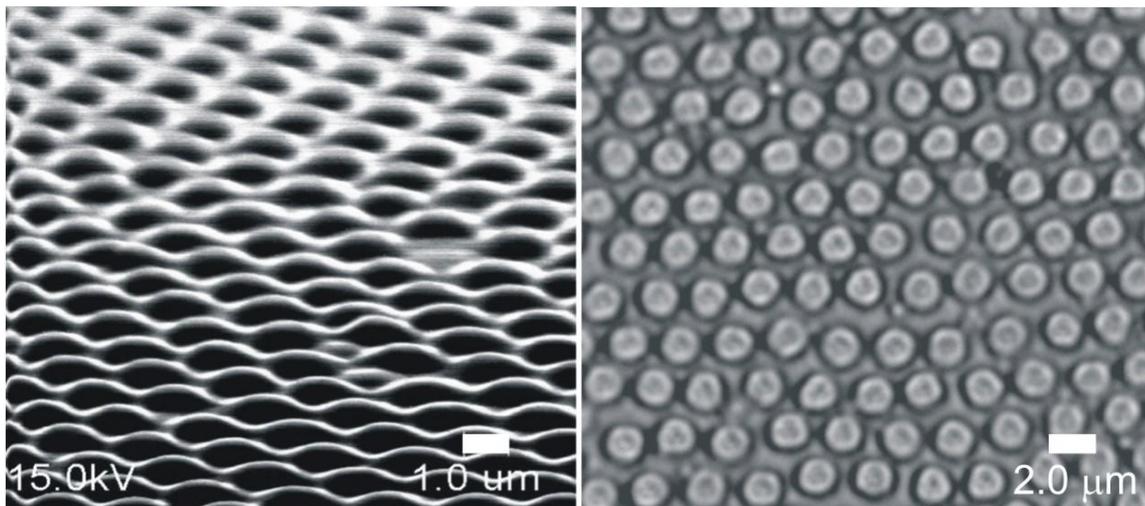
Figure 1. Representative Hydrogel Crystal

Figure 2. Hydrogel particles (2 μm diameter) particles in the de-hydrated state: scanning electron microscopy image on the left, differential interference contrast image on the right.
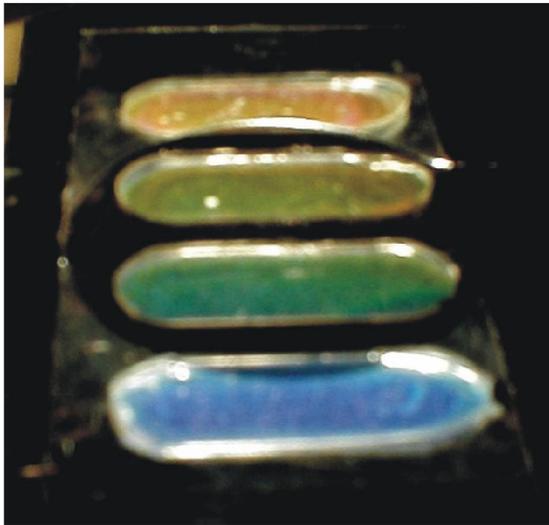
Figure 3. An initial set of hydrogel Bragg films created using the procedures outlined in the text: the left image shows an oblique view, the right image shows a normal incidence view.
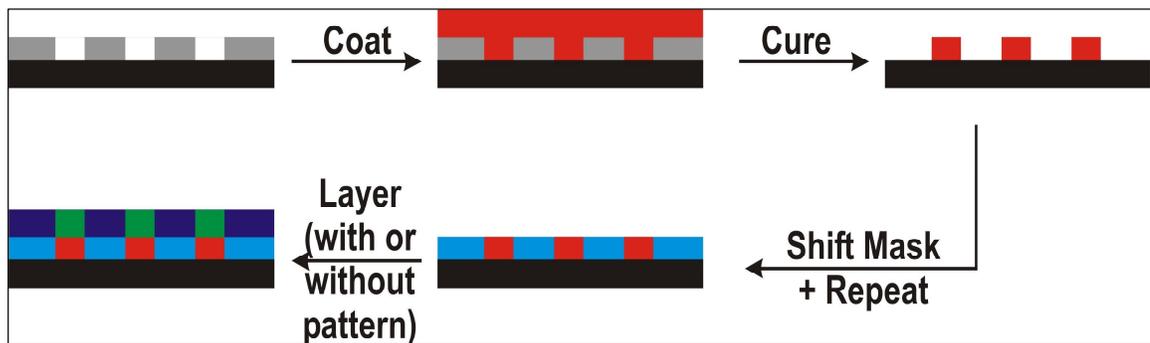

