# Broadband infrared reflecting thin films inspired by quasi-ordered photonic structures in squid tissue

Roy Rotstein[1,2], Alison M. Sweeney[2], Amanda Holt[2], Galen D. Stucky[1,2], and Daniel E. Morse[2]

[1]Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, 93105, USA
[2]Institute for Collaborative Biotechnologies, University of California, Santa Barbara, CA, 93105, USA

## ABSTRACT

Recent work on photonic crystal films has largely focused on the synthesis of highly ordered structures with emphasis on achieving structures with a complete photonic bandgap.[1, 2] In contrast, optical properties of quasi-ordered photonic structures have been relatively uninvestigated. The silver-colored tissue covering the eyes of Loliginid squid is a recent, interesting example of one of these structures with exciting potential applications[3]. Here we present a novel device and synthesis method that replicates the optical properties of this quasi-ordered structure. We use modified self-assembly techniques to build colloidal films that mimic the quasi-order assembly found in the squid system, making significant progress toward a method for fabricating quasi-ordered bio-inspired reflectors.

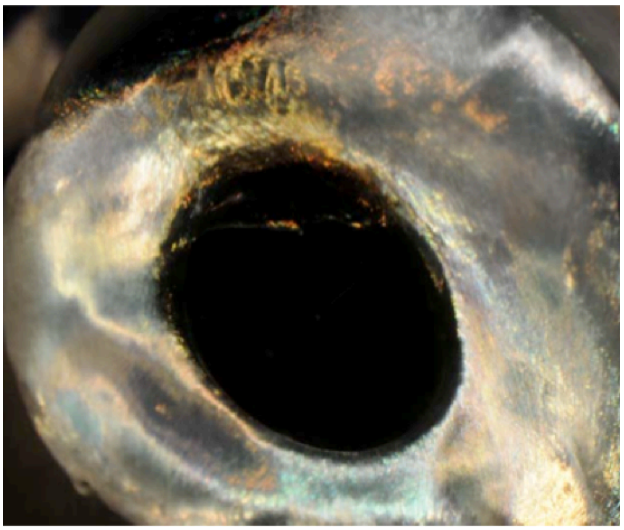
***Keywords***: self-assembly, bio-inspired, photonic cyrstals, thin films, anisotropic particles

## 1 INTRODUCION

Novel photonic structures found in biological organisms have inspired new designs for a wide variety of optical devices ranging from anti-reflective coatings to displays.[2] Recently, our research group has characterized the photonic properties of the tissue surrounding the eye in Loginid squid.[3] The tissue acts as an omni-directional broadband reflector for wavelengths in the visible spectrum (Figure 1a). The source of the broadband reflection is due to the presence high-aspect ratio tapered cells that self-assemble in a quasi-ordered fashion forming a distributed Bragg reflector (Figure 1b). Analyses of the squid system show that a wide, continuous variation in spatial frequencies of refractive index regions gives rise to the observed broadband reflectance in the visible spectrum.[3]

In this work, we seek to mimic the visible-frequency quasi-order of the squid system by self-assembling anisotropic polystyrene colloidal particles into thin films. We demonstrate that these particles self-assemble in a quasi-ordered fashion closely approximating the squid structure that inspired this fabrication.

