Nanocomposite Polymeric Microspheres Containing Ni Nanoparticles with Controlled Microstructures

Kensuke Akamatsu,*,[†,‡] Satoshi Adachi,[†] Takaaki Tsuruoka,[†] Shingo Ikeda,[†]
Satoshi Tomita,[§] and Hidemi Nawafune[†]

*Faculty of Science and Engineering and Graduate School of Science, Konan University, 8-9-1 Okamoto,
Higashinada, Kobe 658-8501, Japan, PRESTO, Japan Science and Technology Agency (JST),
3-5 San-ban-cho, Chiyoda-ku, Tokyo102-0075, Japan, and Graduate School of Materials Science,
Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan*

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A synthesis method for nanocomposite microspheres containing Ni nanoparticles via chemical surface modification has been developed, by which particle size and interparticle distance for embedded Ni nanoparticles can be systematically controlled. The process relies on introduction of carboxyl acid groups via hydrolysis of matrix polymer, incorporation of Ni ions via ion exchange reaction, hydrogen-induced reduction of doped Ni ions in the sphere followed by Ni nanoparticle-catalyzed decomposition of the surrounding polymer matrix. We demonstrate the formation of Ni nanoparticles in polymer microspheres and structural change of polymer matrix upon reaction by FT-IR, SEM, and cross-sectional TEM studies, and show that initial Ni ion loading determines final nanoparticle size ranging from 3 to 8 nm, which are homogeneously distributed in the whole of the microspheres. The heat-treatment in a hydrogen atmosphere at fixed temperature causes decomposition of the polymer matrix via catalytic reaction of Ni nanoparticles, resulting in a gradual increase in the volume fraction of the Ni phase in the spheres and thus decrease of the average interparticle distance. The process reported herein allows, therefore, one to independently control size and interparticle distance of Ni nanoparticles and is an effective methodology for preparing high-quality nanocomposites with a tailored microstructure which further allows control of functions.

1. Introduction

Nanocomposites consisting of inorganic nanoparticles embedded in dielectric matrices have recently been the subject of intensive research, with the aim of developing nanoscale devices with functions determined by the properties and arrangement of the individual nanoparticles.[1–4] Among various types of nanoparticle, there has been increasing interest in magnetic nanoparticles because of their potential technological applications, such as ultrahigh-density data storage media,[5,6] microwave filters,[7] and magnetic resonance imaging.[8,9] To fabricate nanodevices with particular properties and functions, it is necessary to have precise control of the microstructure of the composites, e.g., nanoparticle size, chemical and physical properties of the surrounding matrix, and spatial distribution of the nanoparticles.

Embedding magnetic nanoparticles into a polymer matrix is an effective method of stabilizing and enhancing the functions of these materials. The merits of polymer matrices are their thermal plasticity, which enables tuning of the nanocomposite microstructure, and the diversity of chemical bonds and structures available, which provides additional possibilities for controlling a variety of physical and chemical properties.[10–12] Over the past few decades, several groups have reported polymer coating of single magnetic nanoparticles using various synthetic routes, including microwave plasma polymerization of monomers,[13] adsorption of passivating polymers, and ligand-initiated growth of polymer shells around the particle.[14–16]

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* To whom correspondence should be addressed. E-mail: akamatsu@center.konan-u.ac.jp.

† Konan University.

‡ PRESTO, Japan Science and Technology Agency.

§ Nara Institute of Science and Technology.

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There have also been several reports on the fabrication of nanoassemblies based on magnetic nanoparticles embedded or organized in polymer films and spheres. One approach to synthesizing these nanostructures is incorporation of preformed nanoparticles during polymerization or inclusion in polymer micelles or spheres.[17–19] Kim and Taton et al. reported controlled encapsulation of metal nanoparticles with monomers followed by polymerization to form metal-containing polymeric spheres.[18,19] An alternative approach to preparing magnetic nanocomposites involves in situ synthesis using ion-doped precursors. For example, our group and several others have reported controlled formation of nanocomposite films using precursor[20,21] and polyelectrolyte films.[22]

