

Robust Preparation of Core-shell type Silica/Polymer Nanocomposites by using Surface-initiated ARGET ATRP

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A facile route for covalent functionalization of silica (SiO_2) nanoparticles with poly(methyl methacrylate) (PMMA) has been investigated. The surfaces of the SiO_2 nanoparticles were treated with 2-bromo-2-methyl-N-[3-(trimethoxysilyl)propyl] propanamide to introduce the initiator moieties on the surface. Subsequently, activators regenerated by using electron transfer atom transfer radical polymerization (ARGET ATRP) of methyl methacrylate were employed for the preparation of SiO_2 /PMMA nanocomposites with a $\text{CuBr}_2/\text{N,N,N',N'',N'''}\text{-pentamethyldiethylenetriamine}$ catalyst system and a tin(II) 2-ethylhexanoate reducing agent. The modification of SiO_2 was confirmed by surface analyses including Fourier transfer infrared spectroscopy and X-ray photoelectron spectroscopy. The morphology of the nanocomposites was investigated by using field-emission scanning electron microscopy and transmission electron microscopy. A thermogravimetric analysis was used to evaluate the thermal properties and the grafting density. The colloidal stability of silica nanoparticles in a common organic solvent was explicitly shown to have been remarkably improved by the grafting process.

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I. INTRODUCTION

Over the past decade, the polymer-inorganic nanocomposites with well-defined core-shell nanostructure have gained increasing scientific interest due to their potential for use in advanced devices in a variety of practical multi-disciplines [1,2]. Such kinds of materials can be utilized for various purposes, such as toughening of plastics, as well as thermal and tribological performance enhancement of polymers [2-5]. Generally, composites of inorganic fillers and polymers can be obtained by simple physical blending [6]. Nevertheless, the physical absorption of polymers onto inorganic nanoparticles is not strong enough to achieve efficient processing of materials and stable device performance [6]. Alternatively, stable chemical bonds between surfaces and polymer chains are expected to overcome the notorious drawbacks of the physical approach [6-8]. There are several

approaches to covalently graft polymer brushes onto particulate core particles. One typical method is the surface modification of core particles with vinyl-containing agents, where this vinyl group co-polymerizes with other dissolved monomers in the reaction medium [9,10]. This method was found to be simple and low cost, but resulted in low control of the polymer shells [11,12].

In this report, we present a robust route for the preparation of nanocomposites composed of silica nanoparticles and poly(methyl methacrylate) (PMMA) by taking advantage of surface-initiated activators regenerated by using electron transfer atom transfer radical polymerization (ARGET ATRP). The core-shell structure of the nanocomposites was demonstrated by using electron microscopies including transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FE-SEM).

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II. EXPERIMENT

1. Materials

Silica nanoparticles (average size *ca.* 100 nm) were synthesized by using the Stober method [13]. 2-bromoisobutyryl bromide (2-BBB, Aldrich) was distilled over calcium hydride (CaH_2) under reduced pressure. Triethyl amine (TEA) was purified by using double distillation over *p*-toluenesulfonyl chloride and CaH_2 , respectively. Methyl methacrylate (MMA, 99.5%, Junsei) was passed through an activated alumina column to remove the inhibitor. Other chemicals and solvents were used as received.

2. Synthesis of Initiator-functionalized SiO_2 Particles

The synthesis of 2-bromo-2-methyl-N-[3-(trimethoxysilyl)propyl] propanamide (BrTMSPA) was carried out using the procedure in the literature [14]. The final product was a colorless oil with a yield of 92.5%.

^1H NMR (400 MHz, CDCl_3): δ 6.84 (s, 1H, NH), 3.55 (s, 9H, SiOCH_3), 3.24 (t, 2H, CH_2N), 1.92 (s, 6H, CH_3), 1.63 (m, CH_2 , 2H), 0.64 (t, 2H, SiCH_2).

