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Seeded Growth of CdS Nanoparticles within a Conducting Metallopolymer Matrix

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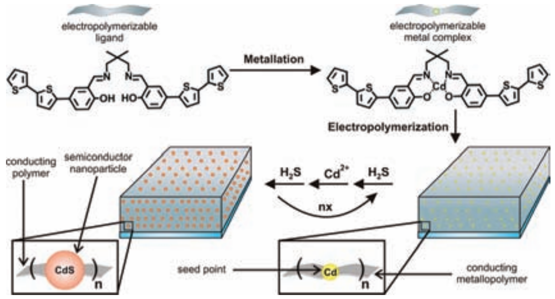
Organic/inorganic hybrid materials are useful for a wide range of applications (e.g., light-emitting materials, photovoltaics, nonlinear optics, sensors, and energy harvesting/storage).[1] The complementary properties of the organic and inorganic components can be exploited to achieve functional materials with enhanced properties.[2] One area of intense interest in recent years has been the development of electronic materials incorporating nanostructured components, particularly for sensors, optoelectronics, and solar cell applications.[3] The use of organic and inorganic components aims to take advantage of the complementary band gaps. The redox properties and stabilities typically lead to the use of organic materials as the p-type component with the inorganic material as the n-type constituent.

One specific class of materials which shows particular promise for a variety of electronic applications is composites of organic conjugated polymers and inorganic semiconducting nanoparticles (NPs). Polymer/NP composites take advantage of the rich optoelectronic properties of conjugated polymers[4] as well as the size and shape dependent band gaps of NPs.[5] As a result, polymer/NP blends exhibit high carrier mobilities as well as an increase in the range of light absorption.[6−8] In addition, these materials are relatively inexpensive to produce and can be cast onto flexible substrates.

Polymer/NP composites are currently synthesized by various methods including postsynthesis mixing of the two materials, attaching metal atoms as pendants to a polymer, impregnating polymers electrochemically with metal centers, and utilizing one-pot syntheses.[6,9−11] Many of these techniques lead to a large size distribution of particles, uneven particle dispersion, passivation of the particle surfaces by surfactants or oxide coatings, and difficulty in controlling the homogeneity of the polymer−nanoparticle blend.[8] Of particular interest when considering these materials for applications in electronic devices is the observation that charge transport increases in these materials with an increase in the physical and electronic interface between the two components. One way this can be achieved is by good dispersion of the nanoparticles throughout the polymer matrix.[12] The use of surfactants/capping agents in the synthesis of nanoparticles has made dispersion throughout the polymer matrix difficult and incorporates an inherent physical barrier to charge transport. However, the use of high aspect ratio nanorods has increased the efficiency of nanoparticle−polymer blends by decreasing the number of particle interfaces in the pathway of electron transport.[7]

With these issues in mind, we have developed a novel approach to synthesize conducting polymer/semiconductor NP hybrid materials which is based on the seeded growth of NPs within conducting metallopolymers.[13] In this synthetic strategy, we first prepare metal complexes that can be polymerized to form conducting metallopolymers with well-defined structures in which metal centers are embedded directly in the polymer backbone. We then utilize the preorganized seed points, or nucleation sites, to initiate the growth of semiconducting NPs directly on the conducting polymer backbone. Through this process we are assured of direct physical and electronic contact between the two active components of the material. Our approach is depicted schematically in Scheme 1.

Scheme 1. Seeded Growth Approach to the Preparation of Hybrid Electronic Materials



The synthetic details for the preparation of monomer **1** shown in Figure 1 can be found in the Supporting Information (SI). The monomer contains polymerizable bithiophene end groups, as well as a salen-type ligand. The salen backbone serves as the binding site for cadmium(II) ions that will act as the seed points for CdS nanoparticle growth (*vide infra*). The solution and gas phase structure and composition of the monomer complex were elucidated by ^{1}H NMR spectroscopy and mass spectrometry, respectively. These data are consistent with a mononuclear cadmium complex with a metal to ligand ratio of 1:1. The solid-state structure was determined by single-crystal X-ray diffraction, and the bulk powder elemental composition was established by X-ray photoelectron spectroscopy (XPS). In the solid state, the structure is a trinuclear complex with a metal to ligand ratio of 3:2, Figure 1. The Cd(II) ions are in two coordination environments in the solid state (Figure S2). The two outer Cd(II) ions have square pyramidal coordination geometries with the salen ligand occupying the four base coordination sites and a bridging acetate occupying the apical site. The central Cd(II) ion lies in a slightly distorted octahedral coordination environment with the oxygen atoms from the salen ligands

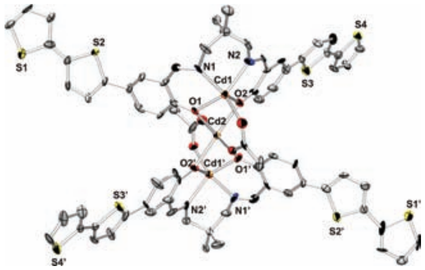


Figure 1. ORTEP diagram of **1** showing the labeling scheme of selected atoms at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