For future magnetic applications, significant advantages are expected on the basis of independent control of the size (which determines the quantum effect) and interparticle distance (which determines particle-to-particle interactions) of metal nanoparticles, which has thus far been difficult to achieve. In addition, the macroscopic morphology of nanocomposites (e.g., films and powders with various particle shapes) may be designed for practical applications. Our group reported the fabrication of polyimide thin films containing several transition metal nanoparticles using a method which relies on chemical surface modification of the polymer matrix to form ion-doped precursors.[20] Although the approach using ion-doped precursors has been used extensively in the fabrication of film-type nanocomposites, there have been few reports concerning other types of nanocomposites such as microspheres,[23] and the ability to control nanoparticle size and volume fraction using these methods is limited. To further the development of design and fabrication of metal/polymer nanocomposites with controlled microstructures via this ion-doped precursor approach, we herein describe a method that allows independent control of nanoparticle size and interparticle distance in nanocomposite materials consisting of Ni nanoparticles embedded in highly cross-linked divinylbenzene (DVB)-based polymer microspheres. By modifying the polymeric microspheres via hydrolysis to generate ion-exchangeable sites, we demonstrate systematic control over the amount of metal ions in the sphere, and the size and amount of embedded Ni nanoparticles. More significantly, the volume fraction of the Ni nanoparticle phase in the spheres (and thus the average interparticle distance between Ni nanoparticles) could be systematically controlled for nanocomposite spheres under conditions in which the size and amount of Ni nanoparticles remain constant. This was achieved by metal-catalyzed decomposition of the surrounding polymer matrices upon thermal annealing. Such control in monodispersed microspheres containing uniformly embedded magnetic nanoparticles is important, not only in terms of potential microelectronic and biomedical applications but also in terms of increasing our fundamental understanding of the relationship between magnetic properties and the composite microstructure.

2. Experimental Section

Materials. The microspheres used in this study were divinylbenzene-based polymers cross-linked via ester groups (4.9 μm in diameter, Micropale, Sekisui Chemical Co., Ltd.). Sodium hydroxide (NaOH) and nickel chloride ($NiCl_2$) were purchased from Wako Chemicals, Ltd. All chemicals were used as received. Distilled water was used for the preparation of all aqueous solutions and for washing steps.

Preparation of Nanocomposite Spheres. The DVB microspheres were initially dispersed in a 7.5 M aqueous NaOH solution at 80 °C for several hours, followed by thorough rinsing with distilled water. To achieve the exchange of sodium ions with nickel ions, we then dispersed the resulting hydrolyzed spheres into a 500 mM aqueous $NiCl_2$ solution at room temperature for 20 min. In this study, the initial hydrolysis reaction was performed for 1.5, 3, 5, 7, or 10 h, yielding ion-doped precursor spheres containing Ni ions at ca. 150, 320, 450, 600, or 740 mmol g^{-1}, respectively. After being rinsed, the precursor spheres were sealed in a quartz tube under a hydrogen gas flow, followed by annealing in a tube furnace, which was heated at a rate of 10 °C min^{-1} up to 370 °C and then maintained at this temperature for several hours, in order to reduce the Ni ions to metallic Ni.

Characterization. The amount of Ni ions in the spheres was quantified using inductively coupled plasma (ICP) atomic emission spectroscopy (SPS7700 plasma spectrometer, Seiko Instruments). To extract Ni ions from the spheres, they were immersed in hydrochloric acid solution (1 vol%) at room temperature for 3 h. Fourier transform infrared (FT-IR) spectroscopy was carried out in order to confirm the changes in chemical structure of the spheres upon hydrolysis and annealing. The spectra were recorded using a FT-IR 670 instrument (Japan Spectroscopic Co.) at a resolution of 4 cm^{-1} and 100 accumulations. The microstructure of the nanocomposites, i.e., sphere diameter, mean size, and size distribution of Ni nanoparticles, was confirmed by scanning electron microscopy (SEM, JSM-6340F, JEOL) and cross-sectional transmission electron microscopy (TEM, JEM-2000EX, JEOL) operating at 15 kV and 200 kV, respectively. The samples for cross-sectional TEM observation were prepared by embedding the spheres into epoxy resin followed by curing and sectioning into slices of about 100 nm thickness using a conventional microtome technique with a diamond knife (Leica, Ultracut R).

