Preparation of Ni-g-polymer core–shell nanoparticles by surface-initiated atom transfer radical polymerization

Renxu Chen [a], Shane Maclaughlin [c], Gianluigi Botton [b], Shiping Zhu [a,b,*]

[a] Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7
[b] Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7
[c] Research and Development, Dofasco Inc., Hamilton, Ontario, Canada L8N 3J5

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ABSTRACT

Surface-initiated atom transfer radical polymerization (si-ATRP) technique was successfully employed to modify Ni nanoparticles with polymer shells. ATRP initiators were covalently bonded onto Ni nanoparticle surfaces by a combination of ligand exchange and condensation reactions. Various kinds of polymers including poly(methyl methacrylate) (PMMA) and poly(n-isopropylacrylamide) (PNIPAM) were grafted from the immobilized initiators. The grated polymer shells gave Ni nanoparticles exceptionally good dispersion and stability in solvents. Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and transmission electron spectroscopy (TEM) were employed to confirm the grafting and to characterize the nanoparticle core–shell structure. Gel permeation chromatography (GPC) studies of cleaved polymer chains revealed that the grafting polymerization was well controlled. The magnetic properties of Ni-g-polymer nanoparticles were also studied.

1. Introduction

In recent years, because of the unique magnetic properties of nanocrystalline metallic nanoparticles such as Fe, Co and Ni, considerable attention has been devoted to the synthesis of these materials. In particular, Ni nanoparticles have received great interest for their potential applications in many diverse fields, including magnetic recording media, biomedical materials, catalysis, and electro-conductive materials. Numerous different physical and chemical preparative routes have been developed to synthesize Ni nanoparticles, such as pyrolysis [1], sputtering [2], microemulsion [3,4], aqueous [5,6] and nonaqueous [7,8,9] chemical reduction, sonochemical deposition [10], and polyol methods [11].

Because of the anisotropic dipolar attraction, Ni nanoparticles have strong tendency to aggregate into large clusters, thus lose their specific magnetic properties associated with the single-domain nanostructures. This greatly limits the uses of Ni nanoparticles in various applications. In order to overcome this problem, it is essential to do some modification work on Ni nanoparticle surface to prevent aggregation. In most preparation methods of Ni nanoparticles,

capping agents like long chain alkyl acids, amines and phosphates were always applied to control growth of nanoparticles; and at the same time, to prevent them from aggregation.

Compared to small molecular capping agents, polymeric shells have their unique advantages. Because of flexibility in control of polymer composition and functionality, polymer shells are not only able to protect nanoparticles from aggregation, but also readily endow nanoparticles with interesting functionalities. Among many approaches for coating nanoparticles with polymer shells, surface-initiated polymerization techniques have recently become very popular choices, especially surface-initiated atom transfer radical polymerization (si-ATRP). By this method, polymer chains are in situ grafted from initiator molecules previously immobilized onto nanoparticle surfaces. The most significant advantage of this "grafting from" method is its ability to produce dense polymer brushes, with grafting densities ranged from 0.1 to 0.7 chains/nm^2. Moreover, ATRP is a well-established controlled radical polymerization technique and can offer good control over polymer molecular weight, and thus polymeric shell thickness, allowing preparation of polymer shells with low polydispersities.

Although si-ATRP has been employed to graft polymers from various nanoparticles, such as SiO$_2$ [12,13], Au [14], MnFe$_2$O$_4$ [15], etc, no successful experiments have been reported on modification of nanocrystalline metallic nanoparticles. Unlike other types of materials, metal surfaces are highly reactive in electrochemical and acid/base reactions that complicate ATRP reactions. Red-ox deactivation of

ATRP catalyst is a particular risk. In our previous study [16], using triethoxysilane-based initiator and iron catalyst, we succeeded in grafting polymer brushes from flat Ni and Cu surfaces. In this paper, we report the first successful study on surface modification of pristine Ni nanoparticles by si-ATRP. A combination of ligand exchange and condensation reaction was employed to covalently immobilize triethoxysilane-based ATRP initiators onto Ni nanoparticle surface. Various types of polymers, like poly(methyl methacrylate) (PMMA) and poly(*n*-isopropylacrylamide) (PNIPAM), were grafted *in situ* from the immobilized initiators. After polymer grafting, both dispersion and stability of the Ni nanoparticles in solvents were greatly improved. The grafted polymer shells were very effective to prevent the Ni nanoparticles from aggregation. The improved dispersion and stability, as well as good compatibility with polymer matrices, are of great benefit to preparation of high quality Ni nanoparticle/polymer composite materials.

2. Experimental

2.1. Materials

Nickel acetylacetonate [Ni(acac)$_2$] (95%), hexadecylamine (HDA) (98%), trioctylphosphine oxide (TPPO) (99%), sodium borohydride (99%), *o*-dichlorobenzene (anhydrous, 99%), acetic acid ($\geq$99.7%), 3-aminopropyltriethoxysilane (99%), 2-bromoisobutyryl bromide (98%), triethylamine (>99%), iron(II) bromide (98%), iron(III) bromide (98%), triphenylphosphine (TPP) (99%), toluene (anhydrous, 99.8%), *N,N*-dimethylformamide (DMF) (anhydrous, 99.8%), *n*-isopropylacrylamide (NIPAM) (97%) were purchased from Aldrich and were used as received. Methyl methacrylate (MMA) (99%) was purchased from Aldrich and distilled over CaH$_2$ under vacuum, then stored at −15 °C before use. Ethanol (anhydrous), hexane (reagent), chloroform (reagent), dichloromethane (reagent), ethyl acetate (reagent), tetrahydrofuran (THF) (HPLC) and hydrochloric acid solution (37 wt.-%) were obtained from Caledon Laboratories Ltd. and used as received. Deionized (DI) water with a resistivity of 18 MΩ cm was prepared from a Millipore Milli-Q filtration system. Ultra-high-purity-grade argon was used in this study.

