An Amphiphilic Poly(phenylene ethynylene) as the Structure-Directing Agent for Periodic Nanoscale Silica Composite Materials

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ABSTRACT

We have synthesized optically active nanostructured composite materials by using an amphiphilic semiconducting polymer, a poly(phenylene ethynylene) (PPE), and a conventional ammonium surfactant as the structure-directing agents. The PPE consists of phenylene units para-substituted with an octyloxy chain and a charged trimethylammoniumethoxy group, resulting in a surfactant-like structure that can assemble into cylindrical micelles. The resulting silica/organic composite material has a hexagonal honeycomb structure with a repeat distance of 45.3 Å, as confirmed by low-angle X-ray diffraction and transmission electron microscopy. Scanning electron microscopy indicates that the larger scale particle size is on the order of micrometers. The incorporation of the polymer into the composite was confirmed by elemental analysis, photoluminescence spectroscopy, and fluorescence microscopy. The polymer retains its photophysical properties in the composite, showing luminescence similar to polymers in the solution phase. The polymer displays a high degree of luminescence polarization anisotropy, indicating that the polymer chains are straight and isolated from each other in the composite.

Mesoporous and mesostructured materials quickly gained attention following their discovery by Kato and co-workers and by the Mobil Research and Development Corporation. Initial interest was due primarily to their potential use as catalysts, supports, and thermal barriers because of the wide range of available pore sizes, high surface area, and thermal stability. However, increasing attention has focused on electronic and optical applications, because the high surface area of these materials allows high doping concentrations, and the tunable size range allows access to a variety of quantum-confined structures. Considerable research has been conducted in order to develop mesostructured materials for optical waveguides, sensors, and photovoltaic cells.

The potential for polymer inclusion for electronic and optical applications became evident as Wu and Bein reported an in situ polymerization of polyaniline within the channels of a hexagonal aluminosilicate. However, the degree of polymerization was low and the DC conductivity of the composite was similar to that of the unloaded host material. Brinker and co-workers also explored in situ polymerization using an amphiphilic diacetylene surfactant as the structure-directing agent in an evaporation-induced self-assembly process to template the formation of silica composite materials with hexagonal, cubic, and lamellar mesoscopic order. Upon exposure to ultraviolet light, the diacetylene monomers polymerized, forming polydiacetylene chains within the silica pores. Recently, the same group demonstrated another in situ polymerization using thiophene monomers in combination with a catalytic palladium complex. The polymerization was initiated by exposure to acetylene gas, forming a poly(2,5-thienylene ethynylene)/silica nanocomposite. Although oligomers did form within the silica channels, their molecular weight was rather low and not well controlled. Nanocomposites containing other conjugated polymers have been synthesized, using poly(phenylene butadiynylene), polythiophene, polypyrrole, and polyacetylene in silica matrices.

Our group has studied the effects of incorporating semiconducting polymers into the pores of calcined mesoporous silica. This technique has the advantage that moderate molecular weight polymers can be synthesized by conventional routes before incorporation in the silica nanopores. When the inside of the silica pores is functionalized with hydrophobic groups, poly[2-methoxy-5(2′-ethoxyhexyloxy)-1,4-phenylenevinylene] (MEH–PPV) chains can be diffused into each pore from solution, separating the polymers and forcing them to adopt elongated conformations. In addition, the pore size can be easily controlled by varying the size of the original surfactant or block copolymer

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template. The PPV chains can therefore be incorporated as isolated single chains within small pore silica (~2 nm pores), as small aggregates of interacting straight chains within medium size pores (~5 nm), or as larger agglomerates consisting of coiled interacting chains within large pores (8–10 nm). This controlled aggregation allows us to direct interchain energy transfer, which in turn enables tuning of the photoluminescence emission spectrum, polarization, and quantum yield. The ability of excitons to split into free carriers or polarons can also be tuned using the pore size; increasing the number of polymer chains within the pores increases the polaron yield, indicating that interchain polaron production is more effective than intrachain production. These results could have applications for nanostructured devices because the straight, interacting chains could be used as molecular wires.

Controlling interchain interactions is useful, but the ability to control the orientation and conformation of the polymers on a larger scale would also be valuable for optical displays and other optoelectronic devices that require a high degree of polarization anisotropy. To this end, we have incorporated semiconducting polymers into thin films of mesoporous silicas with a high degree of pore alignment produced using a rubbed polyimide substrate. For these aligned materials, a high filling fraction is achieved (>40%), indicating the presence of multiple polymer chains within each pore. More importantly, aligning the polymer chains creates films with highly polarized absorption and luminescence.