The SiO_2 nanopowder (1.00 g) and the BrTMSPA (0.50 g) were dispersed in toluene (50 mL). The mixture was stirred for 72 h at room temperature under the protection of flowing nitrogen. SiO_2 -Br nanoparticles were obtained by centrifugation and were washed thoroughly using five centrifugation-redispersion cycles with toluene as the solvent. Finally, the product was dried under vacuum at 45 °C until a constant weight was achieved.

3. Surface-initiated Polymerization of the SiO_2 Macro-initiator

SiO_2 -Br particles (0.500 g), N,N,N',N'',N'' -penta-methyldiethylenetriamine (PMDETA) (8.6 mg), CuBr_2 (1.11 mg), MMA (5.00 g) and anisole (4 mL) were added to an open-capped vial equipped with a magnetic stir bar. The SiO_2 -Br particles were stirred and ultrasonicated for 30 min. The system was degassed by nitrogen bubbling for 15 min. To this solution, a mixture of the reducing agent tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) in 1 ml of anisole was injected rapidly. The polymerization was stopped by exposing the reaction solution to air. The products were then diluted with tetrahydrofuran (THF) and collected by centrifugation with THF four times and methanol twice sequentially. The PMMA-grafted SiO_2 nanocomposites (PMMA-g- SiO_2) were dried under vacuum at room temperature for 24 h. Three separate experiments with interval reaction time were conducted in order to study the kinetics of the polymerization process.

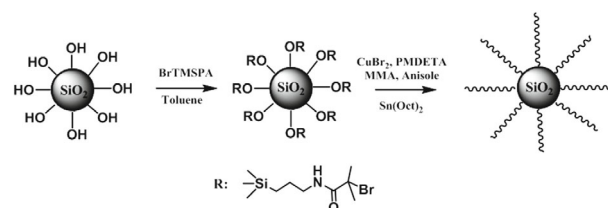


Fig. 1. Synthetic approach for PMMA-g- SiO_2 nanocomposites by using surface-initiated ARGET ATRP.

To evaluate the dependence of number-averaged molecular weight (M_n) and polydispersity index ($\text{PDI} = M_w/M_n$) values of the grafted PMMA on the polymerization time, we cleaved PMMA chains from the SiO_2 surface as follows: 50 mg of the PMMA-g- SiO_2 and 50 mg of tetrabutylammonium bromide (TOAB) were dissolved in 5 mL of toluene in a polyethylene flask. A 5% HF aqueous solution was then added to the mixture. The mixture was stirred vigorously for 24 h. The cleaved PMMA in the organic layer was precipitated in cold ethyl ether.

4. Characterization

TEM images were recorded using a Hitachi H-7500 instrument operating at 80 kV. A drop of the sample dispersed in distilled toluene was placed on a copper grid and dried. The changes in the surface chemical bonding of the functionalized SiO_2 nanoparticles, SiO_2 -Br, and PMMA-g- SiO_2 hybrid particles were captured by using Fourier transformed infrared (FT-IR) spectrophotometry with a BOMEM Hartman & Braun FT-IR spectrometer in the frequency range of 4000 – 400 cm^{-1} . The morphologies of the hybrids were investigated by using FE-SEM images (Hitachi JEOL-JSM-6700F system, Japan). A thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer Pyris 1 analyzer (USA). Before the test, all the samples were carefully ground into fine powder. The samples were scanned within the temperature range of 50 – 800 °C at a heating rate of 10 °C min^{-1} under continuous nitrogen flow. The surface composition was investigated using X-ray photoelectron spectroscopy (XPS, Thermo VG Multilab 2000) in ultra-high vacuum with $\text{Al K}\alpha$ radiation. Gel permeation chromatography (GPC) was performed using an Agilent 1200 Series instrument equipped with PLgel 5- μm MIXED-C columns, with a THF solvent at 30 °C. The solution flow rate was 1 mL/min. The calibration was carried out using PMMA standards.

III. RESULT AND DISCUSSION

The general approach to the preparation of PMMA grafted SiO_2 nanocomposites is illustrated in Fig. 1.