3. Results and Discussion

Synthesis of Ion-Doped Precursor Spheres. The approach to synthesizing nanocomposite spheres containing superparamagnetic Ni nanoparticles involves hydrolysis of DVB microspheres (which contain cross-linking ester groups) to form carboxylic acid groups that act in a subsequent step as ion-exchange sites for the incorporation of Ni ions, followed by formation of Ni nanoparticles upon hydrogen

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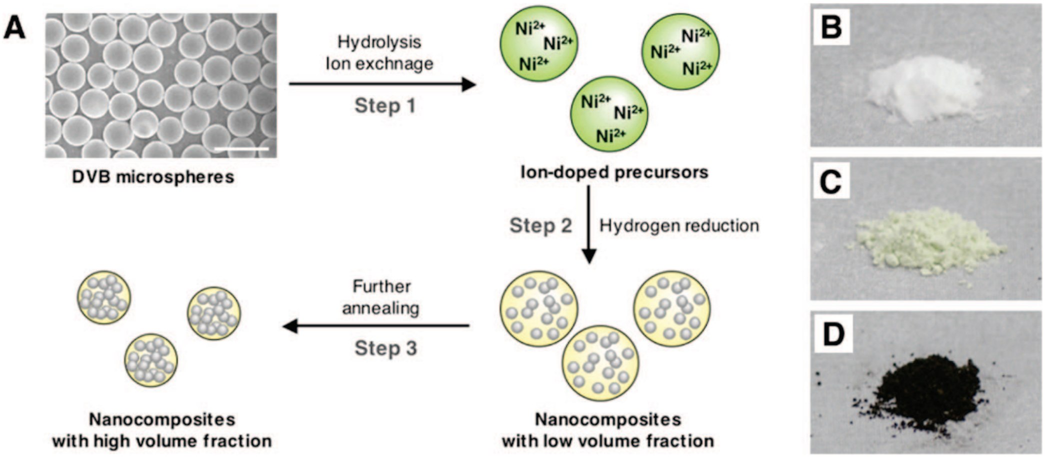

Figure 1. (A) Schematic representation of the synthetic process for DVB microspheres containing Ni nanoparticles. Scale bar in photograph of DVB microspheres: 10 μm. (B) Photographs of untreated DVB powders; (C) material obtained after hydrolysis and incorporation of Ni ions by ion exchange reaction; (D) product obtained by subsequent heat treatment at 370 °C for 30 min in a hydrogen atmosphere.

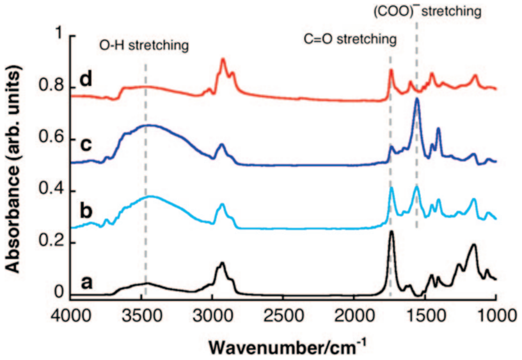

Figure 2. (a) FT-IR spectra of untreated DVB powders; material obtained after hydrolysis using aqueous NaOH solution at 80 °C for (b) 3, and (c) 10 h; (d) product obtained by subsequent incorporation of Ni ions and heat treatment at 370 °C for 30 min in a hydrogen atmosphere.

