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COMMUNICATIONS

From Monomeric Nanofibers to PbS Nanoparticles/Polymer Composite Nanofibers through the Combined Use of γ-Irradiation and Gas/Solid Reaction

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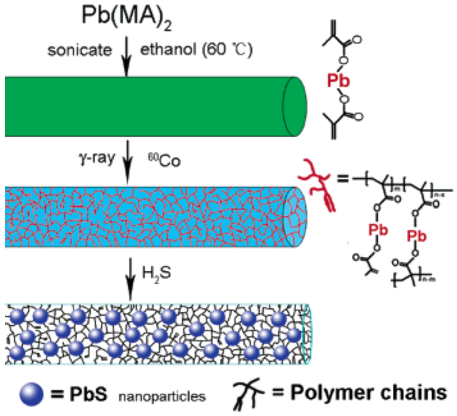
One-dimensional (1D) nanostructures, such as nanowires and nanofibers, have been intensively studied in recent years because of their intriguing properties and potential applications.[1] Much effort has been devoted to the synthesis of various 1D nanoscale materials, such as semiconductors,[2] metals,[3] oxides,[4] chalcogenides,[5] and so forth. Apart from inorganic materials, polymer nanowires or nanofibers are promising 1D nanostructured materials for various kinds of applications because of their lightweight, chemical specificities, low cost, mechanical flexibility, and scalable productions. Examples of chemical synthesis,[6] electrochemical synthesis,[7] nanolithography,[8] and even including physical methods, such as electrospinning[9] and mechanical stretching,[10] have been used to prepare polymer nanowires or nanofibers. By incorporating electrical, optic, and magnetic nanoparticles into these nanostructures, multifunctionalized composite polymer nanofibers can be synthesized.[11]

Among the inorganic nanoparticles, PbS nanoparticles have received great attention because of their unique electrical and optical properties as well as extensive applications.[12] If PbS nanoparticles/polymer composites were fabricated in the form of a 1D nanostructure, they would be found to have potential applications in electroluminescent devices, such as light-emitting diodes, and optical devices, such as optical switches, as they combined the advantages of both a low-dimensional system and PbS nanoparticles/polymer composites. So the synthesis of 1D PbS nanoparticles/polymer nanostructures is a meaningful objective.

Herein, we report for the first time on the preparation of organic metal−salt (lead dimethacrylate ($Pb(MA)_2$)) nanofibers, and that these $Pb(MA)_2$ monomeric nanofibers are successfully converted into PbS nanoparticles/polymer composite nanofibers through the combined use of γ-irradiated polymerization and gas/solid reaction. The lead ions are introduced into nanofibers before polymerization and sulfuration, which allows the generation of nanoparticles without aggregation in the polymer fibers. Since it is known that there are two C═C bonds in each $Pb(MA)_2$ molecule, cross-linked structures are produced in the polymerization procedure, which enhance the mechanical strength and the thermal and chemical stability of the polymer nanofibers.[13] In addition, the morphology of the nanofibers is kept in the process of converting the monomeric nanofibers into composite nanofibers.

Scheme 1 illustrates the synthetic pathway for the preparation of PbS nanoparticles/polymer composite nanofibers. (I) $Pb(MA)_2$ powder was dissolved in ethanol solution by heating and ultrasonication, then $Pb(MA)_2$ molecules could self-assemble into nanofibers in this system. (II) Monomeric $Pb(MA)_2$ nanofibers were polymerized and formed poly(lead dimethacrylate) ($P-Pb(MA)_2$) nanofibers by ^{60}Co γ-ray irradiation. (III) PbS nanoparticles were generated in situ by exposing the $P-Pb(MA)_2$ nanofibers to H_2S gas at room temperature.[14]

Scheme 1. Synthetic Pathway for the Preparation of PbS Nanoparticles/Polymer Composite Nanofibers



The size and morphology of the $Pb(MA)_2$ nanofibers were examined by scanning electron microscopy (SEM). As shown in Figure 1A, the $Pb(MA)_2$ products consist of nanofibers with diameters of 200−300 nm and lengths ranging from tens to hundreds of micrometers, in contrast to that of the starting material. We found that these nanofibers were stable in water and most organic solvents. However, the starting $Pb(MA)_2$ precursor can dissolve in hot water and numerous polar organic solvents. The nature of the very different properties between the $Pb(MA)_2$ powder and nanofibers is mainly attributed to the change on the crystal structure. Besides ethanol, $Pb(MA)_2$ molecules also have the tendency to self-assemble into nanofibers in many other monohydric alcohols. Although the exact mechanism for the formation of these nanostructures is still under investigation, we believe that solvent plays an important role in the process of obtaining the nanofibers.

To convert the $Pb(MA)_2$ nanofibers into $P-Pb(MA)_2$ nanofibers without altering their morphology, we employed a γ-irradiation method to polymerize the $Pb(MA)_2$ monomers. Figure 1B shows an SEM image of the sample after γ-irradiation, indicating no obvious morphological change has happened. To confirm the successful preparation of the $P-Pb(MA)_2$ nanofibers from the $Pb(MA)_2$ nanofibers, ^{13}C solid-state NMR was used to determine the structural change of the samples before and after irradiation. Compared with the ^{13}C NMR spectrum of the $Pb(MA)_2$ nanofibers, it is found that some peaks in the range of 25−60 ppm emerge in the spectrum of the nanowires after γ-irradiation. These extra peaks are attributed to the secondary carbon atoms, tertiary carbon atoms, and quaternary carbon atoms in the polymer chains, which confirm

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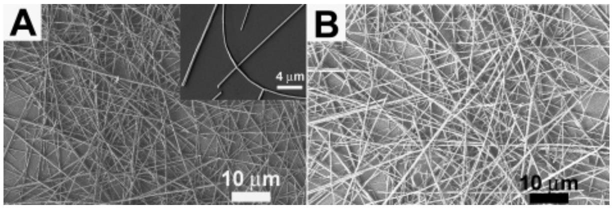

Figure 1. SEM images of $Pb(MA)_2$ (A) and $P-Pb(MA)_2$ (B) nanofibers.