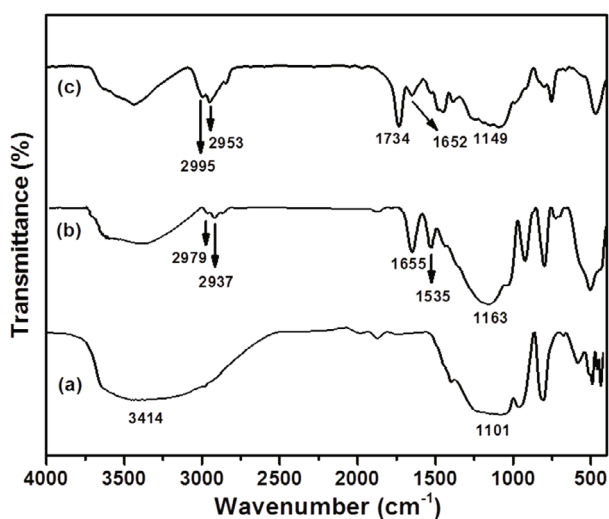


Fig. 2. FT-IR spectra of (a) bare SiO₂, (b) SiO₂-Br and (c) PMMA-g-SiO₂.

Firstly, SiO₂-Br particles were prepared by treating SiO₂ with BrTMSPA. Then, surface-initiated ARGET ATRP of MMA was carried out from the modified initiator particles.

Figure 2 shows the FT-IR spectra of (a) SiO₂, (b) SiO₂-Br, and (c) PMMA-g-SiO₂. For bare SiO₂ particles, the absorption peaks at 1101 cm⁻¹ was due to the stretching vibration of siloxane (Si-O-Si) groups, and the peak at 3414 cm⁻¹ was related to the free-hydroxyl-group stretching vibration. From Fig. 2(b), new adsorption peaks at 1655 cm⁻¹ and 1535 cm⁻¹ were assigned to the >C=O stretching vibration and the N-H bending vibration, respectively. These peaks could be related to the formation of the initiator layer on the silica surface. The bands in the range of 3000 – 2850 cm⁻¹ correspond to C-H stretching vibrations of the CH₃ and the CH₂ groups of the grafted PMMA. In addition, a very strong peak due to the carbonyl groups (>C=O) in the polymer backbone was observed at 1734 cm⁻¹. This could be assumed to be due to the successful attachment of polymer chains onto the silica surface by covalent bonds.

XPS measurements were performed to investigate the surface compositions of the nanocomposites, as shown in Fig. 3. The wide scan XPS spectra over a large energy range at a low resolution were used to identify the elements present in the grafted hybrid nanoparticles. In Fig. 3(a), the sharp peaks at 285.16, 400.47 and 70.64 eV are assigned to C1s, N1s and Br3d, respectively, in the nanoparticles, indicating successful immobilization of the ATRP initiator on SiO₂. Upon surface-initiated polymerization, the C1s intensity increased significantly due to the formation of polymer chains surrounding the SiO₂ nanofillers (see Fig. 3(c)). The C1s regions of the narrow scan XPS spectra for materials are very sensitive to the chemical environment surrounding the element, and thus can provide important information on obtain-

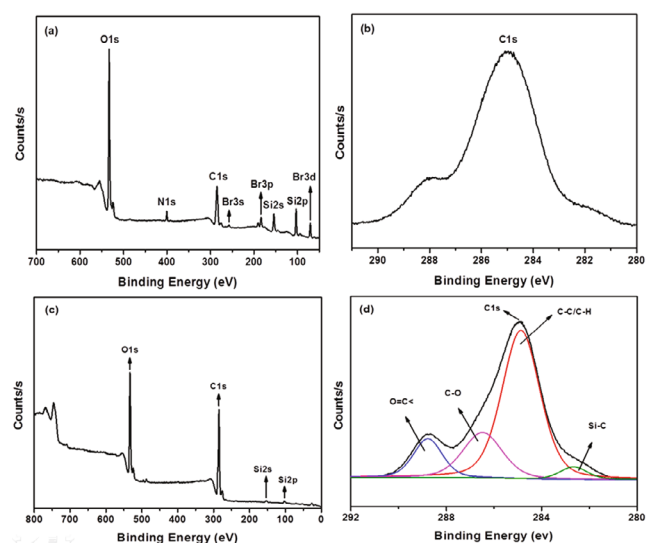


Fig. 3. (Color online) XPS wide scan spectra of (a) SiO₂-Br and (c) PMMA-g-SiO₂; XPS narrow scan spectra of (b) SiO₂-Br and (d) PMMA-g-SiO₂.