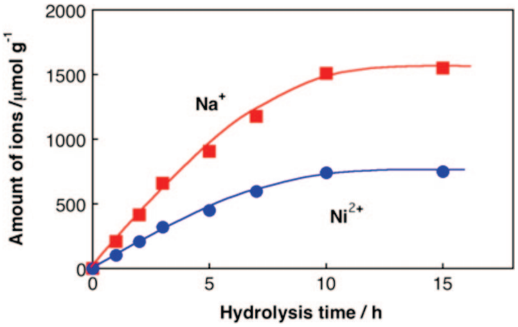

Figure 3. Amounts of Na ions in DVB spheres hydrolyzed using aqueous NaOH solution at 80 °C and Ni ions incorporated by subsequent ion exchange reaction using 500 mM aqueous $NiCl_2$ solution as a function of initial hydrolysis time.

reduction (Figure 1). The DVB polymer particles are spherical in shape, with a diameter of 4.9 μm (standard deviation: 0.29 nm). In a typical procedure, the DVB spheres were treated in aqueous NaOH solution for set periods. This treatment yielded hydrolyzed spheres, as characterized by FT-IR spectroscopy (Figure 2). Upon treatment with aqueous KOH solution at 80 °C for 3 h, bands at 3400 cm^{-1} (OH) and at 1670 cm^{-1} (COO^{-}) appear, and the band at 1750 cm^{-1} (C=O) decreases (spectrum b in Figure 2). This confirms hydrolysis of the cross-linking ester groups in the DVB spheres to form hydroxide groups and sodium salts of carboxylic acids. The degree of hydrolysis can be controlled simply by varying the reaction time, as evidenced by the increase in the carboxylate anion band (1670 cm^{-1}, spectrum c in Figure 2). Longer hydrolysis times led to the greater degree of hydrolysis. This is also confirmed by changes in the amount of sodium ions as a function of hydrolysis time (Figure 3), in which the amount is measured to be nearly proportional to hydrolysis time at early stage of reaction and then saturated. After ion exchange, the same dependence of adsorbed Ni ions with respect to initial hydrolysis time is observed, and no sodium ions can be detected. Importantly, the amount of adsorbed Ni ions is almost half as that of sodium ions adsorbed initially, indicating that the incorporation of Ni ions can be achieved through exchange of monovalent sodium ions with divalent Ni ions in a 2:1 stoichiometric manner. Typically, the amount of adsorbed Ni ions reaches ca. 750 μmol g^{-1} for the spheres initially hydrolyzed for 15 h.

Formation of Nanocomposite Spheres Containing Ni Nanoparticles. The following experiments were designed to investigate the effect of initial Ni ion loading on the microstructure of the nanocomposite spheres containing Ni nanoparticles. After heat treatment of the Ni-ion-doped precursor spheres at 370 °C in a hydrogen atmosphere, the light-green powder became an intense black (Figure 1D). The formation of fcc Ni nanoparticles in the DVB spheres was confirmed by cross-sectional transmission electron microscopic (TEM) observation and electron diffraction analysis. As shown in Figure 4A, small Ni nanoparticles were found to be embedded uniformly in thin cross-sections of the composite sphere. Based on our observations of 100 nm thick sections of the 3.0 μm spheres, it was shown that the hydrolysis reaction occurred even at center of the DVB spheres, and doped Ni ions were uniformly distributed in the precursor spheres. It is important to note that, as shown in Figure 4F, the size of the Ni nanoparticles varied depending on the initial Ni ion loading; the greater the amount of Ni ions in the sphere, the smaller the Ni nanoparticle size (Figure 4 B–E). Under these experimental conditions, the size of the nanoparticles could be