a



b

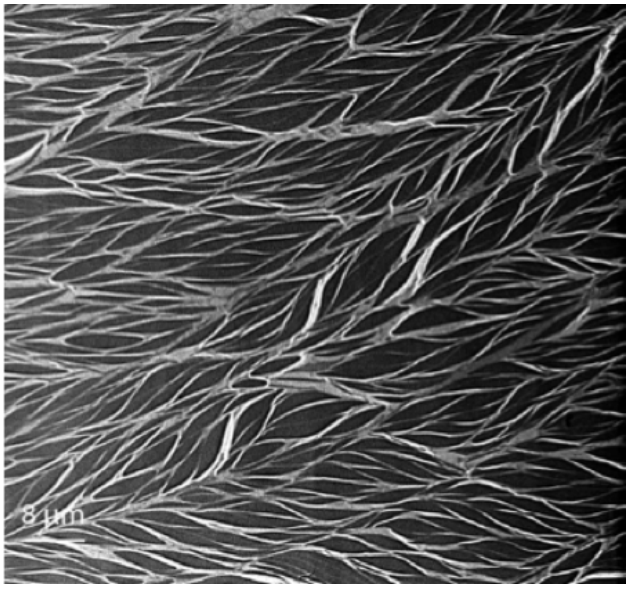



Figure 1. Broadband "silver" reflectance in eyes of Loligo squid. a) Photograph of a squid eye showing the silver broadband reflecting tissue. b) Transmission electron micrograph of silver eye tissue showing large areas of homogeneously quasi-ordered spindle-shaped cells. Figures used with permission from reference [3].

## 2 MATERIALS AND METHODS

### 2.1 Particle synthesis

Rod-shaped polystyrene colloidal particles were synthesized according to a film stretching procedure detailed in refererence [3]. Polystyrene microspheres (purchased from Bangs Laboratories) with a diameter of 300 nm were imbedded in a polyvinyl alcohol film. 3.8 grams of 70k polyvinyl alcohol (Sigma) were added to 60 mL deionized $H_2O$. The mixture was stirred vigorously at 100° C for 30 minutes or until the solution became transperent. 0.3 mL glycerol (Fisher Scientific) was then added to the solution. After letting the solution stir for and additional 5 mintues, 1mL of 5% by volume suspension of polystyrene spheres was added to the solution. The solution was filtered and poured onto a level plate and allowed to dry overnight. The film was cut into 7 x 5 cm strips, mounted onto a mechanical stretching apparatus, and placed in a hot oil bath at 125° C. The films were immersed in the oil bath for 5 minutes prior to stretching to allow for liquefication of the polystyrene particles. Films were stretched to an aspect ratio of 2.5 while immersed in the oil bath. A schematic of the stretching procedure is shown below in Figure 2.

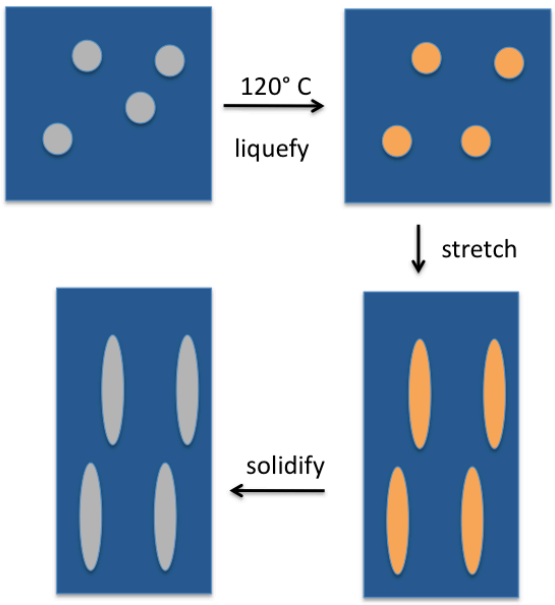



Figure 2. Film sretching process. Polystyrene spheres (grey) are imbedded in polyvinyl alcohol film. The film is stretched in a hot oil bath heated to 125° C. This temperature is above the glass transition temperature of polystyrene and below the melting point of poly-vinyl alcohol. After completion of stretching, the film is removed from the oil bath and allowed to cool back to room temperature over the course of 30 minutes.

The stretched films were subsequently removed from the mechanical stretcher and placed in a 50 mL conical tube containing 20mL de-ionized $H_2O$. The conical tube was immersed in a hot water bath at 80° C, causing the polyvinyl alcohol matrix to dissolve. Particles were isolated by centrifugation and suspended in de-ionized $H_2O$. Particles were subsequently purified by repeated centrifugation and suspension in $H_2O$.