The results summarized above show that it is possible to control polarization and interchain energy transfer in semiconducting polymer containing composite materials, but the synthesis of the materials is a multistep process, involving surfactant templated synthesis of the host material, followed by calcination, silylation, and incorporation of the guest polymer. This synthesis could be facilitated by using an amphiphilic semiconducting polymer to directly template synthesis of the host material, followed by calcination, silylation, and incorporation of the guest polymer. This synthesis could be facilitated by using an amphiphilic semiconducting polymer to directly template formation of the silica framework. In this approach, a high-quality moderate molecular weight polymer is incorporated into the composite, but the synthesis still involves only one step, taking advantage of self-assembly. Our current research has therefore focused on using a polymer as the structure-directing agent, thereby forming the final composite material in a single synthetic step. This paper demonstrates the feasibility of this approach using an amphiphilic poly-(phenylene ethynylene) (PPE) structure-directing agent. Areneethynylene conjugated polymers are attractive for use in nanocomposite materials because of their high quantum yields and stability in air. In addition, the rigid rod structure of this polymer should produce composite materials with long, straight domains.

The polymer selected for this investigation was 4-octyloxy-1-(2-trimethylammoniummethoxy)-2,5-poly(phenylene ethynylene) chloride (PPE), whose structure is shown in Scheme 1. It was synthesized by Sonogashira coupling of neutral para-substituted diethynyl and diiodo monomers, followed by methylation and ion exchange to make the final ionomer. The synthesis will be described in detail in an upcoming publication. This polymer is the ideal candidate for this application since its surfactant-like structure allows it to act as a template, while its conjugated backbone allows long-range charge conduction. Since we are familiar with hexagonal mesoporous materials templated with alkylammonium surfactants, the polymer was designed with the same functionality. The para-substituted side chains on the phenyl ring of each repeat unit are a nonpolar octyloxy chain and a polar trimethylammoniumethoxy group. This structure causes the PPE molecules to assemble into cylindrical aggregates in solution, as shown in Scheme 1. Since the polymer chain axes are parallel to the cylindrical axis of each pore, the polymers can conduct along the pore axes, potentially resulting in wire-like long-range conduction.

Composite materials were synthesized in basic aqueous solution by adapting a standard procedure for making hexagonal mesoporous silica using cetyl trimethylammonium bromide (CTAB) as the surfactant and silica source tetraethyl orthosilicate (TEOS). This procedure was modified by replacing 1–5% (by mass) of the CTAB with PPE (see Scheme 1). The presence of the surfactant in addition to the polymer was necessary because the solubility of the polymer was insufficient to drive inorganic/organic co-assembly. The synthesis was carried out by first mixing the base and surfactant together in deionized water. The presence of CTAB aids in solubilizing the polymer; therefore PPE was added after the CTAB. This mixture was stirred under mild heating (50 °C) until the polymer dissolved completely. TEOS was then added, and the mixture was allowed to continue stirring for another 3 h at room temperature. The
resulting precipitate was then filtered and dried. The final mole ratios were 100:0.1:0.45:8.5 H$_2$O:CTAB/PPE:NaOH:TEOS.

The ratio of CTAB/PPE was dictated by the solubility of the polymer in aqueous solution; the maximum amount of PPE relative to CTAB was 5% by mass, but in all cases the concentration of quaternary ammonium groups (whether from CTAB or PPE) was kept constant. Although PPE could dissolve at a ratio of up to 5% relative to CTAB, some polymer inevitably precipitated out of solution upon addition of TEOS when working at the limit of solubility. This produced composite materials incorporating inconsistent amounts of polymer. To determine how much polymer was incorporated into the composite, C–H–N elemental analysis was performed by Desert Analytics and was used to calculate the monomer-to-surfactant ratio. For a synthesis containing 1% polymer relative to CTAB, elemental analysis indicates that the actual composition is closer to 8%. The preferential incorporation of polymer over surfactant is expected, because the limited solubility of PPE forces the majority of the polymer chains into the micelles. In addition, the smaller CTAB molecules gain more entropy by leaving the ordered composite than the polymer because of the greater number of degrees of freedom available to a large number of small molecules compared to a small number of large molecules. Therefore, entropy also preferentially drives the polymer into the micelles. Solutions containing modest PPE concentrations (~1%) yielded composite samples with consistent amounts of polymer incorporation (~8%) with essentially no PPE left in solution after composite precipitation. All measurements were taken on samples containing 8% PPE unless otherwise noted.

