Colloidal Dimers for Reduced Symmetry Photonic Crystals

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Abstract:

The primary concentration of this project was to synthesize monodispersed, non-spherical, high refractive index colloids with a well-defined, asymmetric shape to be used as building blocks for photonic crystal structures with stable three-dimensional bandgaps. To achieve this aim, crosslinked polystyrene seed particles with varying levels of divinylbenzene (DVB) were synthesized. A seeded dispersion polymerization technique was utilized to swell the seed particles and create polystyrene dimers. Samples containing the asymmetric particles, along with other morphology types, were synthesized. Parallel to the dimer synthesis, we have successfully coated polystyrene seed particles with materials of high refractive index, such as zinc sulfide and titania. These core-shell particles were used to create hollow high refractive index shell structures by dissolving the polystyrene core with toluene. Polystyrene/DVB and coated particles were characterized via SEM.

Introduction:

Photonic crystals are dielectric structures with a periodic variation in the refractive index which may permit the manipulation of light in the same manner as semiconductors do for electrons. This property can lead to applications in zero-threshold lasers, coherent LED emission and low-loss waveguiding for all optical circuits. Computational studies have shown that using non-spherical building blocks in constructing the face-centered cubic lattice can break the symmetry-induced degeneracy of the photonic band structure. An additional condition under which a photonic crystal will exhibit a complete bandgap is a minimum contrast in refractive index between the two dielectric materials. In order to satisfy this condition, particles may be coated with high refractive index materials and then turned into hollow particles through dissolution of the core.

Experimental Section:

Polystyrene Seed Particles Crosslinked with DVB: Monodispersed particles of 400-500 nm dia. were obtained by combining the following reagents: 50 mL ethanol, 20 mL deionized water, 3 mL purified styrene, 73.3 mg sodium lauryl sulfate (SLS), and 66.7 mg potassium persulfate (KPS). Crosslinking densities from 0.5% to 3% were achieved by substituting DVB for the corresponding percentage of styrene. The mixture was then magnetically stirred and polymerized at 70°C for 24 hours before being washed and resuspended in ethanol.

Polystyrene Peanuts using Seeded Dispersion Polymerization: Crosslinked polystyrene/DVB spheres were first resuspended into a 2 wt% EtOH/H_2O solution. Then, 35 mL of EtOH/H_2O solution, 5 mL P(S/DVB) solution, 0.4 mL styrene, 47.5 mg SLS, and 33.3 mg KPS were mixed in a 100 mL bottle. The solution was stirred for 24 hours to allow swelling of the crosslinked particles. Then, polymerization was initiated by raising the temperature to 70°C for an additional 24 hours. Refer to Figure 1.

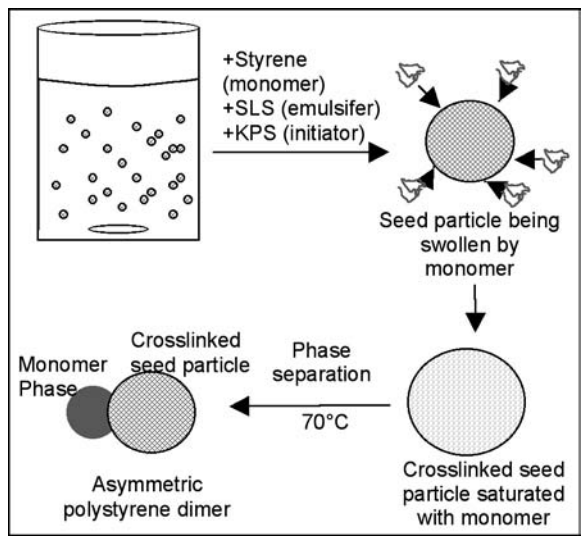

Figure 1: Synthesis schematic for polystyrene peanuts via seeded dispersion polymerization.