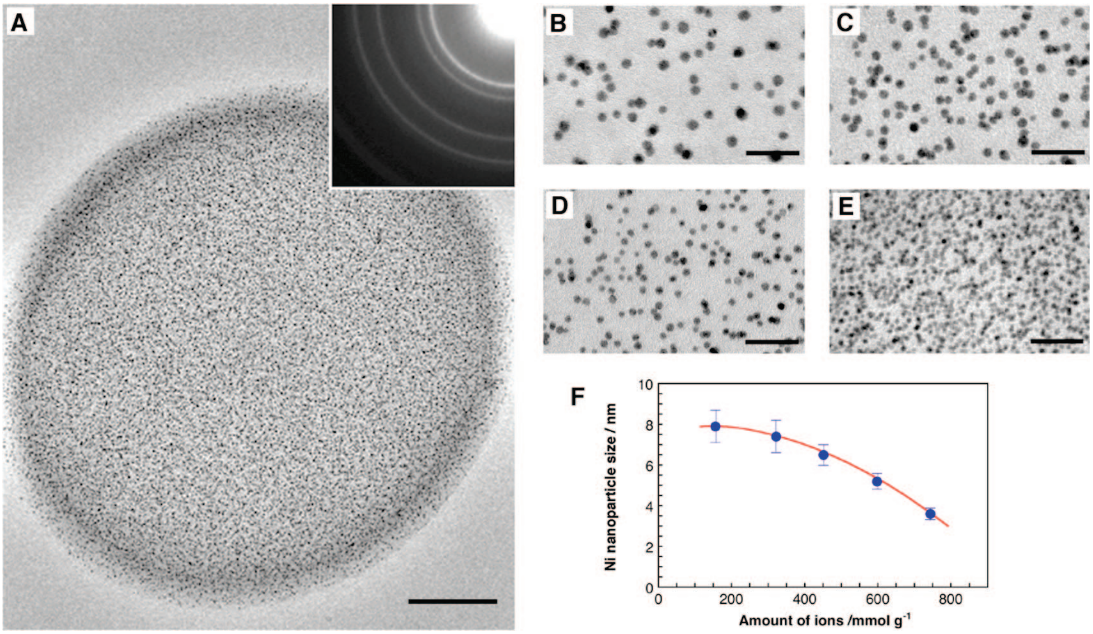

Figure 4. (A) Cross-sectional TEM image of DVB nanocomposite sphere containing Ni nanoparticles. Initial Ni ion loading: 720 mmol g^{-1}. Inset: electron diffraction pattern of the nanocomposite. Scale bar: 500 nm. (B−E) Cross-sectional TEM images of DVB nanocomposite spheres with initial Ni ion loadings of (B) 320, (C) 430, (D) 600, and (E) 740 mmol g^{-1}, obtained after heat-treatment at 370 °C for 30 min. Scale bar for images B−E, 50 nm. (F) Plots of mean Ni nanoparticle diameter as a function of initial ion loadings. Heat treatment was performed at 370 °C for 30 min in a hydrogen atmosphere for all samples.

controlled in the range 3.5−8.0 nm, with a standard deviation of less than 10% for all samples. This remarkable relationship between ion loading and nanoparticle size may be due to the balance in nucleation and growth of metal nanoparticles, as has been suggested in relation to the formation and growth of inorganic nanoparticles in solution.[24,25] When ion loading is high, there is a greater likelihood of the reduced Ni atoms coming into contact with each other to form Ni clusters due to large number of Ni sources per unit volume (thus, nucleation of Ni clusters is dominant), resulting in the formation of large numbers of small Ni nanoparticles (high nucleation density). In contrast, Ni nanoparticle growth is dominant under conditions of low ion loading, which results in the formation of small numbers of large Ni nanoparticles (low nucleation density). Preliminary experiments showed that high temperature heat treatment (e.g., 400 °C) resulted in the formation of nanoparticles smaller than those prepared by annealing at lower temperature, presumably due to higher reduction rate of Ni ions at higher temperature (results not shown). Since the cohesive energy of metal atoms is generally higher than the adhesive energy between metal atoms and polymer molecules, the metal atoms tend not to dissociate once they have formed metallic nanoparticles. In addition, because of the lower rate of reduction from Ni ions to Ni atoms by hydrogen gas and the smaller diffusion coefficient of Ni atoms or clusters in a solid polymeric matrix,[26] the growth of Ni nanoparticles is considered to be kinetically controlled, resulting in the formation of monodispersed nanoparticles, which are uniformly embedded in the spheres. The coalescence of Ni nanoparticles hardly occurs because of rigid structural nature of highly cross-linked DVB matrix. The XPS results showed that Ni nanoparticles were not oxidized when the samples were stored at room temperature in air for a week (see the Supporting Information, Figure S1), which might indicate the passivation of Ni in DVB spheres to prevent oxidation. The overall reaction process is suggested as follows

$$\mathrm{R1{-}COO{-}R_2 + NaOH \rightarrow R_1{-}COONa + HO{-}R_2} \qquad \text{(hydrolysis)} \quad (1)$$