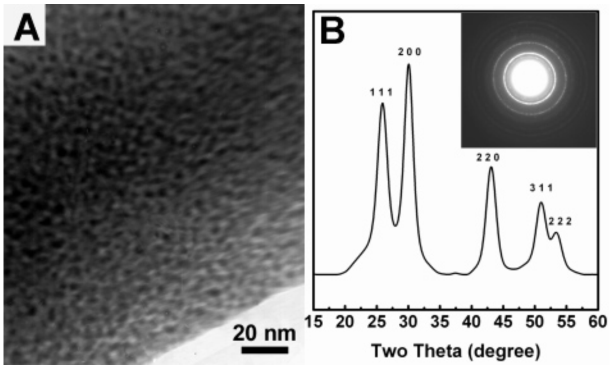

Figure 2. (A) TEM image of PbS nanoparticles/polymer composite nanofibers. (B) Powder XRD pattern recorded from the corresponding composite nanofibers. (Inset) SAED patterns of the PbS nanoparticles in the $P-Pb(MA)_2$ nanofibers.

the successful polymerization of $Pb(MA)_2$ monomers upon γ-irradiation. It should also be noted that the signals at 142.19 and 141.61 ppm, which are assigned to the carbon atoms attached directly to the (carbon−carbon) double bonds, do not disappear completely after irradiation, illustrating that the polymerized reaction is incomplete. Fourier-transform infrared (FTIR) experiments further confirmed the successful polymerization upon γ-irradiation. The intensity of the peak of the C═C bond at 1645 cm^{-1} decreases obviously after γ-irradiation. To perform quantitative analysis, the carboxylate band at 1520 cm^{-1} was selected as the internal standard peak. By comparing the intensities of the C═C bond peak before and after irradiation, we calculated that the degree of polymerization amounted to 76%. The $P-Pb(MA)_2$ nanofibers have excellent thermal stability, and we cannot see any endotherm or exotherm before 300 °C in their differential scanning calorimetry (DSC) curve. The $P-Pb(MA)_2$ nanowires are stable in most organic solvents as are the $Pb(MA)_2$ nanofibers. The polymer nanofibers are even quite stable in concentrated hydrochloric acid, in which the monomeric nanofibers can be easily dissolved.

The Pb ions (54.9 wt % in $P-Pb(MA)_2$ nanofibers) act as metal centers in the polymer chains for the further introduction of densely dispersed functional PbS nanoparticles into the polymer nanofibers. PbS nanoparticles are prepared in situ by exposing the $P-Pb(MA)_2$ nanofibers to H_2S gas at room temperature. The samples rapidly turn from white to black. In the FTIR spectrum of the $P-Pb(MA)_2$ nanofibers after reaction with H_2S gas, the presence of the expected characteristic bands at around 1700 cm^{-1} attributed to the protonated carboxylic groups indicates the successful formation of PbS nanoparticles. A transmission electron microscopy (TEM) image of the composite nanofibers is presented in Figure 2A. We can see that the dense PbS nanoparticles with diameters of approximately 4 nm are separated from each other and are well dispersed in the polymer nanofiber. This is mainly because, after reaction with H_2S, some carboxyls are still bonded to the Pb ions on the particle surface; the compact polymer networks can prevent the PbS particles from growing further after nucleation.[15] Data obtained from the selected-area electron diffraction (SAED) pattern (inset of Figure 2B) prove that the PbS nanoparticles have a cubic fcc rock-salt structure. Detailed structural analyses of the PbS nanoparticles in nanofibers were further carried out with XRD pattern (Figure 2B). All the diffraction peaks can be indexed to the cubic fcc rock-salt structure of the PbS phase with the cell parameter $a = 5.936$ Å for PbS nanoparticles (JCPDS 05-0592). Furthermore, the average size of the PbS nanoparticles calculated by the Debye−Scherrer diffraction formula ($d = k\lambda/\beta \cos \theta$) is about 4.2 nm, which is in good agreement with the result of the TEM image.

In summary, we have demonstrated a novel strategy for the facile synthesis of PbS nanoparticles/polymer composite nanofibers through combining γ-ray irradiation and gas/solid reaction. In this approach, γ-irradiation offers an ideal means to fabricate polymer nanofibers without obvious changing of the morphology and introducing any other reagent. In addition, the cross-linked structures and the bonds between the particle surface and the carboxyls not only enhance the mechanical strength and thermal and chemical stability of the composite nanofibers but also favor formation of uniform PbS nanoparticles in the entire polymer matrix. This approach could also be extended to methacrylates containing other metal ions (such as Zn^{2+}) and some rare earth metal ions (such as Eu^{3+}). We anticipate that this method would provide a platform for the fabrication of diverse and multifunctional polymer nanocomposite fibers, which would have potential applications in fabricating devices with optical, electrical, and magnetic properties.

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Supporting Information Available: Experimental procedures, DSC, NMR, FTIR, and XRD analyses, SEM and microscopy images, SAED data. This material is available free of charge via the Internet at http://pubs.acs.org.

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