### 2.2 Self-assembly of colloidal films

The rod-shaped colloidal particles were assembled into thin films using a modified convective assembly technique. A 3 mL suspension of particles was diluted down to a concentration of 0.1% volume. This suspension was placed inside a 3 mL volume well from a 12 well multiwell tissue culture plate (Fisher Scientific). Wells were rinsed with deionized $H_2O$ prior to use. Glass or silicon substrates were cleaned prior to use by immersion in a pirnha bath (2:1 sulfuric acid:30% hydrogen peroxide) for a period 3 hours. Substrates were then washed with deionized water and dried under a stream of nitrogen. To ensure hydrophilicity, substrates were subjected to plasma treatment for 30 seconds. A glass or silicon substrate was then placed in the colloidal suspension and supported vertically with binder clips. The microwell plate was placed inside an oven kept at a temparature of 65° C. The suspension was allowed to evaporate over the course of 12 hours.

Inverse silica films were synthesized using a cooperative assembly technique based on a procedure detailed in referenced [5]. 10 µL of a TEOS solution (1:1:1.5 by weight TEOS:0.1M HCl:ethanol) were added to 3mL of a 0.1% volume colloidal suspension. The films were assembled using the same technique described above. After the suspension had completely evaporated, the film was calcined at 500° C for 3 hours to remove the polymer template.

### 2.3 Structural characterization

The structural features of the films were characterized with a FEI XL30 Sirion FEG scanning electron microscope (FEI Co., Hillsboro, OR). Samples were sputtered with gold and imaged using a beam voltage of 5 keV.

## 3 SEM CHARACTERIZATION

SEM images of both the polystyrene colloidal film and the silica inverse film are shown in Figure 3. Both images were taken at a 30° tilt angle.

a


b

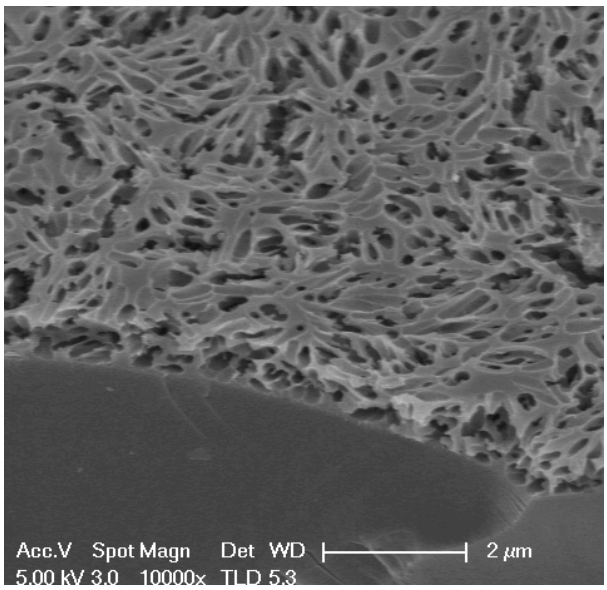



Figure 3. Scanning electron micrographs of the synthetic films. a) Self-assembled polystyrene rods with aspect ratios of 2.5. b) Inverse silica films. The silica fills the interstitial space between the rods during the assembly process, and the film is subsequently calcined at 500° C to remove the polymer rods.

The polystyrene rods assemble in a quasi-ordered fashion. The orientation of individual rods is confined to the plane of the substrate such that the major axis of individual rods aligns parallel to the plane of the substrate. While no long-range order is present in the the structure, a small degree of local ordering occurs between nearest neighbor rods. Small domains comprising a few neighboring rods preferentially align in the same direction. These domains orient independently of each other and do not posses a preferred direction of alignment in the film. Similar alignment behavior can be observed for the silica film.

## 4 CONCLUSIONS

In summary, we have successfully mimicked the architecture and optical propertiesof a novel quasi-ordered structure found in broadband reflecting tissue of Loliginid squid. We synthesized rod-shaped anisotropic colloidal particles and assembled them into thin films. The optical properties of these films, along with the corresponding silica inverse films, exhibit broadband reflectance extending into the near-infrared. These films have potential applications as semi-reflective coatings for the near-infrared.

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