

Controlled Fabrication of Cross-Linked Nanoparticles/Polymer Composite Thin Films through the Combined Use of Surface-Initiated Atom Transfer Radical Polymerization and Gas/Solid Reaction

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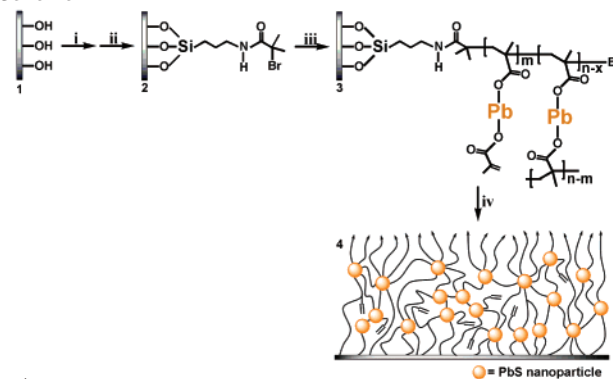
The functionality of polymer films by the incorporation of semiconductor nanoparticles is of great importance in current chemistry, physics, and materials science because of their potential applications in fabricating devices with optical, electric, and magnetic properties.¹ Nanoparticles/polymer composite thin films can usually be prepared by various useful approaches, such as the Langmuir–Blodgett method,² the layer-by-layer assembly method,³ chemical deposition,⁴ and spin coating.⁵ These approaches are often challenging, however, in terms of the stability of composite films, the high density of semiconductor nanoparticles, and the aggregation of particles in the thin films which are required for most of the applications. Alternatively, surface-initiated atom transfer radical polymerization (ATRP) is one of the most robust and versatile approaches for the synthesis of pure polymer films, due to its ease of controlling the thickness, the low polydispersity, the homogeneity, the surface density, and the composition of grafted polymer films.⁶

We have combined surface-initiated ATRP of a new monomer, lead dimethacrylate (LDMA), with a gas/solid reaction to establish a promising strategy for the controlled synthesis of cross-linked nanoparticles/polymer composite thin films. To our knowledge, this is the first time that surface-initiated ATRP has been applied to the fabrication of nanoparticles/polymer nanocomposite thin films. The polymer films are grown directly from the substrates by covalent bonds, which offers a basis for enhancing the stability of composite films. To further increase the density of PbS nanoparticles, the homopolymerization of LDMA is utilized in the synthesis of the composite films. Furthermore, bulk poly(lead dimethacrylate) (PLDMA) is difficult to manufacture mechanically into film materials because of its rigidity and its cross-link, which can be effectively overcome by our approach.

Scheme 1 illustrates the synthetic pathway for the preparation of cross-linked PbS nanoparticles/polymer composite film on a silicon wafer by surface-initiated ATRP and gas/solid reaction. Initially, the initiator monolayer was formed according to a literature procedure⁷ by the reaction with the surface Si–OH groups of a silicon wafer. Subsequently, controlled surface-initiated polymerization of LDMA was accomplished by immersing the initiator surfaces in the polymerization bath containing monomer, sacrificial initiator, catalyst, ligand, and solvent in a three-necked flask with continuous stirring under a high-purity nitrogen stream at 90 °C. Finally, nanoparticles were generated in situ by exposing the PLDMA films to H₂S gas at room temperature.

Since there are two C=C bonds in each LDMA molecule, a cross-linked PLDMA film is produced in this polymerization procedure, which also enhances mechanical strength and thermal and chemical stability.⁸ Baker and co-workers^{6c} point out that, in

Scheme 1^a



^a Conditions: (i) 3-aminopropyltriethoxysilane, toluene; (ii) 2-bromo-2-methylpropionic acid, DCC, DMAP, CH₂Cl₂; (iii) lead dimethacrylate, *p*-toluenesulfonyl chloride, Cu(I)Cl, 2,2'-bipyridine, DMF; (iv) H₂S gas.

the solution, the formation of insoluble polymers that precipitate onto the substrate results in a heterogeneous film. Although we added sacrificial initiator *p*-toluenesulfonyl chloride to our system to control the polymerization reaction, we succeeded in overcoming this problem by suspending the silicon wafer in the diluted solution under continuous stirring. Furthermore, the slow polymerization rate in the solution kept the concentration of insoluble polymers low in the whole synthetic fabrication of homogeneous, cross-linked PLDMA films so that no polymers deposited on surfaces from solution (For more details see Supporting Information).

In addition, because we added CuCl as a catalyst to this system, there exists the possibility of the coordinated competition between copper ions and lead ions, which could poison the catalyst or contaminate the resulting polymers. We found, however, that the catalyst was not poisoned: as soon as the reaction started, the solution became viscous and dark brown; during the entire polymerization process, the solution remained dark brown, indicating that the polymerization proceeded continuously. After we terminated the polymerization reaction by pouring the reaction solution into a large amount of alcohol at air ambience, its color slowly changed from dark brown to blue, suggesting the very strong binding ability of the coordination of Cu(I) ions with 2,2'-bipyridine (bpy). Furthermore, X-ray photoelectron spectroscopy (XPS) of the PLDMA films and inductively coupled plasma (ICP) analysis of the free PLDMA powders produced in the solution revealed no copper, proving that the final product was not polluted.

