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Facile Synthesis of Oligothiophene-Capped CdS Nanoparticles

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CdS nanoparticles functionalized by electroactive oligothiophenes, with narrow size distribution, have been prepared and characterized. The structure of the hybrid product was investigated by TEM, XRD, optical and FTIR spectroscopy. The modified nanoparticles consist of a few tens of oligothiophene units attached to the CdS core. The grafting of conjugated oligomers to nanoparticles was made possible by complexing the dangling cadmium ion on the nanoparticle surface.

Introduction

The design of nanostructured hybrid materials, with novel physical properties, has emerged as one of the most exciting areas of scientific endeavour in this decade, in which material and chemical research are playing a dominant role.[1] Nanocrystals (NCs) have a well-documented array of properties that differ from those of the corresponding bulk materials. Surface modification was shown to optimize the intrinsic optical properties, producing highly luminescent NCs, and also serves as a means of tuning their solubility. On the other hand, π-conjugated oligomers and polymers are a relatively new class of electronic materials that are revolutionizing important technological applications including large-area electronics, owing to their compatibility with low-temperature processing, the simplicity of thin-film device fabrication and the tunability of their electronic properties.[2] The richness of the synthetic organic chemistry allows the fabrication of π-conjugated materials with a degree of control unattainable with conventional inorganic semiconductors. Grafting conjugated polymers and oligomers onto the surface of nanoparticles provides a means of controlling not only the final surface functionality of the material, as one could do also with ligands, but also of introducing new optoelectronic and enhancing charge-transport properties.[3] Such physical properties have motivated many studies on π-conjugated systems and NC composites.

The encapsulation of inorganic nanoparticles by conjugated polymers has its origin in work by Greenham et al. which dates back over one decade.[4] Although much attention has been devoted to the study of the photovoltaic properties of these materials, there have been studies reporting the elaboration and the characterization of well-organized NCs embedded in conjugated polymers, as can be seen from reports of the Lahav group who studied the organization of $(Pb_{1-x}Cd_x)S$ nanoparticles within an oligo(*p*-phenyleneethylene)dicarboxylate matrix.[5] In optoelectronic devices, inorganic semiconductor NCs have been combined with π-conjugated systems in order to take advantage of the ease of processing, characteristic of many π-conjugated polymers, and their complementary properties. The inorganic semiconductor NCs have high electron affinities and the organic semiconductors show high hole mobilities, so charge transfer occurs rapidly in such systems. Photoinduced charge transfer can result in enhancement of the photoconductivity and photovoltaic effects. A major problem which arises in the fabrication of these composites is the immiscibility of the two materials due to differences in their polarities. In composites heavily loaded with NCs, phase segregation occurs even when the NCs are stabilized by hydrophilic ligands.[4]

To overcome this problem and to obtain a three-dimensional interpenetrating network of nanocomposites, many approaches have been used, in which NCs and conjugated polymers are intimately associated. In these approaches the conjugated systems are directly connected to the quantum dot surface. Milliron et al. reported the preparation of novel soluble oligothiophene-CdSe NCs, wherein electronic interaction between functional components was facilitated by attaching the binding group directly to the conjugated backbone.[6] Mutual fluorescence quenching of oligothiophenes and CdSe NCs indicates photoinduced charge transfer, which is essential for their potential utility as an active component in photovoltaic devices. Similarly, Sun et al. have

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