A schematic diagram of the coassembly reaction is shown in Scheme 1. The first step shows the assembly of amphiphilic PPE molecules with CTAB in solution to form cylindrical micelles. These aggregates associate electrostatically with silica oligomers, which then condense to form a continuous framework. The resulting composite materials were formed as yellow powders, providing initial visual evidence of polymer incorporation in the composite. Low-angle X-ray scattering measurements (Figure 1) indicate that the materials have two-dimensional (2D) hexagonal order with a (10)$_{\text{hex}}$ peak position of 39.2 Å, which corresponds to a lattice constant of 45.3 Å. This correlates well with CTAB-only composite materials made by a similar procedure, which typically have center to center pore distances of 39–40 Å.

Chem3D molecular models predict that the distance between the ends of the amphiphilic side chains on the PPE phenyl groups should be approximately 17 Å. Since this is similar to the length of a CTAB molecule (~14 Å), the polymer chains should pack efficiently into micelles with CTAB. The greater length of the polymer side chains compared to CTAB surfactant correlates with the difference in pore–pore spacing between the CTAB-only composite and the PPE–CTAB materials. The calculated intramolecular distances are based on the assumption that the length of an alkyl chain in a self-organized liquid crystal phase with limited mobility is typically 0.7 times the distance predicted by the idealized bond angles of the elongated chain. This is derived from thermodynamic and geometric analysis of the molecular packing of surfactants in self-assembled structures. We believe this assumption to be valid in the composite materials under investigation, because the presence of the condensed silica matrix surrounding the organic domains substantially decreases the fluidity of the alkyl chains of both surfactant and polymer.

We employed several types of microscopy in order to elucidate the morphology of the PPE/silica composite. High-resolution transmission electron microscopy (TEM) images of calcined versions of the samples are presented in Figure 2. Images were collected using a JEOL 2000FX operating at 200 kV. While the calcination process destroys the semiconducting polymer, it Improves the TEM contrast and improves the stability of the sample to the electron beam without significantly altering the nanoscale architecture. The TEM images confirm the well-defined nanometer scale architecture also demonstrated in low-angle diffraction measurements. The primary structural elements visible in TEM are stripes with a center-to-center spacing of approximately 4 nm, corresponding to the (10) lattice spacing. Unfortunately, the rigid rod nature of the polymers makes the composites inherently form elongated structures that tend to be deposited parallel to the substrate, making it difficult to find grains with the pores oriented normal to the TEM grid. However, it is clear that the structure is hexagonal as opposed to lamellar, which could also show stripes in TEM, because a lamellar structure would collapse during calcination.

The larger scale morphology of the composite is revealed in Figure 3. Scanning electron microscope (SEM) images (Figure 3a) reveal particles on the scale of tens of micrometers. The particle size distributions were consistent across different samples. Figure 3b is a confocal fluorescence microscope image of another composite particle, showing a similarly sized particle. The fluorescence images also showed
consistent size distributions in agreement with the SEM data. Since the contrast is due to fluorescence of the PPE, the homogeneous brightness of this image also suggests that the polymer is distributed uniformly throughout the material. In these images, the lattice spacing is found to be 4 nm, in excellent agreement with the (10) diffraction spacing observed in low-angle X-ray diffraction.

Photoluminescence (PL) measurements also confirmed the presence of PPE in the composites. Photophysical measurements were performed on composite samples suspended in glycerol, which was used to match the index of refraction of the silica framework and thus to decrease scattering.14,17 Fluorescence was measured with a Jobin-Yvon Horiba Spex Fluorolog-3 spectrofluorometer with samples held in 1 cm quartz cuvettes. As shown in Figure 4a, the photoluminescence peak of PPE in the composite lies between those of the polymer in solution and in a drop-cast film, although the peak is much closer to that observed for PPE in solution.

