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Preparation and characterization of polyaniline microwires containing CdS nanoparticles

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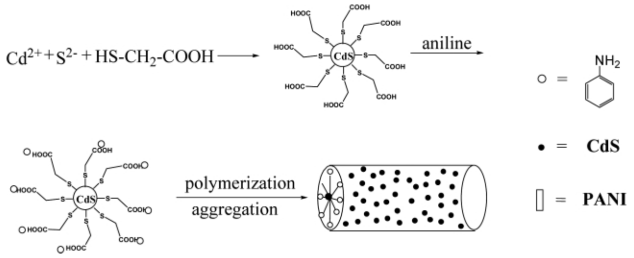
Polyaniline(PANI) microwires containing CdS nanoparticles have been prepared by introducing hydrogen bonding and/or electrostatic interaction between mercaptocarboxylic acid capped CdS nanoparticles and PANI. SEM and TEM proved them to be wire-like structures. PL spectra of the PANI/CdS complex is blue-shifted by 14 nm compared to CdS nanoparticles in *N*-methylpyrrolidinone(NMP).

Polyaniline (PANI) is one of the most frequently investigated (semi)conducting polymers for use in electronic applications.[1,2] In recent years, one-dimensional (1-D) polyaniline nanostructures, including nanowires, rods, and tubes have been studied with the expectation that such materials will possess the advantages of both low-dimensional systems and organic conductors. Examples of template method,[3] template-free method[4] and even including physical methods such as electrospinning[5] and mechanical stretching[6] have been used to make polyaniline nanofibers and nanotubes. In addition, the multifunctionalized PANI nanotubes or nanowires have also been synthesized blending with inorganic electrical, optical, and magnetic nanoparticles to form composite nanostructures.[7]

Among those inorganic nanoparticles, CdS nanoparticles have received great attention because of their unique electrical and optic properties as well as extensive application in diverse areas. We know that CdS nanoparticles are n-type semiconductors, while PANI is a p-type semiconductor. It is therefore expected that useful photoconducting nanocomposites can be created by combination PANI and CdS nanoparticles. While techniques for incorporating highly fluorescent nanocomposites in thin films are well developed,[8] stabilizing these nanocomposites in bulk polymer matrices remains a challenge. Although many papers on PANI/CdS composites have been published in the literature,[9] the main problem of incompatibility of nanoparticles with PANI matrices still remain. Recently, the way to obtain nanocrystal–polymer composites using alkylammonium surfactants[10] and using a polymerizable surfactant to transfer water-soluble nanocrystals into a radical monomer solution which is then polymerized[11] has been reported. But obviously it is not applicable to PANI. In this paper we demonstrate a method to synthesize PANI microwires containing CdS nanoparticles by introducing hydrogen bonding and/or electrostatic interaction. The synthetic strategy involves three steps: (1) For the CdS nanoparticles that are not treated with a surfactant or bonded to polymer chains and form large aggregates, mercaptocarboxylic acid was used to stabilize the CdS nanoparticles. Thus carboxy group capped CdS nanoparticles formed. (2) Physically adsorb (through hydrogen bonding and/or electrostatic interaction.) aniline molecules (An) onto carboxy group capped CdS nanoparticles to form the adduct $(An)_x/CdS$.[12] (3) Add an oxidant to polymerize the adsorbed aniline monomers to form an interpolymer complex. During the synthesis, the interpolymer complexes aggregate to form PANI–CdS microwires (Scheme 1).

Fig. 1 shows that the scanning electron microscopy (SEM) images of PANI–CdS microwires. We can see that most of the resulting PANI–CdS composites are in the form of wires with diameter about 200 nm and length several micrometers (Fig. 1a, b), It was also found that the molar ratio of CdS to aniline strongly affected the morphology of the resulting PANI–CdS composites. When the molar ratio of CdS to aniline was lower than 1 : 75, PANI/CdS composites were wires (Fig. 1a, b); however, no wire-like PANI–CdS composites were observed when the molar ratio was higher than 1 : 37.5(Fig. 1c). Moreover, the diameter of PANI–CdS wires were related to the molar ratio of CdS to aniline as shown in Fig. 1. It shows that when the molar ratio of CdS to aniline was 1 : 150, a minimum diameter (about 90 nm) for PANI–CdS is observed. TEM images proved that those wires are solid (Fig. 2). PANI–CdS microwires might be formed by an aggregated process



Scheme 1 Simplified schematic representation of PANI nanowires containing CdS by introducing hydrogen bonding and/or electrostatic interaction between mercaptocarboxylic acid capped CdS and PANI.