$$\mathrm{2(R_1{-}COONa) + NiCl_2 \rightarrow (R1{-}COO)_2Ni + 2NaCl} \qquad \text{(ion exchange)} \quad (2)$$

$$\mathrm{(R_1{-}COO)_2Ni + H_2 \rightarrow 2(R_1{-}COOH) + Ni\ (atom)} \qquad \text{(reduction of Ni ions)} \quad (3)$$

$$n(\mathrm{Ni\ atom}) \rightarrow (\mathrm{Ni})_n\ (\mathrm{nanoparticle}) \qquad \text{(nanoparticle formation)} \quad (4)$$

$$\mathrm{R_1{-}COOH + HO{-}R_2 \rightarrow R_1{-}COO{-}R_2 + H_2O} \qquad \text{(dehydration)} \quad (5)$$

In Figure 2, FT-IR measurements of the samples obtained after hydrogen reduction comfirms that the carboxylate groups were reprotonated via reduction of Ni ions with hydrogen molecules (eq (3)), and a dehydration reaction occurred simultaneously to form ester groups during heat treatment at 370 °C (eq (5)). These results demonstrate that the process under investigation involves reformation of the initial cross-linked DVB matrix. The process should also be applicable to other metals which can be doped via ion-exchange reaction.

Independent Control of Size and Volume Fraction of Ni Nanoparticles. Next, to control the volume fraction of Ni with fixed nanoparticle size, we conducted long-term

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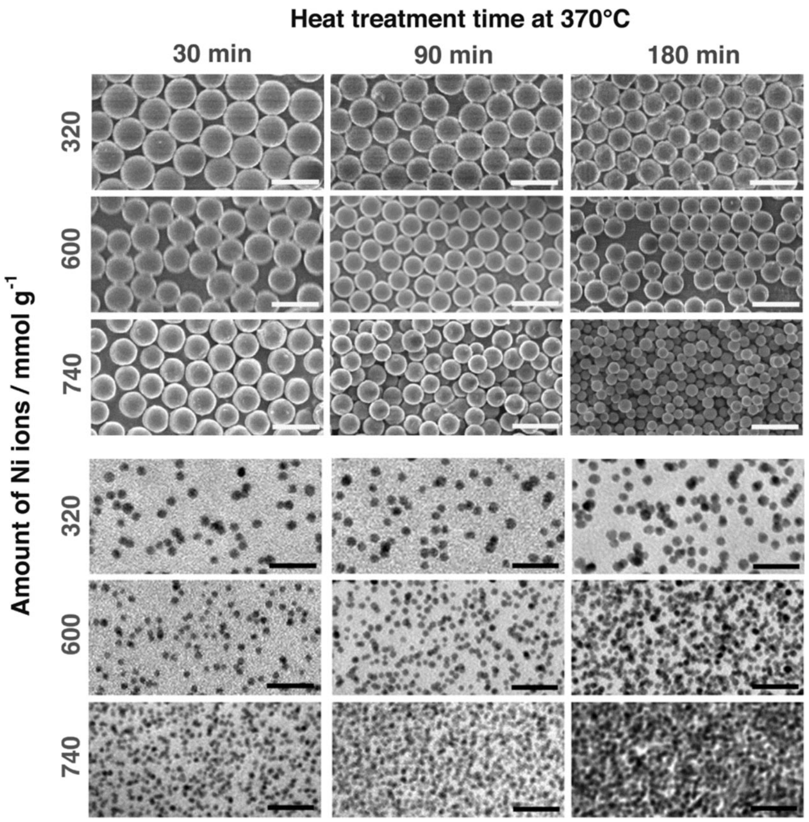

Figure 5. SEM (upper 9 images) and cross-sectional TEM (lower 9 images) images of DVB nanocomposite spheres with different initial ion loadings and treatment times after heat treatment at 370 °C in a hydrogen atmosphere. Ion loadings and heat-treatment times are indicated in the figures. Scale bars: 5 μm for SEM images; 50 nm for TEM images.

