Size-Selective Synthesis of CdS Nanoparticles on Polyethylene Films

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Size-selective CdS nanoparticles were synthesized on polyethylene (PE) films with surface-grafted poly(acrylic acid) (PAAc) chains by the stepwise immersion of the films into aqueous solutions of cadmium acetate and sodium sulfide. By varying the surface density of the PAAc chains, the soaking time, and the number of cycles, it was possible to control the degree of coverage of the film and the size of the CdS nanoparticles.

The synthesis and characterization of semiconductor nanoparticles have been under intensive investigation over the past several years, owing to their size-dependent nonlinear optical, physical, and electronic properties.[1–4] One of the most recent research goals is directed designing and assembling semiconductor nanoparticle films. These nanostructured materials have many potential applications as photocatalysts in photoreactions,[5] electro-luminescent devices,[6] and photoelectrodes.[7]

Polymers are able to passivate various materials and prevent particle agglomeration, while maintaining a good spatial dispersion of the particles. Polymers are also expected to provide good mechanical properties, conferring high kinetic stability to nanoparticles. Polymers have already been employed as steric stabilizers, and as a means of controlling nanoparticle growth and their spatial arrangement in films. Up to now, most of the research has focused on the formation of semiconductor nanoparticles in a polymer matrix, by taking advantage of the microphase separation in a polymer blend or copolymer films.[8,9] The polymer generally acts as an encapsulant for the particles, and is also capable of controlling the particle size by providing the slow release of group 12 precursors and by binding to surface metal atoms to terminate particle growth. We report here a novel alternate soaking process to prepare size-selective CdS nanoparticles on polyethylene (PE) films. The degree of coverage of the PE films and the CdS particle size can be easily controlled by changing the surface density of the grafted poly(acrylic acid) (PAAc), the soaking time and the number of cycles.

A PE film with PAAc chains grafted to the surface (PAAc-*g*-PE) was prepared by sequential coronal discharge and graft polymerization steps.[10] The coronal discharge treatment was performed on PE films under 17 kV gap voltage for 2 min in dry air. The corona-treated PE films were then immersed in a 10 wt% aqueous solution of acrylic acid in a glass ampoule. Each batch of graft polymerization was vigorously degassed, sealed off, and then placed in an incubator at 60 °C for 2–8 h. The amount of grafted PAAc on the surface of the PAAc-*g*-PE film, which was determined by gravimetry, depended on the polymerization time. Three PAAc-*g*-PE films with different PAAc surface densities of 50, 180, and 300 μg cm^{-2} were prepared.

CdS nanoparticles on the PAAc-*g*-PE film were synthesized using an alternate soaking process, which is analogous to the method used in hydroxyapatite formation.[11] The PAAc-*g*-PE film was immersed in a 4 mM cadmium acetate ($Cd(OAc)_2$) aqueous solution for an adequate time period (from 1 min to 10 min). The film was then taken out and rinsed with distilled water thoroughly. The film was next immersed in a 4 mM sodium sulfide aqueous solution for the same time, followed by rinsing with distilled water. This stepwise cycle was repeated to increase the particle size.

Figure 1 shows the FTIR spectra of an untreated PE film, and PAAc-*g*-PE films with and without the loading of Cd(II) ions or CdS nanoparticles. The appearance of a peak at 1710 cm^{-1}, assigned to C=O stretching vibration, in the spectrum of the PAAc-*g*-PE film (Figure 1b) confirmed the grafting of the PAAc layer onto the corona-treated PE surface. The immersion of the PAAc-*g*-PE film into a $Cd(OAc)_2$ solution leads to the conversion of the carboxylic acid groups to a cadmium carboxylate form. A new peak at 1550 cm^{-1}, which was attributed to the asymmetric stretch of the carboxylate anions in CO_2, was clearly observed in the spectrum of the cadmium-loaded PAAc-*g*-PE film (PAAc-*g*-PE-Cd(II)). The PAAc-*g*-PE-Cd(II) film was colorless and transparent. The CdS nanoparticles were generated on the film surface following the immersion of the PAAc-*g*-PE-Cd(II) film into the Na_2S solution. The PAAc-*g*-PE film with the CdS nanoparticles on their surface (PAAc-*g*-PE-CdS) was light yellow. Owing to the presence of the CdS particles on the film, the UV–vis spectrum of PAAc-*g*-PE-CdS showed an absorption onset at 460 nm. This significant blue shift of the absorption onset with respect to bulk CdS (520 nm) can be attributed to quantum-size effects, corresponding to an

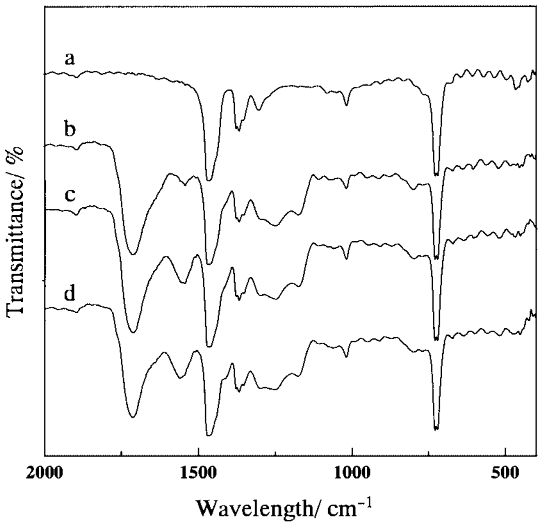

Figure 1. FTIR spectra of PE (a), PAAc-*g*-PE (b), PAAc-*g*-PE-Cd(II) (c) and PAAc-*g*-PE-CdS (d) films. Conditions: grated PAAc, 300 μg cm^{-2}; soaking time, 1 min; cycle number, 1.