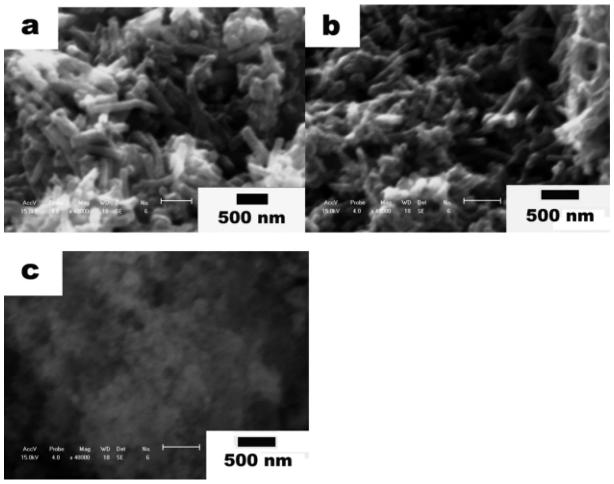


Fig. 1 SEM images of PANI/CdS nanocomposites synthesized under different molar ratio of CdS to aniline. (a) CdS : aniline = 1 : 150. (b) CdS : aniline = 1 : 75; (c) CdS : aniline = 1 : 37.5.

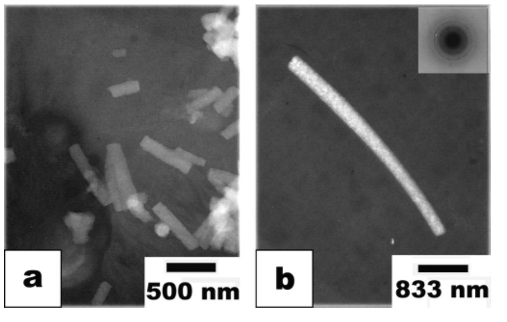


Fig. 2 TEM images of PANI/CdS synthesized under different molar ratio of CdS to aniline. (a) CdS : aniline =1 : 150, (b) CdS : aniline = 1 : 75

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associated with the formation of micelles formed by carboxy group capped CdS nanoparticles and aniline by using hydrogen bonding and/or electrostatic interaction as templates.[4] Free aniline existing in the reaction solution might diffuse into the micelles to form micelles filled with free aniline that act as templates in the formation of PANI–CdS microwires. In addition, the contents of carboxy group capped CdS nanoparticles and aniline existing in the reaction solution are affected by the molar ratio of aniline to CdS nanoparticles, resulting in variations in the morphology of the resulting PANI–CdS nanocomposites.

The molar ratio of CdS to aniline not only affects the morphology of the resulting PANI–CdS composites but also affects the dispersion of the CdS nanoparticles in PANI matrices. Fig. 2a shows that when the molar ratio of CdS to aniline was 1 : 150, no CdS particles was in the PANI wires. While as the molar ratio was 1 : 75, TEM image reveals that the CdS nanoparticles are well dispersed in PANI matrices (Fig. 2b). The electron diffraction pattern indicated that the nanocrystallites were cubic CdS with (111), (220), and (311) planes, the same as that of aqueous CdS nanoparticles,[13] which further confirms the existence of CdS nanoparticles in PANI matrices. The size and morphology of the CdS nanoparticles are similar to the appearance of the aqueous CdS nanoparticles[13] and they suggest that the PANI polymer chain prevents the CdS nanoparticles from aggregation.