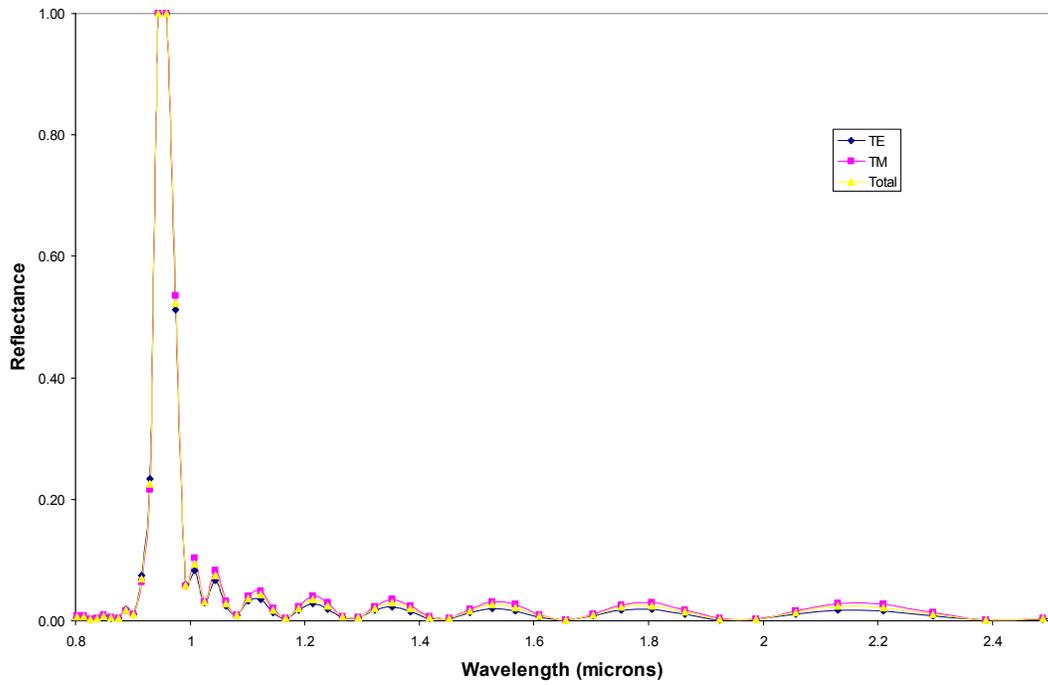Figure 4. Lithography-based concept for generating patterned optical tags.

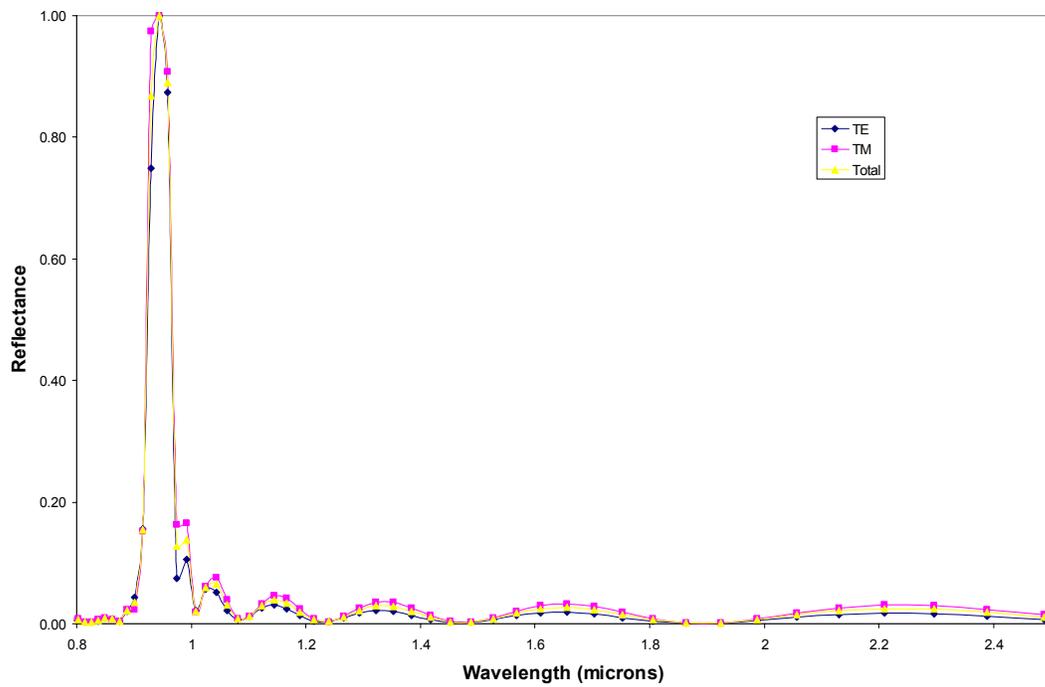Figure 5. Normal incidence reflectance of hydrogel thin film in the dehydrated state.