To test the successful preparation of the PLDMA films, XPS was used to determine the surface composition. The Pb 4f_{7/2} and 4f_{5/2} peaks are observed at 138.5 and 143.3 eV, respectively, corresponding well with the expected values for Pb bound to

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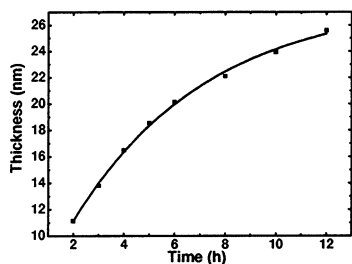


Figure 1. Plot of the PLDMA films thickness vs polymerization time.

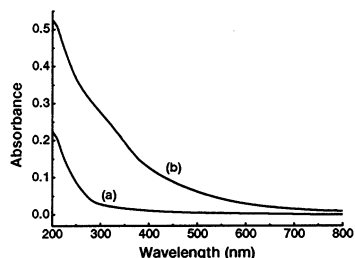


Figure 2. Absorption spectra of nanoparticles/polymer composite thin films on quartz slides before (a) and after (b) exposure to H_2S gas.

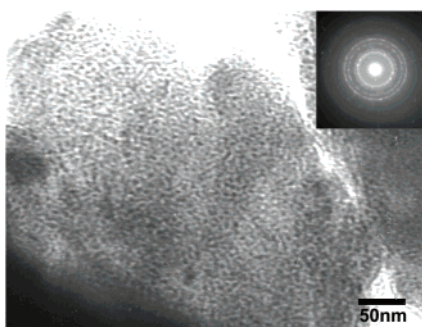


Figure 3. TEM image of PbS nanoparticles formed in the PLDMA film. (Inset) Selected area electron diffraction patterns of the PbS nanoparticles in the PLDMA film.

oxygen. Moreover, the XPS quantitative analysis for the films gives rise to a molar ratio of 1 Pb:3.8 O:9.8 C, in good agreement with the value (a molar ratio of 1 Pb:4 O:8 C) based on the monomer formula. These effects all suggest the addition of the PLDMA film to the surface of the silicon wafer and the high density of lead ions in the film.

To further demonstrate the “controlled” character of the PLDMA films, the surface-initiated ATRP of LDMA was performed on various silicon wafers removed from the same reaction system every 2 h. Atomic force microscopy (AFM) was used to determine the film thickness through imaging across the scratch boundary.⁹ Figure 1 displays the thickness of the PLDMA films plotted against the polymerization time: the film thickness increased with the polymerization time. Simultaneously, we observed the PLDMA film polymerized for 2 h at different locations by contact mode AFM: the surface roughness (RMS) was about 2.5 nm in a $10 \times 10 \mu m^2$ scanning area. These results indicate the successful growth of a homogeneous, controlled PLDMA film on the surface of silicon wafers.

Exposure of the PLDMA films to H_2S gas at room temperature is used to prepare PbS nanoparticles in situ. The films rapidly turn from colorless to light yellow. Figure 2 shows typical UV–visible absorption spectra of the PLDMA film polymerized for 10 h before (a) and after (b) reaction with H_2S gas. Compared with the absorption spectrum of the pure PLDMA film, it is found that an obvious absorption of the PLDMA film after reaction with H_2S

gas emerges in the visible region, confirming the formation of PbS nanoparticles. The corresponding transmission electron microscopy (TEM) image of the fragment of the composite film removed from the quartz slide is presented in Figure 3. Overall, the dense PbS nanoparticles are roughly spherical in shape and are separated from each other, each having a diameter of approximately 4 nm. Since some carboxyls are still bonded to the Pb ions on the particle surface after reacting with H_2S , the compact polymer networks can prevent the PbS particles from growing further after nucleation, resulting in their small size and uniform dispersion.^{2,8} Furthermore, the results of contact mode AFM show that before and after reaction with H_2S the surface roughness of the composite films (RMS was ca. 2.8 nm in a $10 \times 10 \mu m^2$ scanning area) is not obviously changed, indicating that they are still homogeneous.

This novel strategy for the facile, controlled formation of cross-linked nanoparticles/polymer composite thin films through combining surface-initiated ATRP and gas/solid reaction exhibits a key feature: the introduction of Pb ions through the extension of surface-initiated ATRP to the monomers containing metal ions, which provides an opportunity to generate nanoparticles in the polymer films. Since surface-initiated ATRP can be applied not only to homopolymerization but also to block or random copolymerization of a wide range of monomers containing metal ions, such as Zn^{2+} , Cd^{2+} and some rare earth metal ions, we anticipate that this technique can be exploited for the fabrication of multifunctional and multilayered polymer nanocomposite films. Extension to other living and controlled polymerization systems will open up a wider route to functionalize surfaces for promoting the fabrication of new types of optical, electric, and magnetic devices.

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Supporting Information Available: Experimental procedures, the characterization of LDMA, XPS curve, and the TEM images at higher magnification (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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