The molecular structure of the resulting PANI–CdS microwires was characterized by Fourier-transform infrared (FTIR) spectroscopy and X-Ray diffraction patterns (XRD). The peak at 3240 cm^{-1} is attributed to N–H stretch vibration. The main peaks at 1583 and 1500 cm^{-1} can be assigned to the stretching vibration of a quinone and benzene rings, respectively. The peak at 1303 cm^{-1} can be assigned to the C–N stretching vibration of a secondary aromatic amine. The peak at 1146 cm^{-1} corresponds to the aromatic C–H in-plane bending mode. The out-of-palne bending of C–H in the 1,4-disubstituted benzene ring is reflected in the 827 cm^{-1} peak. The weak peak vibration absorption of Cd–S bond at 405 cm^{-1} is observed and this also convinces that the existence of CdS in the wires. Fig. 3b shows typical X-ray diffraction patterns synthesized at two different molar ratio of CdS to aniline. It shows that they are all amorphous, quite different from PANI–β-naphthalene sulfonic acid (NSA) with high crystallinity.[14] The difference in crystallinity between PANI–NSA microtubes and our PANI/CdS wires may due to the relatively small size of CdS to the contour length of PANI and the hydrogen bonding and/or electrostatic interaction between carboxy group capped CdS nanoparticles and imine group in PANI domain. CdS is tethering to the PANI chain and appears to destroy the crystallinity of the PANI domain.

UV/Vis spectra of PANI/CdS in *N*-methylpyrrolidinone (NMP) solution shows two distinctive absorption bands at 340 and 620 nm, which coincide with those of neat PANI reported earlier. The former peak was attributed to the π–π* transition in the benzenoid ring and the latter was associated with a benzenoid to quinoid excitonic transition.[15] Since the absorption of colloidal CdS overlaps with that of PANI, the peak centered around 340 nm becomes substantially broadened.

Photoluminescence spectra of CdS nanoparticles and the PANI–CdS nanowires in NMP solution are shown in Fig. 4(2). It was found that the molar ratio of CdS to aniline did not affect the photoluminescence spectra of the PANI/CdS complex. CdS nanoparticles in NMP emit blue light with a maximum intensity located at 488 nm. While the peak maximum of CdS in PANI matrices is blue-shifted by 14 nm compared to CdS nanoparticles in NMP. The blue shift in the luminescence of CdS nanoparticles might be caused by the different chemical environment.[16]

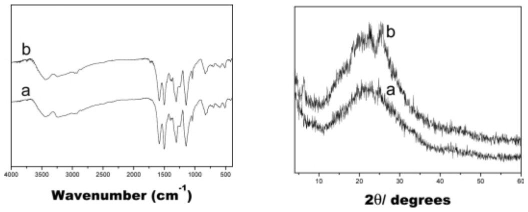
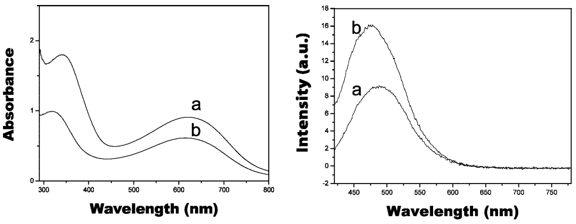


Fig. 3 IR spectrum and XRD scattering patterns of PANI/CdS complexes under different molar ratio of CdS to aniline. (a) CdS : aniline = 1 : 75, (b) CdS : aniline = 1 : 150.



(1) (2)

Fig. 4 (1) UV/Vis spectrum of PANI/CdS complexes under different molar ratios of CdS to aniline. (a) CdS : aniline = 1 : 75, (b) CdS : aniline = 1 : 150 (2) Photoluminescence spectrum of (a) CdS nanoparticles and (b) PANI/CdS complex in NMP solution.

In conclusion, semiconductor CdS nanoparticles can be dispersed in PANI microwires by using hydrogen bonding and/or electrostatic interaction between the carboxy group capped CdS nanoparticles and the polyaniline molecules. The SEM, TEM, FTIR and X-ray characterized the PANI/CdS composite microwires and proved that the CdS nanoparticles are dispersed in the PANI matrices. The photoluminescence of CdS is slightly affected by incorporation in the PANI matrix.

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