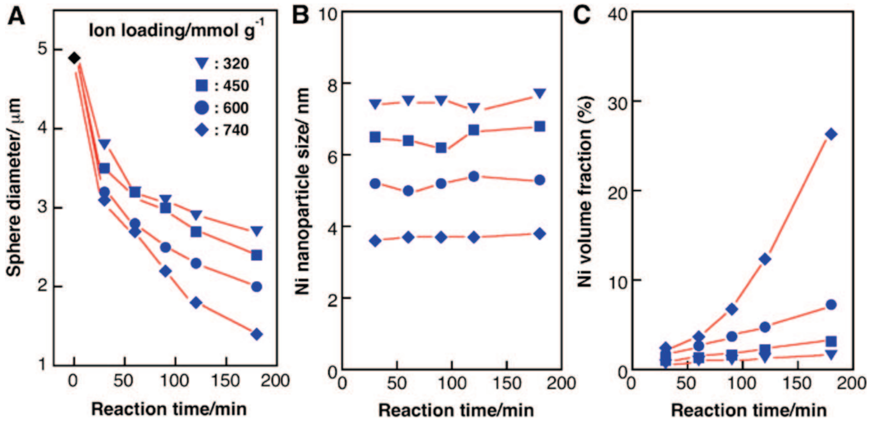

Figure 6. Plots of (A) sphere diameter, (B) Ni nanoparticle size, and (C) Ni volume fraction in nanocomposite spheres after heat treatment at 370 °C in a hydrogen atmosphere as a function of treatment time and initial Ni ion loading. The Ni volume fractions were calculated using the equation given in ref.[27]

annealing of the precursor spheres in a hydrogen atmosphere. Microstructural changes in the sphere diameter were characterized using scanning electron microscopy (SEM), and Ni nanoparticle size was determined by TEM. Typical results for spheres with different initial ion loadings are shown in Figure 5 and summarized in Figure 6. The sphere diameter decreases upon heat treatment at 370 °C for several hours, but the Ni nanoparticle size remains unchanged, and the volume fraction of Ni nanoparticles appears to increase in the cross-sectional TEM images (cross-sections are 100 nm thickness for all samples). Interestingly, the decrease in sphere diameter occurs more quickly in composites with smaller Ni nanoparticles (Figure 6A). It may be noted that the weight of the composite powders decreased upon annealing, and degradation products with a waxlike texture were deposited on the inner wall of the quartz tube used for hydrogen reduction. FT-IR analysis revealed that these products contained aldehyde groups (Figure 7) and contained less carboxylic acid and ester groups. Because the sphere diameters did not decrease when annealing was performed for samples without Ni ions (i.e., without Ni nanoparticles), or for Ni-ion-containing samples in the absence of a hydrogen gas flow, it is thought that the process is mediated by metal-catalyzed decomposition of the polymer matrix by hydrogen molecules. The mechanism may be

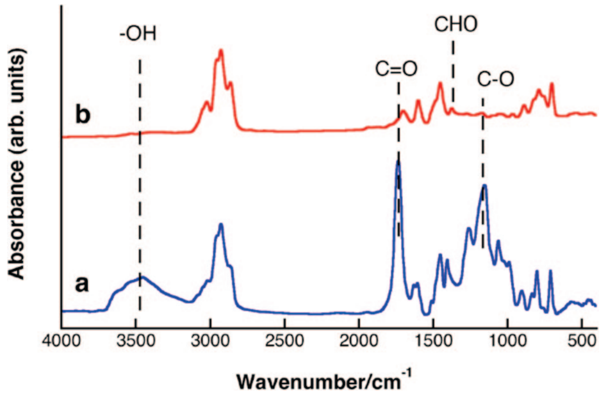

Figure 7. FT-IR spectra of untreated DVB spheres (a), and decomposition products obtained on the inner wall of the quartz tube after annealing at 370 °C for 10 h in a hydrogen atmosphere (b).

considered as follows: the Ni nanoparticles catalyze cleavage of existing and/or reformed ester groups by hydrogen molecules at the metal/polymer interface, forming oligomeric decomposition products bearing aldehyde groups, which are released from the composite spheres. This process is similar to that observed in polyimide films containing several transition metal nanoparticles.[20]

$$R_1{-}COO{-}R_2 + H_2 \rightarrow R_1{-}CHO\ (g) + HO{-}R_2(s) \quad \text{(Catalyst: Ni nanoparticle)} \tag{6}$$

