

POLYMER-BASED COMPOSITE MATERIALS IN THE SHAPE OF COLLOIDS, FIBERS, AND THIN FILMS

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Introduction

Hybridizing organic or inorganic nanostructured materials with polymers is a good strategy to provide multi functions with a single material or to obtain new properties that are not available from single-component materials. Nano-sized or micro-sized polymer-based hybrid materials embedding nanostructured organic or inorganic materials have been long studied. Recently we reported the formation of composite materials such as a microscale polymeric colloids or fibers containing with nanoparticles of polymers or ceramics. And we published polymer thin films in which semiconductor nanowires grow *in-situ* and form a network structure. In this talk, structural control and compositional variation of the hybrid materials in the form of colloids, fibers, and thin films.

Results and Discussion

Composite formation of colloids and fibers has been carried out by using electrohydrodynamics, including electrospinning and electrospraying, which is a good way to produce uniform-sized colloids and fibers in a continuous process. The dimension can be controlled from tens of nanometers to a few micrometers. The structure of the colloids and nanofibers from electrohydrodynamics has been diversified according to the uses.

Especially, core-shell structure and hybridization with functional nanomaterials are fascinating due to their possible uses in drug-delivery systems, multifunctional scaffolds, organic/inorganic hybrids with new functions, and highly sensitive gas- or bio-sensors.

Figure 1 shows SEM images (A-C) and a confocal laser scanning microscope image (D) of the PS@PCL core-shell microcapsules. The PCL solution was fed by 6 $\mu\text{L}/\text{min}$ through the inner nozzle and the PS solution was supplied by 3 $\mu\text{L}/\text{min}$ through the outer nozzle. The voltage was fixed at 10.5 kV to form a cone-jet mode. In order to optically monitor the location of the polymer molecules, a green dye (coumarin 6) was dissolved in PS solution and a red dye (rhodamine B) was mixed with PCL solution. The concentration of rhodamine B and coumarin 6 in both solutions was kept 0.018 wt% in chloroform. Figure 1A shows the as-produced spherical colloids with good size uniformity. The diameter of the colloids was about 3 μm . The higher magnification of the colloids, as displayed in Figure 1B, revealed the embossing pattern like a golf ball on the colloidal surface.

The surface morphology is attributed to the decreased solubility of PCL in chloroform as the concentration increased due to the fast evaporation of the solvent.¹⁸ In the late stage of the solvent evaporation, the polymer molecules crystallize and thus the solvent is localized at the surface of the microparticle. The evaporation of the solvent leaves the humps on the colloidal surface. The same morphology has been reported in PCL particles obtained by electrospraying chloroform solutions.^{18b} On the other hand, the golf ball shape was not observed when PCL was highly miscible with solvents.^{18a} The structure of the core and shell of the colloids was examined by dissolving PCL with a mixture solvent of 2,2,2-trifluoroethanol (TFE)/deionized water (1:2, v/v) for 60 min. PCL was readily dissolved within a few min in the mixture solvent. Figure 1C shows the crosslinked PS particles after dissolving PCL. They still maintained the spherical shape and the size was reduced about 18 % from the as-produced colloids, indicating the core-shell structure of electrosprayed colloids. The golf ball structure on the surface was not observed in the PS core, which informs that the two solutions were well separated and the interface was sharply maintained during the electrospraying. The core-shell structure of the colloids was optically confirmed as shown in Figure 1D. The simultaneous excitation of the dyes at 488 nm and 543 nm revealed that the green dye was confined in the core and the red dye was localized in the shell. The position of the dyes reflects the location of the polymer molecules, which clarifies the core-shell structure of the colloids. Even when the dyes appear mixed each other, the polymer molecules are still probable to be separated because the small dye molecules can diffuse faster through the interface between the polymer solutions [1].

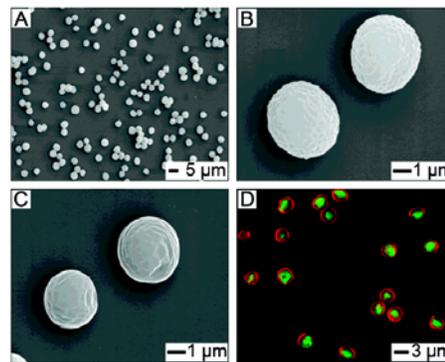


Fig. 1 SEM images (A-C) and confocal laser scanning microscope image (D) of the microcapsules prepared

d by co-axial electrospinning.