average particle diameter of ~3 nm.[12] One would expect that the sodium would essentially displace all of the Cd(II) ions bound to the carboxylic acid groups upon the formation of the CdS nanoparticles. The increase in the intensity of the peak at 1550 cm^{-1} of the PAAc-*g*-PE-CdS film may be due to the formation of more carboxylate anions from the carboxylic acid groups by sodium. The shoulder at 1415 cm^{-1} assigned to the CO_2 symmetric stretch, was also observed in the spectrum of the PAAc-*g*-PE-CdS film. The untreated and corona-treated PE films were also immersed in the $Cd(OAc)_2$ and Na_2S solutions successively, and yet CdS nanoparticles did not form on their surfaces. These data indicate that strong ion–ion interactions between the carboxylate groups of the grafted PAAc and Cd(II) ions are necessary for the loading of the Cd(II), and for the formation of CdS nanoparticles on the surface. Moreover, the surface density of PAAc has a profound influence over the uptake of cadmium and the control of the size of the CdS nanoparticles.

In Figure 2, the amount of CdS formed on the surface is given as a function of the cycle number for three kinds of PAAc-*g*-PE films. It is very clear that the formation of CdS is highly dependent on the reaction conditions, such as the surface density of the grafted PAAc and the number of cycles. Almost complete CdS generation is achieved after 3 cycles for a PAAc film with a surface density of 50 μg cm^{-2}, with the final amount of CdS being only 10 μg cm^{-2}. Under the same conditions, however, the degree of CdS surface coverage increases to 173 μg cm^{-2} after 10 cycles for a film with 300 μg cm^{-2} grafted PAAc. By varying the concentrations of the $Cd(OAc)_2$ and Na_2S solutions and the soaking time, one can vary the rate of CdS formation and the particle size as well.

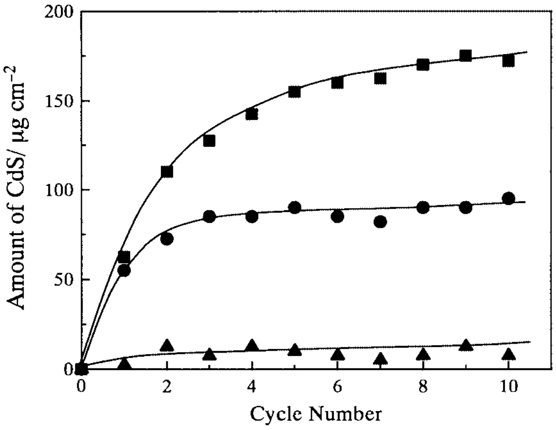

Figure 2. Plots of the amount of CdS formed on PAAc-*g*-PE films at different PAAc surface densities of 50 (▲), 180 (●), and 300 μg cm^{-2} (■), as a function of the cycle number. Conditions: soaking time, 1 min.

Tapping-mode AFM images of CdS particles on PAAc-*g*-PE films with grafted PAAc surface densities of 50 and 300 μg cm^{-2} are shown in Figure 3. After 10 cycles, smaller CdS particles are generated on the surface of the PAAc-*g*-PE film at 50 μg cm^{-2} grafted PAAc, in a sparsely-packed arrangement. Based on the corresponding cross sections, the particle size as determined by the step height corresponds to approximately 3.3 ± 0.2 nm. The film with a high PAAc surface density of 300 μg cm^{-2} exhibited a heavy coverage of CdS particles, as shown in Figure 3b. The cross sections showed particles roughly circular in shape, with a height of 5.3 ± 0.3 nm.

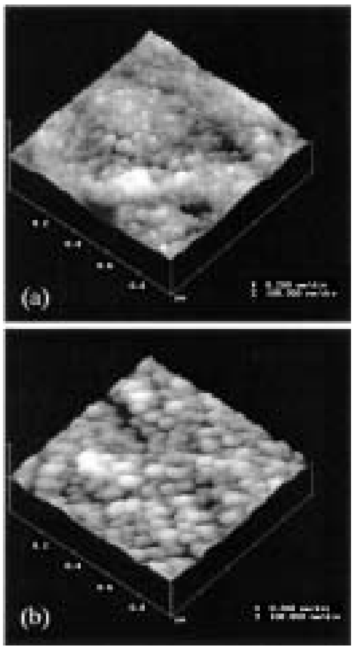

Figure 3. Tapping-mode AFM images of CdS nanoparticles on PAAc-*g*-PE films at different PAAc surface densities of 50 (a) and 300 μg cm^{-2} (b). Conditions: soaking time, 1 min., cycle number, 10.

In conclusion, the formation and growth of CdS nanoparticles on polyethylene films were successfully performed by the combined use of surface graft polymerization and an alternate soaking process. Using this system, the degree of coverage of the PE films and the size of the CdS nanoparticles can be controlled by varying the surface density of poly(acrylic acid), the soaking time, and the number of cycles. The ease and flexibility of the present approach may enable the facile production of doped or mixed semiconductor nanoparticles while controlling their sizes and doping levels. This increases the potential applications of these nanoparticles in various devices.

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