As a result, the sphere diameter decreases as a function of annealing time, resulting in a relative increase in the volume fraction of the Ni phase. We performed these experiments using samples with Ni nanoparticles of four different sizes, and calculated the average volume fraction of the Ni phase in the spheres (Figure 6C).[27] The volume fraction of the Ni phase (f) in the phases is calculated using following equation: f = (mass volume of Ni)/(volume of composite sphere). The mass volume of Ni is given by the following equation: $V_{\mathrm{Ni}} = CV_{\mathrm{DVB}}d_{\mathrm{DVB}}M_{\mathrm{w}}\,d_{\mathrm{Ni}}^{-1}$, where C is the initial ion loading, V_{DVB} is the volume of DVB spheres used (6.5×10^{-11} cm^{-3}), d_{DVB} is the density of the DVB spheres (1.19 g cm^{-3}), M_{w} is the atomic weight of Ni (58.69 g mol^{-1}), and d_{Ni} is the density of Ni (8.908 g cm^{-3}). In these experiments, the volume fraction was controllable in the range ca. 1.5% − 20%, depending on the initial amount of doped ions and the annealing time. The greater rate of decrease in sphere size (i.e., rate of decomposition) for spheres with smaller Ni nanoparticles is thought to be due to the larger total interfacial area between Ni nanoparticles and the surrounding DVB matrix, because the catalytic decomposition reaction takes place at the interface. It is important to note that the fact that the Ni nanoparticle size remains intact when the sphere diameter decreases indicates a gradual decrease in the interparticle distance for neighboring Ni nanoparticles, as shown in Figure 1A. This observation demonstrates that nanoparticle size and interparticle distance can be independently in the present system of nanocomposite spheres. The average interparticle distance varied from a few tens of nanometers for lower volume fractions to a few nanometers for higher volume fractions; in the current system, for example, f could be controlled in the range ca. 3.0−20% for Ni nanoparticles of 3.5 nm, and ca. 1.5−2.0% for nanoparticles of 8.0 nm (Figure 6C). These values give average interparticle distances (surface-to-surface distances) of 5.6−1.3 nm (3.5 nm Ni nanoparticles) and 18.1−14.1 nm (8.0 nm Ni nanoparticles).[27] These values are within coupling range for magnetic dipole moments.[21] The systematic characterization of the magnetic properties of these materials as a function of their microstructural parameters is worthy of examination and currently underway.

5. Conclusion

In conclusion, we have developed a method for synthesizing cross-linked DVB microspheres containing Ni nanoparticles, in which the size and volume fraction of Ni nanoparticles are independently and highly tunable on a nanometer scale. This method takes advantage of the hydrolysis ability of the polymeric host, and subsequent ion exchange and annealing in hydrogen atmosphere induces both reduction of the doped metallic ions and reformation of the initial polymeric structures via dehydration. Some analytical experiments revealed that initial loading of Ni ions controls mean size of Ni nanoparticles which are monodisperse and distributed homogenerously in microspheres. Importantly, volume fraction of Ni nanoparticles increases with heat treatment time in hydrogen atmosphere because of the decrease in sphere diameter that is caused by metal-catalyzed decomposition of the polymer matrix, providing an effective way of independently controlling size and average interparticle distance of Ni nanoparticles. For the following reasons, the present work forms a basis for new research on mesoscopic composite materials: (1) the synthesis method is expected to be applicable to other noble and transition metal nanoparticles; (2) it furthers our understanding of the fundamental origins of the physical properties of nanocomposites though systematic investigation of the controlled microstructures (i.e., particle size and interparticle distance); (3) the method may be extendable to allow construction of other types of mesostructure, such as photonic materials consisting of magnetic nanocomposite spheres.

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Supporting Information Available: Figure S1, XPS results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] The average interparticle distance between Ni nanoparticles is estimated on the basis of f and the particle size, assuming that the particles are arranged in a simple cubic lattice.