In Figure 2 using electrospinning process, crosslinked PMMA colloids were dispersed in a dense polyvinylacetate (PVAc)/titanium isopropoxide solution in DMF and in a concentrated PAN solution in DMF for their electrospun fibers. Figure 1 shows the electrospun nanofibers wrapping the PMMA colloids. Figure 2A provides the result of PVAc/TiO_x composite nanofibers produced from PVAc/Ti(OiPr)₄ mixture solution in DMF including PMMA colloids. The sol-gel process of Ti(OiPr)₄ during the electrospinning vitrifies the extended polymer jet faster than without Ti(OiPr)₄. All the PMMA colloids were wrapped by the composite without being located at the air interface. Since the diameter of the fibers was comparable with the colloidal size the undulating morphology of the nanofibers is natural. Figure 2B and 2C display PAN nanofibers embedding small amount of PMMA colloids (B) and large amount of colloids (C). Small amount of PMMA colloids formed a string and large amount of the colloids assembled to make continuous colloidal packing. In both cases, the PMMA colloids were completely wrapped by PAN which tells good affinity of the swollen PMMA colloids to concentrated PAN solution. Fibers thicker than 1 μm had smooth surfaces without noticeable roughness, indicating the PMMA colloids were located in the core and fully surrounded by PAN. When the PAN fibers were thermally stabilized at 400°C the PMMA colloids were removed and left hollow fibers as shown in Figure 2D, which obviously verifies the core-sheath structure of the as-spun fibers [2].

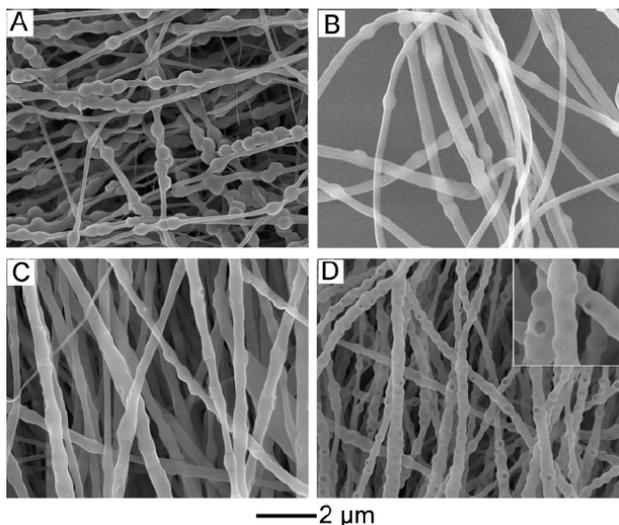


Fig. 2 SEM images of nanofibers wrapping crosslinked PMMA colloids: (A) PVAc/TiO_x fibers with small amount of PMMA colloids, (B) PAN fibers with small amount of PMMA colloids, (C) PAN fibers with large amount of PMMA colloids, (D) PAN fibers after thermal annealing.

Figure 3 shows the growth of the Se nanowires in a PCL thin film. A drop of uniform *a*-Se colloidal suspension in ethanol was placed on a 300 nm-thick PCL film and dried in air. The sample was annealed at 70°C in a heating cell.

Figure 3A, 3B, and 3C demonstrate the nanowire growth in 5 min, 2 h, and 10 h after the annealing. The colloids sank in the polymer thin films because the annealing temperature was higher than the melting temperature of PCL (~60°C). Surprisingly, many nanowires were already observed to grow in 5 min. Figure 3C shows the nanowires after complete dissolution of *a*-Se colloids. For the clear view of the nanowires, the picture was taken after removing PCL with chloroform. Dense population of nanowires could be obtained starting with more colloids as displayed in Figure 3D. Since all the nanowires should grow within the polymer thin films, the growing nanowires met the others and formed a chemical junction, finally producing 2D network structure as shown in the magnified inset. The nanowires were a single crystalline characterized by TEM and diffraction studies [3].

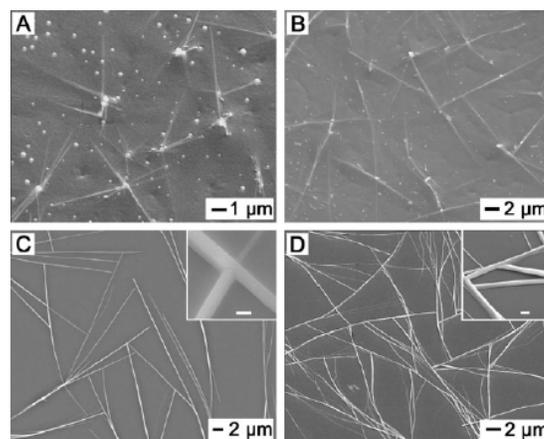


Fig. 3 Transformation of *a*-Se colloids on poly(ε-caprolactone) (PCL) into *t*-Se nanowires according to the annealing time: (A) 5 min, (B) 2 h, (C) 10 h. (D) Dense nanowires from large amount of *a*-Se colloids.

Conclusion

Polymer-based composite materials in the form of colloids and fibers were prepared by electrohydrodynamics. The in-situ growth of semiconducting nanowires in polymer thin films can provide new aspect of nanowire synthesis.

References

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