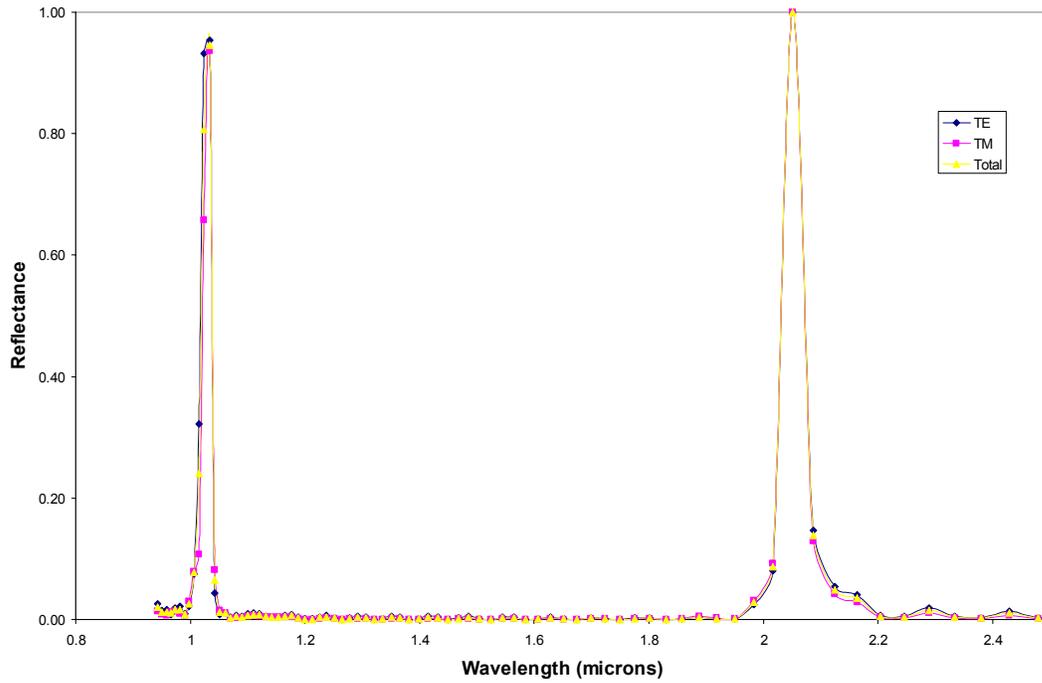Figure 6. Reflectance at 10° to normal for hydrogel film in the dehydrated state.

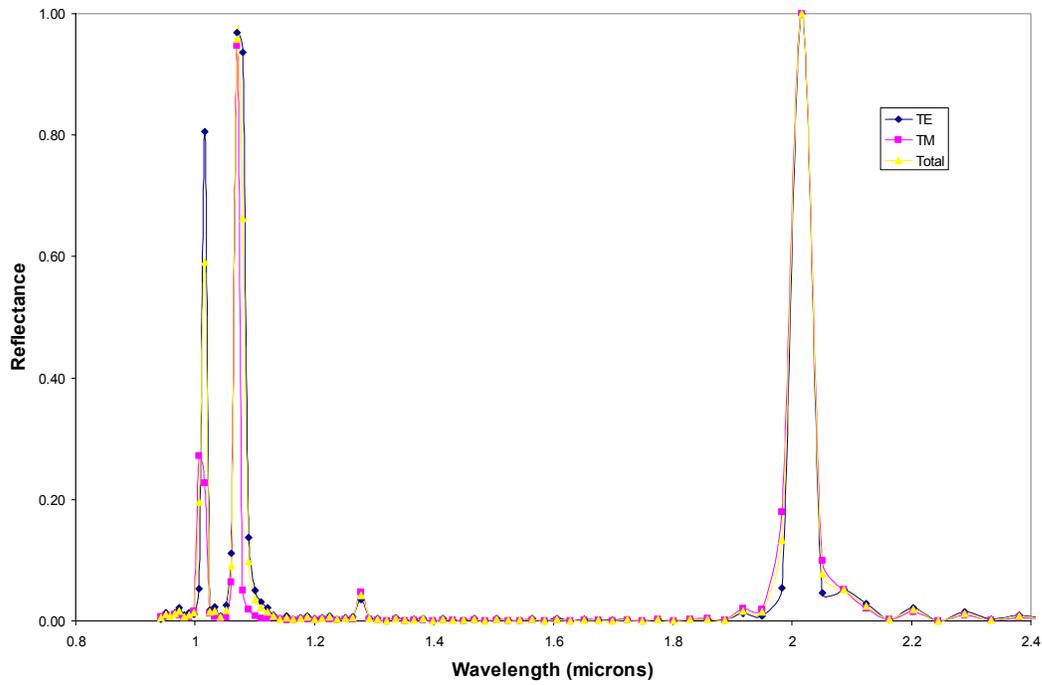Figure 7. Normal incidence reflectance for hydrogel film in the hydrated state.

Figure 8. Reflectance at 10° to normal for hydrogel film in the hydrated state.