The shifts in peak position can be attributed to the conformation of the polymer chains, as well as to interactions between chains. In the solid state, the PPE molecules are packed closely together, allowing neighboring chains to be close enough to achieve π-orbital overlap. This allows excited state species to migrate to the lowest energy sites via Förster transfer and generates lower energy interchain species, strongly redshifting the PL emission.27 In solution, the PPE molecules aggregate due to the solubility of the charged trimethylammonium groups in the polar solvent and the insolubility of the alkoxy side chains. However, electrostatic repulsion forces neighboring chains too far apart to achieve effective π-overlap. Therefore, the redshift in the luminescence is not observed. In the composite, the chains should also be fairly well isolated, both because there is only a modest amount of PPE relative to CTAB and because electrostatic repulsion and packing frustration should again separate any chains that assemble into the same domain. Since the interchain interactions are small in both cases, we conclude that the shift in PL between the solution phase samples and the composite is likely attributable to chain conformation. In solution, the polymers are confined to the

Figure 2. Parts (a) and (b) show representative TEM images of calcined PPE/CTAB/silica composite. While the calcination process destroys the optically active polymer in the composites, it produces materials which are more stable in the electron beam without significantly altering the nanometer scale architecture of the material. In these images, the lattice spacing is found to be 4 nm, in excellent agreement with the (10) diffraction spacing observed in low-angle X-ray diffraction.

Figure 3. (a) SEM image showing a piece of PPE/silica composite. Particle sizes are fairly consistent across samples. (b) Confocal fluorescence microscope image of a composite grain similar to that in part (a), showing that PPE is incorporated into the composite, making it fluoresce. The uniform fluorescence intensity suggests that the polymer is fairly homogeneously distributed throughout the composite.
photons if the chains are randomly oriented. Similar intensities of polarization memory between the incident and emitted light are selectively excited. In this experiment, the incident light is linearly polarized, and the emitted light is polarized either parallel or perpendicular to the incident beam. Therefore, even though individual grains of sample are randomly oriented, the PPE micelles, but they can still move because of the dynamic nature of the micelles. Therefore, they can twist and bend slightly, lowering the effective conjugation length. However, the composite locks the polymers into a rigid, coplanar conformation, ensuring that they are in the lowest energy conformation.

To further characterize the environment of the PPE in the composite, we performed polarized fluorescence measurements. In this experiment, the incident light is linearly polarized, and the emitted light is polarized either parallel or perpendicular to the incident beam. Therefore, even though individual grains of sample are randomly oriented, the PPE chains with transition dipoles parallel to the polarization direction of the incident light are selectively excited. In semiconducting polymers such as PPE, excitations can hop between chains via Förster energy transfer if the chains are in electronic communication with each other. If this hopping is fast, Förster transfer can result in a complete loss of polarization memory between the incident and emitted photons if the chains are randomly oriented. Similar intensities are thus observed for light emitted both parallel and perpendicular to the excitation polarization in polymer films. If the polymer chains are isolated, however, this process cannot occur, resulting in increased polarization memory. Similarly, if the neighboring chains are all parallel to each other, Förster transfer can occur, but it does not result in polarization scrambling.

As shown in Figure 4b, the composite displays approximately twice the emitted intensity with the excitation and emission polarizers oriented parallel to each other as it does when they are perpendicular. Taking into account the monochromator grating factor, the polarization anisotropy is high, reaching nearly 0.4 at 450 nm. An anisotropy of 0.4 is the highest value that can be achieved for a system like ours which lacks macroscopic alignment and has parallel absorption and emission transition dipoles. The large polarization ratio indicates that either the polymers are isolated or they are parallel to each other in the composite. An 8% polymer loading should statistically result in more than one polymer chain in each cylinder at any given linear position, and typical Förster radii for semiconducting polymers are larger than our pores (for poly(phenylene vinylene) [PPV], these Förster radii are generally found to be 4–5 nm, which is larger than the pore diameter of ~3 nm). Therefore, we would expect some energy transfer to occur in these composites. The high luminescence anisotropy thus suggests that the polymer chains are indeed oriented parallel to each other and to the hexagonal cylinder direction, as predicted by simple packing models. The wavelength dependence of the anisotropy also shows a slight decrease in anisotropy at lower energy. This indicates that as excitations migrate between chains to lower energy sites, they lose some of their polarization memory. This result confirms that Förster transfer is still occurring in these materials and thus that the high anisotropy stems primarily from the straight, parallel alignment of polymer chains.

In summary, we have demonstrated a single-step synthesis of mesoporous silica that incorporates semiconducting polymers into the 2D hexagonal architecture. Although the presence of some CTAB surfactant is required to drive self-assembly, we believe that altering the polymer side-chain structure has the potential to significantly improve the polymer solubility, allowing for synthesis of composites with a higher PPE to surfactant ratio and improving the optical and electronic properties. Future work will also focus on combining these direct polymer templating methods with semiconducting matrix materials in an effort to produce semiconductor-semiconductor heterostructure devices. Experiments are currently in progress to optimize the amount of PPE in the composites and to further investigate their optoelectronic properties.

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