

Preparation of polystyrene/SiO₂ nanocomposites by surface-initiated nitroxide-mediated radical polymerization

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Abstract Polystyrene/SiO₂ composite nanoparticles (PS-g-Silica) were prepared by an *in-situ* surface-initiated nitroxide-mediated radical polymerization. After SiO₂ nanoparticles were treated by thionyl chloride (SOCl₂), peroxide initiation groups were immobilized on their surfaces through a reaction with tertiary butyl hydroperoxide (TBHP). Then surface nitroxide-mediated radical polymerization was initiated and polystyrene was grafted on the surface of SiO₂ particles. Composite nanoparticles were characterized by IR spectra, transmission electron microscopy (TEM), atomic force microscopy (AFM) and thermogravimetry (TGA) and the results indicated that the surface-initiated nitroxide-mediated radical polymerization could be successfully used to synthesize well-dispersive PS/SiO₂ nanocomposites.

Keywords: surface-initiated nitroxide-mediated radical polymerization, nanocomposites, SiO₂ nanoparticles, grafted modification, polystyrene.

As nanoscopic science, technology, and engineering have been rapidly developed in recent years, nanomaterials have attracted widespread attention for their specific capability in the optics, electrics, calorifics, magnetics, catalysis and mechanics because of their high activity, good selectivity, tremendous specific surface and small size. Especially, silica nanoparticles occupy a prominent position in scientific research, because of their easy preparation and wide applications in various

industrial fields, such as catalysis, pigments, pharmacy, electronic and thin film substrates, electronic and thermal insulators, and humidity sensors. However, their agglomeration and incompatibility with the organic matrix are impeding problems, which limit their efficient use. As a kind of composite material prepared from organic polymers and inorganic compounds, organic-inorganic hybrids have attracted much attention in recent years because they have a controllable combination of the properties of both polymers and inorganic compounds. Grafting of polymers onto inorganic particles such as silica can improve effectively the surface properties because the grafted polymer chains on the surface interfere with the aggregation of these particles and increase the affinity of the surface for solvent and polymer matrix^[1,2]. In recent years, as an important model surface grafting technique, surface-initiated polymerization (SIP)^[3] has been successfully applied in modifying inorganic surfaces with polymers, and preparing of well-defined, polymer-grafted silica particles. Tsubokawa *et al.*^[4] reported the radical grafting polymerization of propylene monomers initiated by the azo groups of polymer chains grafted onto the nanometric silica surface. Fukuda and co-workers^[5] studied the mechanism and kinetics of reversible addition-fragmentation chain transfer reaction (RAFT)-mediated graft polymerization of styrene initiated on a silica particle. Advincula *et al.*^[6] investigated the formation of covalently attached polystyrene on silica nanoparticle surfaces by living anionic surface-initiated polymerization (LASIP). The use of surface-initiated atom transfer radical polymerization (ATRP) for polymerizing polystyrene on silica nanoparticles was also reported^[7,8]. In the above reports, the use of specific silane coupling agent is very important to modify inorganic surfaces when the initiator was anchored onto silica nanoparticle. But the difficult synthesis of those specific silane coupling agents limited their industrialized manufacture and applications.

Herein, with the common industrialized reagent, thionyl chloride (SOCl₂) and tertiary butyl hydroperoxide (TBHP), replacing the specific silane coupling agent, a new structurally well-defined, polymer-grafted hybrid nanocomposite was prepared by introducing peroxide groups onto the surface of ultrafine silica and employing surface-initiated nitroxide-mediated radical polymerization. After SiO₂ nanoparticles were treated by SOCl₂, peroxide initiation groups were immobilized on their surfaces through a reaction with TBHP. 2,2,6,6-

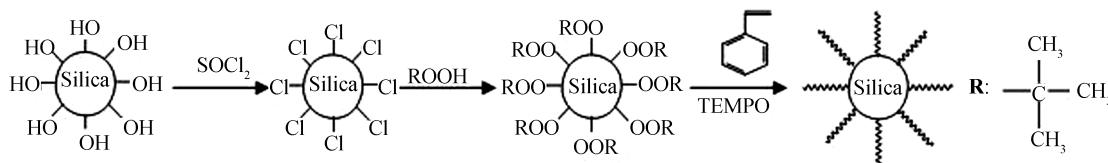


Fig. 1. Synthetic steps for forming PS/SiO₂ hybrid nanocomposites.

tetramethylpiperidinoxy (TEMPO), and polystyrene (PS) were grafted onto silica by nitroxide-mediated living free radical polymerization. Fig. 1 shows the synthetic steps for forming organic-inorganic hybrid nanocomposites.