2.2. Synthesis of Ni nanoparticles

Ni nanoparticles were synthesized following the published procedure [17]. The synthesis was conducted using a standard airless technology. 0.2 g of Ni(acac)$_2$ was dissolved in 5 mL *o*-dichlorobenzene at 100 °C, and the solution was quickly injected into a mixture containing 40 mL dichlorobenzene, 1.5 g TOPO, 1.5 g HDA, and 0.15 g sodium borohydride at 140 °C during vigorously stirring. The mixture was quickly heated to 180 °C and stirred for 30 min under Ar atmosphere. It was then cooled to room temperature. 100 mL ethanol was added to precipitate Ni nanoparticles. The nanoparticles were separated by centrifugation (3500 rpm, 1 h) and dried in vacuum. The dried nanoparticles were redispersed into toluene and re-precipitated in ethanol. The cycle was repeated for three times to remove excess ligands. Finally, Ni nanoparticles were dispersed in toluene with a concentration of 10 mg/mL.

2.3. Immobilization of initiators

The surface-attachable initiator was synthesized following the same procedure as in our previous work [16]. The initiator was immobilized onto Ni nanoparticles as follows: 0.25 mL initiator, 50 μL acetic acid and 50 mL toluene based Ni nanoparticle dispersion were mixed in a 100 mL round-bottom flask. The mixture was stirred at room temperature for 72 h under argon protection. 100 mL *n*-hexane was added into the mixture to precipitate the initiator-

modified Ni nanoparticles. The nanoparticles were separated by centrifugation (3500 rpm, 1 h) and dried in vacuum. The dried nanoparticles were redispersed into toluene and re-precipitated by *n*-hexane. The wash cycle was repeated for five times to remove excess initiators. Finally, the initiator-modified Ni nanoparticles were dispersed in toluene with a concentration of 10 mg/mL.

2.4. Surface-initiated ATRP on Ni nanoparticle

The typical procedure for ATRP of MMA from Ni nanoparticle surface is as follows: 64.7 mg (0.300 mmol) FeBr$_2$, 8.9 mg (0.030 mmol) FeBr$_3$ and 259.6 mg (0.9900 mmol) triphenylphosphine were placed into a 25 mL flask containing a magnetic stir bar. The flask was deoxygenated through several evacuation/backfilling cycles of argon. 6.0 g (60 mmol) MMA and 6.0 g initiator-modified Ni nanoparticle dispersion in toluene were purged with Ar for 1 h before added into the flask containing iron catalyst via a double-tipped needle. The mixture was stirred intensively, degassed with argon for another 10 min, and put into an oil bath of 60 °C. After the desired reaction time was reached, the polymerization solution was taken out from the oil bath, diluted with 50 mL THF. The Ni-*g*-PMMA nanoparticles were collected by centrifugation (20,000 rpm, 1 h). The nanoparticles were repeatedly rinsed with large amount of THF to remove residual monomer and free polymer. Finally, the samples were dried in vacuum at 50 °C for 6 h. The polymerization of NIPAM was performed at 40 °C in DMF. After the reaction, the polymerization solution was diluted with methanol at a solution/methanol ratio of 1/4. The Ni-*g*-PNIPAM nanoparticles were also collected by centrifugation (20,000 rpm, 1 h), washed intensively with methanol and then dried in vacuum.

2.5. Cleavage of PMMA chains from Ni nanoparticles

Grafted PMMA brushes were cleaved from the Ni nanoparticle surfaces with the method described by Matsuno et al. [18]. Hydrochloric acid solution was used to dissolve the Ni nanoparticles. PMMA was extracted with chloroform. The chloroform was then removed under vacuum and PMMA was subjected to GPC measurement.

2.6. Characterization

Fourier transform infrared analysis was performed on a Bio-Rad FTS-40 FT-IR spectrometer. All samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15,000 psi. The spectra were scanned over the range 4000–400 cm^{-1} in the transmission mode, accumulating 16 scans at a resolution of 2 cm^{-1}. TEM was carried out on a Philips CM-12 transmission electron microscope. The samples were dispersed in appropriate solvents with ultrasonication for 2 min and then dropped onto the copper grid to dry. Magnetic studies were carried out using a Quantum Design MPMS SQUID magnetometer at 5 K and 298 K.

TGA was performed on using a Thermowaage STA409, at a scan rate of 10 °C/min, up to 800 °C in nitrogen atmosphere. The initiator density on nanoparticle surfaces and the grafting densities of polymer chains were calculated from the TGA results according to the following equation:

$$\text{Density}\left(\text{molecules/nm}^2\right) = \frac{W \times r \times N_A \times d_{\text{Ni}}}{M(1-W) \times 3 \times 10^{21}}$$

where W is the weight loss of sample, r is the radius of Ni nanoparticles, N_A is Avogadro's constant, d_{Ni} is the density of nickel (8.90 g/cm^3), and M is the polymer molecular weight.