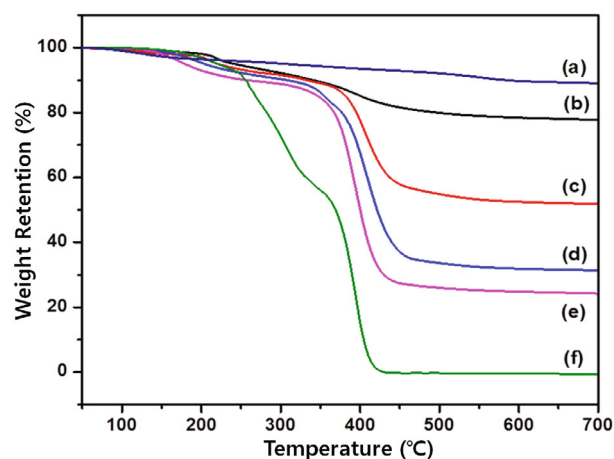


Fig. 4. (Color online) TGA curves of (a) bare SiO₂, (b) SiO₂-Br, (c) PMMA-g-SiO₂ after 6h, (d) 12h, (e) 24h and (f) the cleaved homopolymer.

ing the strength of the interaction between SiO₂ and the polymer chains. Figure 3(d) shows the C1s region of a narrow scan XPS spectrum for the nanoparticles. For the grafted nanoparticles, the binding states of C1s can be deconvoluted into four contributions, which correspond to the C-H/C-C species, the Si-C species, the >C=O species and the O-C species in the polymer backbone.

The result from the TGA analysis of as-synthesized nanocomposites is shown in Fig. 4. The initial weight loss observed in the vicinity of 150 °C is due to the continued loss of water. The TGA result for SiO₂-Br is shown in Fig. 4(b). The weight loss at around 200 °C (*T_{onset}*) corresponds to the ATRP initiator being anchored on the silica nanoparticles. For the polymer-grafted SiO₂, two main weight-loss regions are observed in the TGA

Table 1. The molecular weight and PDI of the cleaved polymer prepared with different polymerization times.

Sample	Reaction time	Molecular weight (g/mol)	PDI (M_w/M_n)
1	6 h	22500	1.45
2	12 h	40600	1.39
3	24 h	50100	1.30

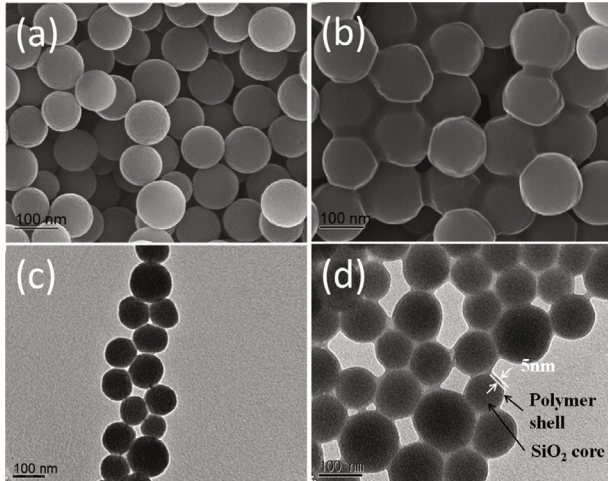


Fig. 5. TEM images of (a) $\text{SiO}_2\text{-Br}$ and (b) SiO_2/PMMA nanocomposites; FE-SEM images of (c) $\text{SiO}_2\text{-Br}$ and (d) SiO_2/PMMA nanocomposites.

curve, as shown in Figs. 4(c)–(e). The weight decrease in the first region (the onset at 200 °C) and the significant weight reduction in the second region (the onset at 360 °C) are attributed to the decomposition of PMMA. The grafting amounts of the polymer were estimated to be 28% for a 6-h reaction time, 48% for a 12-h reaction time and 60% for a 24-h reaction time.