The dried ultrafine silica 8.0 g was added to a mixture of 75 mL chloroform and 75 mL SOCl₂ and refluxed for 36 h under stirring. After the reaction, unreacted SOCl₂ and chloroform were removed by distillation. Then dried in vacuum, 5.0 g of this chloride-functionalized silica was transferred to a flask, and mixed with 65 mL 1,4-dioxin, 15 mL TBHP, and 0.25 g NaHCO₃. The mixture was stirred under nitrogen at room temperature for 12 h, and then the peroxidated particles were washed with methanol and dried at room temperature under vacuum. Polymerization was carried out as follows: 1.0 g of peroxide-functionalized silica and 20 mL of xylene were put into a dry flask equipped with a magnetic stirrer. The mixture was ultrasonicated for 30 min. Then 0.063 g of TEMPO and 8 mL of styrene were added. The flask was subsequently evacuated and flushed with nitrogen three times. The graft polymerization was carried out at 130°C for 72 h with stirring in nitrogen. After polymerization, the viscous mixture was diluted with THF and the polymer-grafted silica nanocomposites were separated by centrifugation. The product was washed several times with THF and then dried in vacuum. Before analysis, the PS modified silica was diluted with THF and extracted for 24 h using a Soxhlet extraction apparatus to remove any unbound polymers from the silica surfaces.

Fig. 2 shows the FT-IR spectra of the untreated silica nanoparticles (1) and PS/SiO₂ hybrid nanocomposites (2). The adsorption peaks at 1090 and 464 cm⁻¹ were attributed to Si-O-Si symmetric stretching of silica. The spectrum for PS/SiO₂ hybrid nanocomposites was characterized by the appearance of some new adsorption peaks at 700, 1453, 1490 and 2800–3100 cm⁻¹. It indicated that the polystyrene had been grafted onto the surfaces of the silica nanoparticles successfully.

The thermal stability of untreated silica nanoparticles

(1) and PS/SiO₂ hybrid nanocomposites (3) was investigated by the TGA analyses (Fig. 3). As expected, the inorganic silicate showed a very high thermal stability at the temperature > 100°C. The weight loss of the bare silica nanoparticles at the temperature < 100°C was due to the desorption of some gases and water adsorbed from the air. The temperature of the weight loss of PS/SiO₂ hybrid nanocomposites (Fig. 3-3) was consistent with the decomposition of the PS (Fig. 3-2) and they were stable at the temperature < 400°C. This clearly indicates the attachment of the PS to the SiO₂

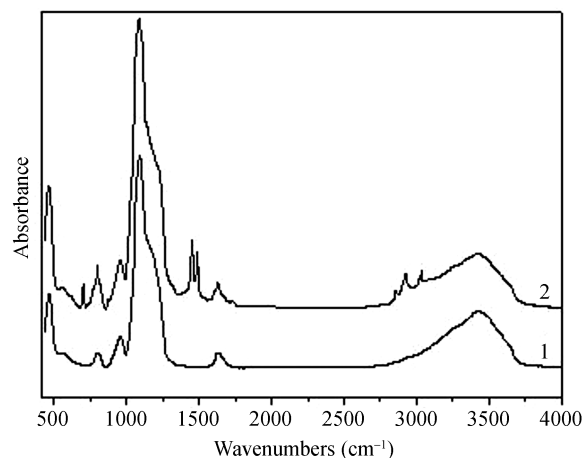


Fig. 2. FT-IR spectra of the nanometric silica (1) and PS/SiO₂ hybrid nanocomposites (2).

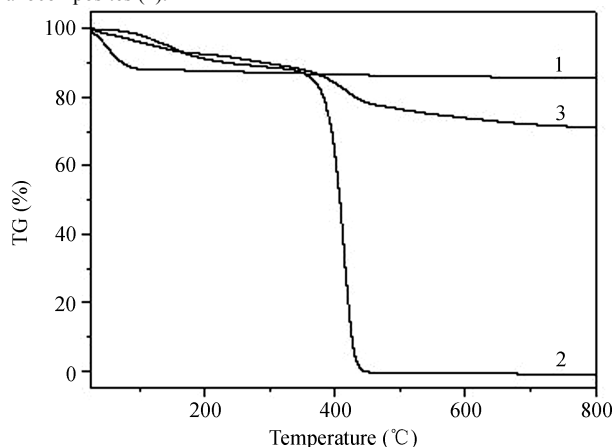


Fig. 3. TGA curves of the nanometer silica (1), PS (2) and PS/SiO₂ hybrid nanocomposites (3).