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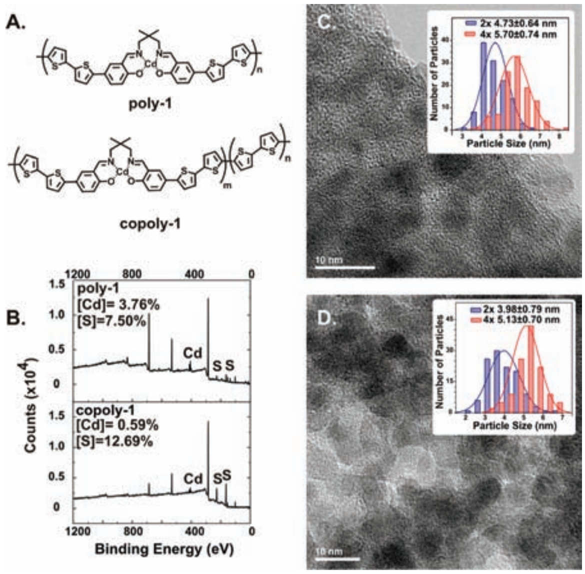

Figure 2. (A) Structures of poly-**1** and copoly-**1**. (B) XPS scans showing Cd:S ratios in poly-**1** and copoly-**1**. (C) CdS NPs grown within a poly-**1** matrix as seen by TEM. (D) CdS NPs grown within a copoly-**1** matrix as seen by TEM. Insets in (C) and (D) show size distributions of CdS NPs.

occupying the four pseudoequatorial sites and the bridging acetate ligands binding in the two pseudoaxial positions. The bond distances and angles are consistent with the data of an isostructural complex lacking the polymerizable groups.[14] Dissolution of this trinuclear complex results in the formation of 2 equiv of the mononuclear complex and 1 equiv of cadmium(II) acetate (SI).

Electropolymerization of **1** yielded conducting metallopolymer films of poly-**1** (Figure 2A) on various working electrodes such as platinum buttons, stainless steel, ITO coated glass, and gold transmission electron microscopy (TEM) grids (SI). The films were characterized using XPS, electrochemistry, profilometry, and four-point probe resistivity. The electrochemical analysis of a typical electrode-confined polymer film (i.e., 20 scans, $t = 84$ nm, $\sigma = 5.7 \times 10^{-3}$ S/cm) exhibits a linear dependence of observed current on applied scan rate within the range 10−500 mV/s (Figure S4). This behavior is consistent with a strongly adsorbed electroactive thin film which is not limited by the diffusion of charge compensating counterions. The ionic porosity demonstrated by the linear scan rate dependence is particularly critical when considering the growth of semiconducting NPs within the polymer film from ionic and gaseous reagents which must diffuse into the film (*vide infra*).

To achieve the growth of CdS NPs, the films were then treated sequentially with a saturated solution of hydrogen sulfide (H_2S) in methylene chloride, a solution of Cd(II) ions in methylene chloride/methanol, and then the same H_2S solution all at room temperature. The metal centers of the conducting metallopolymers act as seed points for crystalline nanoparticle growth directly in the polymer film without high temperature annealing. There is no visible change in the color, thickness, or mechanical stability of the polymer film, but the presence and composition of NPs were confirmed through TEM and energy dispersive X-ray spectroscopy, respectively (Figure 2C). CdS NPs with an average size of 4.7 nm were observed after two growth cycles, and this average size can be increased to 5.7 nm by doubling the growth cycles (2× and 4×, respectively, Figure 2C inset). It is noted that the growth of metal NPs within polymers has been reported.[15]

To show that the metal centers in the conducting metallopolymers are acting as seed points for CdS NP growth, a film of polybithiophene (polyBT) was prepared by electropolymerization onto a TEM grid using conditions identical to those for the preparation of poly-**1**. The polyBT film was treated with the same NP growth procedure described above, and TEM experiments showed no NPs present throughout the film confirming that the metal centers in the metallopolymers are acting as the seed points for nanoparticle growth (Figure S7).

Random alternating copolymers of **1** and BT were prepared by electropolymerization from solutions containing a 1:50 ratio mixture of **1**:BT (e.g., 20 scans, $t = 224$ nm, $\sigma = 2.2 \times 10^{-3}$ S/cm). XPS analysis of the copolymer film reveals that the Cd:S ratio decreases as expected relative to poly-**1** (Figure 2B). Therefore, by electrocopolymerization the composition of the conducting metallopolymer film and the density of the seed points (Cd(II) ions) can be altered. These films, with more dilute concentrations of Cd(II) ions, were subjected to the same NP growth procedures. CdS NPs are formed in copoly-**1** with an increase in average NP size depending on the number of growth cycles (Figure 2D). However, the relative density of the NPs throughout the polymer film was decreased due to the decrease in the concentration of Cd(II) seed points.

The results presented herein demonstrate the first example of the seeded growth of semiconducting NPs within a conducting polymer matrix. The metal centers of a conducting metallopolymer are used as the seed point for size controlled NP growth. Size control of the NPs allows for tuning of the NP band gaps to optimize material properties. Also, the monomer can be copolymerized with BT to give films of different compositions in which NPs can be grown granting control over NP density. By growing the NPs directly in the backbone of the conducting polymer, use of surfactants is eliminated which allows for direct interaction between the two materials. The enhanced component interface should allow for increased electronic and optoelectronic material properties for use in various applications including photovoltaics, light-emitting diodes, and sensors. Future work will focus on systematic studies of NP distribution, NP growth mechanism, and electronic/optoelectronic characterization.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet http://pubs.acs.org.

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