DIRECT GROWTH OF SEMICONDUCTOR NANOPARTICLES WITHIN A CONDUCTING POLYMER MATRIX

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Introduction

The search for new polymer-based electronic materials has lead to research of hybrid polymer-nanoparticle blends. Conducting polymers are well known for their use in devices due to their ability to transport excitons. One drawback is that electron transport in conducting polymers is much slower than hole transport. In order to transfer electrons more efficiently and exploit their tunable bandgaps for exciton generation, preformed nanoparticles have been directly blended with conducting polymers. By doing so, the exciton will be separated at the interface between the two materials, and the electron transport will transport holes while the nanoparticles will transport the electron. Achieving good communication between the two materials prepared by this method has proven difficult as a result of passivation of the nanoparticles surface by surfactant molecules or oxide coatings, uneven size distribution, and uneven distribution of particles throughout the polymer, and uneven size distribution. In an effort to improve interfacial interactions, a novel conducting method has been synthesized. After polymerization, the incorporated metal center serves as the seed point for semiconductor nanoparticle growth. The growth of the nanoparticles directly into the polymer backbone will enhance interactions between the two materials, which should lead to increased exciton separation and transport.

Experimental

General Methods. The following chemicals were used as received: 5-bromosalicylaldehyde (Alfa Aesar), 2,2'-bithiophene (Aldrich), tributyltin chloride (Alfa Aesar), 2,2-dimethyl-1,3-propanediamine (TCI), 1,2-phenylenediamine (TCI), 2,2'-ethylenedioxybis(ethylamine) (Aldrich). All solvents were dried using an Innovative Technology, Pure Solv solvent purifier with a double purifying column. All reactions were performed using standard Schlenk techniques.

Instrumentation. NMR spectra were obtained using Varian Unity+300. TEM pictures were taken using a JEOL 2100F microscope. Samples were prepared on gold grids with a carbon support film purchased from Electron Microscopy Sciences.

Electrochemistry Methods. All electrochemistry was performed using an Autolab Potentiostat. Experiments were run in 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride. A nonaqueous reference electrode of 0.1 M silver nitrate in acetonitrile was used. A platinum button was used as the working electrode and a platinum coil was used as the counter electrode. XPS samples were prepared on 0.002" thick Stainless Steel.

Quantum Dot Growth. Polymerized films were treated with subsequent solutions of metal salts (MNO₃) and a saturated solution of sodium chloride (NaCl). The polymerizable metal precursors were metallated using metal salts of Cd, Ga, and Pb. The polymerizable metal complexes were then electropolymerized as conducting metallopolymer films were characterized by electrochemistry, UV-vis spectroscopy, XPS, and UV-vis spectroelectrochemistry.

Results and Discussion

In the first step of the synthesis, 5-(tributylstannyl)-2,2'-bithiophene was synthesized following literature preparation which was then coupled with 5-bromosalicylaldehyde as seen in Scheme 1. Once coupled, a condensation reaction was carried out to give Schiff-base ligands. Ligands bearing three different backbones, phenyl, dimethyl propyl, and a crown ether derivative have been synthesized. All ligands have been identified by ¹H NMR spectroscopy as well as by mass spectrometry. The ligands were then metallated using metal salts of Cd, Ga, and Pb. The polymerizable metal complexes were characterized by X-ray photoelectron spectroscopy (XPS), mass spectrometry, and single-crystal X-ray diffraction.

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Table 1. XPS of electropolymerized 3 (M = Cd):bithiophene on Stainless Steel. Theoretical values are shown in parenthesis.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>1:1</th>
<th>1:2.5</th>
<th>1:50</th>
<th>1:100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd:S</td>
<td>1.25</td>
<td>1.4</td>
<td>1.8</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>(1:4)</td>
<td>(1.26)</td>
<td>(1.19)</td>
<td>(1.36)</td>
</tr>
</tbody>
</table>

The new Schiff-base metal complexes were then electropolymerized as seen in Scheme 2 to give electrode confined thin films. The resulting conducting metallopolymer films were characterized by electrochemistry, UV-vis spectroscopy, XPS, and UV-vis spectroelectrochemistry. Representative XPS data for poly-3 (M=Cd) is shown in Table 1. In addition to the homopolymers, a series of random alternating copolymers have been synthesized and characterized, Scheme 3. These copolymers incorporate differing amounts of bithiophene in order to vary the spacing and

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concentration of the metal seed points in the conducting metallopolymer films. Films were prepared by electropolymerization of stock solutions that contained the following ratios of metal complex:bithiophene: 1:1, 1:25, 1:50, and 1:100. Although it is not a direct dependence, as the ratio of monomer to bithiophene is increased, there is an increase in the Cd:S ratio in the resulting films.

Conducting metallopolymer films were also prepared by electropolymerization directly onto carbon coated gold TEM grids. Semiconductor nanoparticles were then grown directly within the polymerized films by exposing the films sequentially to a source of sulfide (H₂S) and metal ions (Cd²⁺, Ga³⁺, or Pb²⁺). This step-wise growth process allows control over the nanoparticle size and terminating surface. Figure 1 shows the presence of 3-4 nm semiconductor nanoparticles that were grown directly in the conducting metallopolymer matrix via this process as observed by TEM.

Conclusions

By synthesizing a metal-containing ligand with polymerizable end groups and then the conducting metallopolymer materials thereof, polymer-nanoparticle blends can be prepared utilizing the metal centers as seed points for semiconductor nanoparticle growth. Because the metal is directly bonded to the backbone of the conducting polymer direct electronic communication between the two materials is ensured. This arrangement provides the appropriate interfacial interactions needed for exciton dissociation and transport opening possible applications in photovoltaic materials. This general synthetic route also allows for the easy synthesis of different metal centered monomers and corresponding semiconductor materials.

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References

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