To obtain the molecular-weight details (M_n and PDI) for the grafted PMMA, we cleaved the polymer chain from the surfaces of SiO_2 nanoparticles by using a HF treatment. The cleaved polymer was analyzed by GPC. Table 1 summarized the GPC data for different polymerization times of 6, 12 and 24 h. The M_n of the grafted PMMA chains ranged from 22500 to 50100, with a relatively narrow PDI. The narrow PDI of the cleaved polymer indicates that the polymer chain grow from the silica surface in a controlled manner.

The morphologies of $\text{SiO}_2\text{-Br}$ and the resulting polymer-decorated nanoparticles in the solid state were analyzed using TEM. Dilute solutions of nanoparticles in toluene were cast onto carbon-coated grids and analyzed after evaporation of the solvent. Figure 5(a) shows the discrete nature of the SiO_2 nanoparticles after the treatment with BrTMSPA. The TEM image of Fig. 5(b) reveals a polymer shell encapsulating a dense silica core, giving rise to a distinctive encapsulated hybrid nanostructure. This result was further confirmed by using

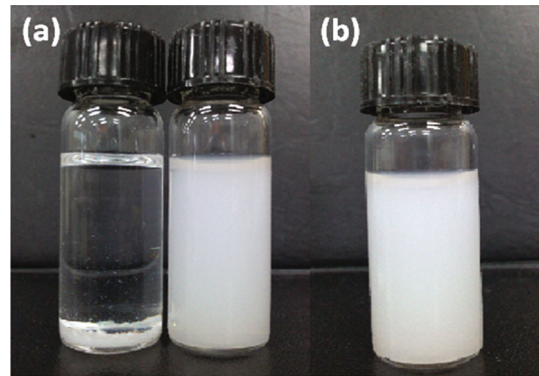


Fig. 6. Digital photographs of (a) bare SiO_2 and PMMA-g- SiO_2 dispersed in toluene at the initial stage and (b) PMMA-g- SiO_2 dispersed in toluene after 1 day.

FE-SEM, as shown in Figs. 5(c) and (d). The surface morphology of the PMMA-g- SiO_2 nanoparticles in the FE-SEM image of Fig. 5(d) suggests that the narrowly dispersed nanoparticles were covered with an amorphous polymer layer. The increase in the size of the nanocomposites from that of the silica nanospheres is readily discernible from the TEM and the FE-SEM images under the same magnification.

The silica nanoparticles were suspended in toluene before and after the grafting of the PMMA brush to compare their colloidal stability in the organic solvent. Photographs of SiO_2 and PMMA-g- SiO_2 dispersed in toluene are shown in Fig. 6(a). The picture on the left is related to bare SiO_2 which settles rather quickly. The extant picture is after the grafting of PMMA to SiO_2 . A good dispersion can be seen to have been formed as a result of the polymer chains from silica surface. Photographs of the solution of PMMA-g- SiO_2 after one day are shown in Fig. 6(b), where the PMMA brush can be seen not to have introduced a reasonable long-time stability to the dispersion of silica nanoparticles.

IV. CONCLUSION

A facile and efficient method to prepare PMMA-g- SiO_2 nanocomposites by using surface-initiated ARGET ATRP has been reported. The polymerization was conducted in a well-controlled manner at room temperature by using PMDETA/ CuBr_2 and $\text{Sn}(\text{Oct})_2$ as a catalyst system and a reducing agent, respectively. The TEM and the FE-SEM analyses showed a core-shell-type morphology for the nanocomposites. This versatile approach can be applied to graft other polymers with increasing complexity and functionality onto the polymeric shells and may pave the way for the design, fabrication, optimization, and eventual application of more functional SiO_2 -based nanocomposites.

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