One-Step Vapor Deposition Polymerization for Polymer Encapsulated Inorganic Nanoparticles

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Abstract

We demonstrated VDP methodology as a new strategy to fabricate the various inorganic colloid–vinyl polymer core–shell nanostructures. This conceptually new and simple process allowed the formation of the highly uniform PMMA shells on the silica and titania nanoparticle surfaces. The shell thickness could be controlled from ca. 2.5 to 40 nm with changing the monomer/inorganic particle weight ratio. In addition, carbon capsules derived from the silica–PDVB nanoparticles realized the encapsulation and selective release property of pyrene in a different environment and can be applied as a novel nanohybrid material in optical and electronic devices. This novel approach might be expanded to allow the preparation of the various core–shell structures, which include metallic, inorganic, and polymer materials.

1. Introduction

The enhanced stability and tunable surface properties derived from the selective polymer coating of inorganic colloids have expedited the development of a variety of methods to fabricate inorganic–polymer core–shell nanostructures.[1] To date, the preparation of polymer–coated inorganic nanoparticles has largely depended upon the solution–based approaches, which include emulsion or dispersion polymerization[2] and adsorption of polymers onto the inorganic particles.[3] However, these methods have often been limited by the large particle–particle aggregations, the formation of the isolated polymer particles from the inorganic colloids, or the requirement for the complicated multistep procedure. Therefore, it is desirable to develop a simple and reliable method to fabricate inorganic colloid–polymer nanoparticles with the well–defined core–shell morphology. Vapor deposition techniques can provide the creation of a smoother and more uniform polymer layer by the consecutive polymerization of vaporized monomer under a vacuum onto the desired surface. While vapor deposition polymerization (VDP) has been performed on the metal and semiconductor with macroscopically flat surfaces by radiation–induced polymerization,[4] considerably less attention has been paid to the coating of inorganic colloids with polymers. Herein we report a facile route for the fabrication of various inorganic colloid–vinyl polymer core–shell nanostructures by one–step VDP. Having demonstrated the feasibility of the above approach, we were prompted to apply it to encapsulate silica and titania nanoparticles with poly(methyl methacrylate) (PMMA) and polydivinylbenzene (PDVB).
parameters to simplify the reaction system such as the reaction time of 24 h and the reaction temperature of 70 °C. The shell thickness could be tuned by varying the MMA/silica weight ratio. As the MMA/silica weight ratio increased, the polymer shell thickness increased gradually. The PMMA shell thickness of about 25 nm was obtained with an MMA/silica weight ratio of 0.75 (Figure 1e) and increased up to about 39 nm at the weight ratio of 1.5 (Figure 1f). VDP provided a uniform PMMA shell regardless of the increment in shell thickness.

Figure 1. SEM images of a) 200 nm silica particles as synthesized and b) silica particles coated with PMMA. TEM images of c) 200 nm silica particle and d) silica–PMMA core–shell nanoparticles with the various shell thickness (MMA/silica weight ratio of 0.25 in d), 0.75 in e), and 1.5 in f).

Titania is well-known for its use in optical and photocatalytic applications. In our experiment, titania nanoparticles of irregular shapes were encapsulated with a PMMA shell to improve their stability and dispersibility for a variety of applications. The representative TEM micrograph of titania–PMMA nanoparticles (MMA/titania weight ratio of 1.5; Figure 2) proved that 200 nm titania nanoparticles were successfully coated with a PMMA shell, and the shell had the same morphology as that of the titania nanoparticles. The shell thickness ranged from 10 to 20 nm. This result suggests that VDP is also available for the encapsulation of the irregularly shaped inorganic particles as well as spherical silica particles.

Figure 2. TEM image of titania–PMMA core–shell nanoparticle. The titania nanoparticle was completely encapsulated with the PMMA layer.

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2. Experimental

Uniform silica spheres of about 200 nm were synthesized according to the method of Stöber et al.[5] Ludox TM–40 solution (Aldrich) was used as a source of 25 nm silica nanoparticle. Titanium dioxide (Junsei Chemical) was chosen as 200 nm titania nanoparticles. Silica and titania nanoparticles (2g) were treated with chlorodimethylvinylsilane (CDVS, 0.2mL) in a mixture solution of ethanol (75 mL) and water (15 mL) overnight, and then dried at 50 °C. A reactor was designed for VDP by connecting two modified round bottom flasks as reaction chambers. The total volume of the reactor was about 200 mL. 0.3 g of CDVS–treated inorganic particle and 0.01 g of a radical initiator was added to the one chamber of the reactor. 2,2′-azobis-(2- (2-imidazolin-2-yl)-propane dihydrochloride or 2,2′-azobisisobutyronitrile (AIBN) was used as a radical initiator. The reactor was evacuated to about $10^{-1}$ torr at room temperature, and then the vacuum valve was closed to obtain the system in a static vacuum. Liquid monomer was introduced into the other chamber of the reactor by injection (0.075–0.6 mL). The monomer was completely vaporized by heating at 70 °C. The vapor deposition polymerization proceeded with magnetic stirring of the inorganic particles in an atmosphere of the monomer vapor for 24 h. After the polymerization, the residual monomer vapor was removed from the reactor by venting and the final product of inorganic–polymer core–shell nanoparticle was obtained.

3. Result and Discussion

A scanning electron microscopy (SEM) image shows 200 nm spherical silica particles (Figure 1a). PMMA–coated silica nanoparticles obtained with an MMA/silica weight ratio of 0.25 are shown in Figure 1b. These nanoparticles have a morphology similar to silica particles, thus indicating uniform PMMA layers on the silica particle surfaces. In transmission electron microscopy (TEM) images, the PMMA–coated silica particles have a uniform and remarkably thin PMMA layer (shell thickness 8 nm) on their outer surface (Figure 1c and 1d). In addition, we did not observe the polymer particle that had not encapsulated the inorganic particle in TEM investigation. The formation of the highly uniform PMMA layer and the absence of polymer particles might result from the nature of the VDP and the high specific surface area of inorganic nanoparticles to be encapsulated. The inorganic nanoparticles provide the considerably large surfaces even with a small number of particles compared to semiconductor or metallic flat surfaces, on which the most of monomers can adsorb from the vapor phase. Under these conditions, polymerization of the monomers proceeds exclusively by growing polymer radicals confined in the adsorbed layers and is not significantly affected by polymerization in the gas phase.[6] The growth of the polymer layer in the particle surfaces leads to the formation of the highly uniform polymer shell. The degree of polymerization depended on the reaction time, the initiators, and the reaction temperature. In the control of the thickness of the polymer, we selected the loading amount of the monomer as a control parameter and fixed other reaction
4. Conclusion

In summary we have demonstrated the VDP methodology as a new strategy to fabricate various inorganic colloid–vinyl polymer core–shell nanostructures. This conceptually new and simple process has allowed the formation of highly uniform PMMA shells on silica and titania nanoparticle surfaces. The shell thickness could be controlled from about 2.5 to 40 nm by changing the monomer/inorganic particle weight ratio. This novel approach might be expanded to allow the preparation of the various core–shell structures, which include metallic, inorganic, and polymeric materials.

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