BRIEF COMMUNICATION

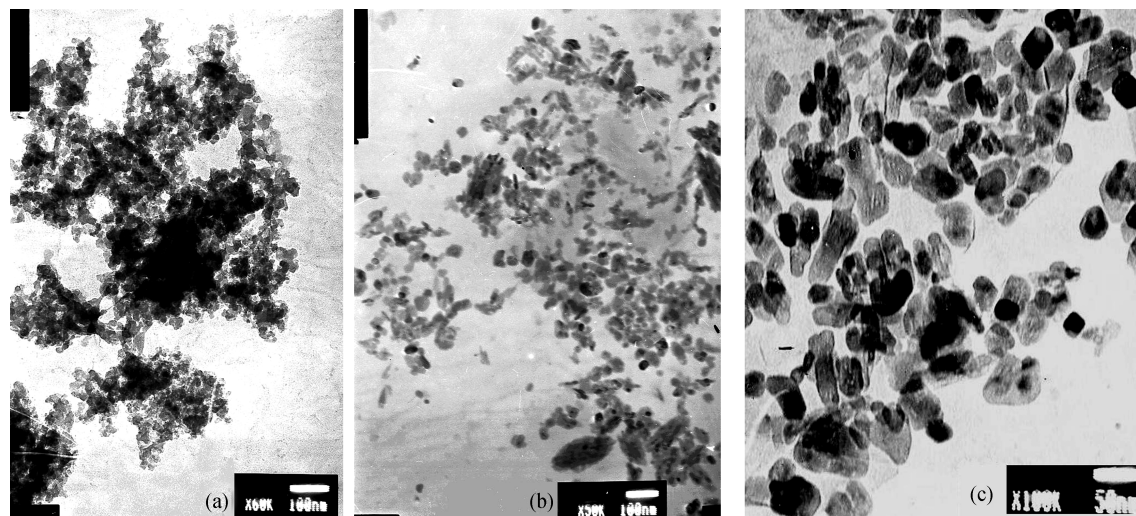


Fig. 4. TEM image of the nanometer silica (a) and PS/SiO₂ hybrid nanocomposites (b), (c).

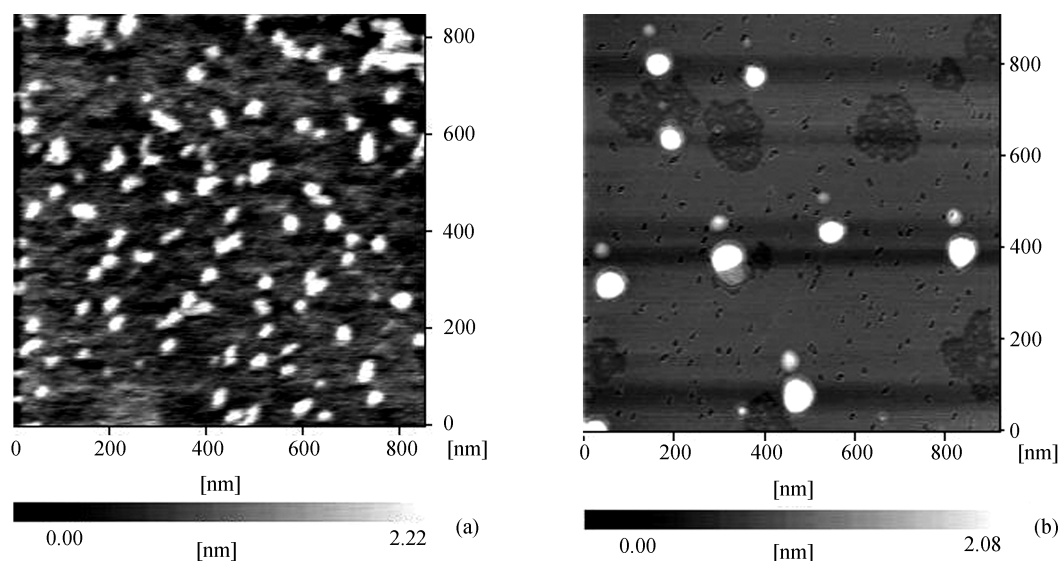


Fig. 5. Tapping mode AFM images of the nanometer silica (a) and PS/SiO₂ hybrid nanocomposites (b).

nanoparticle surface and interface. Apparent grafting percentage can be calculated to be 40% from the TGA weight loss of PS/SiO₂ hybrid nanocomposites.

The morphologies and the surface topography image of untreated silica nanoparticles and PS/SiO₂ hybrid nanocomposites were investigated using TEM (Fig. 4) and AFM (Fig. 5). As shown in Fig. 4, silica nanoparticles dispersed badly, formed large aggregates and had an average effective diameter (D_e) of 20 nm; the size of the PS/SiO₂ hybrid nanocomposites is in the range of 30 to 50 nm with an averaging grain size of 40 nm, and the average interparticle distance is much larger than that of the silica nanoparticles. Furthermore, it can also

be found that the hybrid nanocomposites are uniformly dispersed without aggregation. Tapping mode AFM could not only take the same conclusion but also give us much more messages of surface topography. Compared with the untreated silica (Fig. 5(a)) with sharp edges and rough surface, after the polymerization, the PS/SiO₂ hybrid nanoparticles (Fig. 5(b)) showed bigger size and very smooth edges. These results were consistent with the previously reported ones^[9]. In summary, the PS/SiO₂ composite nanoparticles can be prepared by an *in-situ* surface-initiated nitroxide-mediated radical polymerization and the dispersedness of nanoparticles can be enhanced.

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