Polystyrene Spheres Coated with Zinc Sulfide: Coating of un-crosslinked polystyrene spheres was done using a chemical bath deposition technique. First, 0.2g poly(vinylpyrrolidone) (PVP), 0.5 mL polystyrene, and 50 mL deionized water were added to a 200 mL volumetric flask and sonicated. Next, 0.6060g zinc nitrate, 0.0430g manganese nitrate, and 1.4370g thioacetamide were dissolved into the flask. Deionized water was added to balance and the solution was transferred to a heated water bath at 85°C for either 1, 1.5, or 2 hours. The reaction was terminated by quenching the solution to below 10°C in an ice bath. To remove the polystyrene cores, an excess of toluene was added to the coated spheres overnight.

Polystyrene Spheres Coated with Titania: Coating of un-crosslinked polystyrene spheres was done through the hydrolysis of titanium tetraisopropoxide (TTIP) in a method

adapted from Imhof [1]. The following reagents were mixed in a 100 mL bottle: 27 mL ethanol, 289 mg PVP, 672.04 μL 5 mM NaCl solution, 10 mL polystyrene, and 302.4 μL TTIP in 4 mL ethanol. Hydrolysis occurred rapidly after 1 minute of stirring and the suspension was allowed to stand for 15 minutes before washing and redispersing in ethanol.

Results and Discussion:

Polystyrene Seed Particles Crosslinked with DVB: Particles with 0.5%, 1%, 1.5%, 2%, and 3% DVB were successfully synthesized. In order to verify monodispersity, the coefficient of variation (standard deviation/mean) was calculated and confirmed to be under 9%. An interesting result of a synthesis of P(S/3%DVB) done at 90°C was that peanut-shaped particles were formed. This is likely due to particle aggregations arising from collisions above the glass transition temperature. This sample contained a large percentage of dimers that may be separated, leading to possibilities of a one-step process of the formation of polystyrene peanuts.

Polystyrene Peanuts using Seeded Dispersion Polymerization: An early experiment using P(S/0.2%DVB) seed particles in 5:2 EtOH:H_2O produced ellipsoidal-shaped particles, trimers, tetramers, and spherical particles speculated to be a new nucleation of seed particles (*See Figure 2: P(S/.2%DVB) seed particles in 5:2 EtOH:H_2O*). Literature has shown that smaller particles require a larger percentage crosslinking in order to exhibit phase separation, so the next experiment was done with P(S/2%DVB). Additionally, the solution was changed from a 5:2 EtOH: H_2O to 2:5 EtOH:H_2O in order to encourage swelling of the monomer in seed particles. The result of the modified experiment was a nearly uniform solution of agglomerated football-shaped particles. While these particles are not useful due to agglomeration, the uniform building block formed is encouraging. Another experiment was run using P(S/3%DVB) in a H_2O solution. Again, some ellipsoids were synthesized in addition to swollen spheres and other morphologies.

Polystyrene Spheres Coated with Zinc Sulfide: Longer experimental times created a more uniform, thicker coating of ZnS on the polystyrene spheres. The coating thicknesses were measured to be 70.5 nm, 84 nm, and 99.5 nm for the 1, 1.5 and 2 hour experiments, respectively (*See Figure 3: Hollow ZnS shells - 2 hour deposition*). Verification for the coating material was conducted using energy dispersive spectroscopy.

Polystyrene Spheres Coated with Titania: The titania coating was fairly uniform with a thickness of 44 nm (*See Figure 4: TiO_2 coated polystyrene.*). Formation of secondary titania particles may be due to the use of anionic polystyrene spheres as compared to the cationic ones reported by Imhof. Thicker coatings may likely be achieved by increasing the TTIP concentration.

Conclusions:

In the future, focus will be placed on creating uniform polystyrene dimers, which may require higher crosslinking densities. Additionally, a one-step peanut process by controlling emulsifier quantity and reaction temperature may be used. Coatings using tin sulfide and noble metals will be done. Once dimers are formed, we will try to assemble them using template-assisted self assembly and proceed to characterize the crystals.

Acknowledgements:

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References:

[1] Imhof, A. Langmuir 2001, 17, 3579-3585.