Articles

NH$_2$-Terminated Poly(ethylene oxide) Containing Nanosized NiO Particles: Synthesis, Characterization, and Structural Considerations

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Highly concentrated nanosized NiO particles have been prepared by means of vacuum evaporation of Ni on NH$_2$-terminated poly(ethylene oxide) matrix film and subsequent purification by removal of a part of the matrix which was soluble in ethanol. TEM observation revealed that the purified composites contain uniformly dispersed NiO particles with an average diameter of less than 5 nm and fairly narrow size distribution. From the analyses including high-resolution TEM, electron diffraction pattern, and X-ray diffraction (XRD), the resultant particles were found to be fcc NiO, and significant lattice expansion was observed. The chemical bonding of amine end groups of the matrix molecules to NiO particle surfaces was suggested by XPS measurements. XRD and differential scanning calorimetry measurements indicate that the matrix structure in the composite is amorphous. This amorphous nature of the matrix could be caused by the restriction of molecular chain mobility through the chemical interaction between NiO particles and matrix molecules, leading to the insoluble nature of the composite in ethanol. On the other hand, the composite is soluble in propionic acid with no evidence for significant aggregation of NiO particles. The maximum content of NiO reaches ca. 50 wt % after purification, which is due to the localization of NiO particles into some parts of the matrix film during formation of NiO particles. The particle growth mechanism is discussed from the effect of initial amount of deposited Ni on the average particle diameter, its standard deviation, and the content of NiO in the composite.

Introduction

Recently, nanosized materials have attracted much attention because of their unusual chemical and physical properties different from those of bulk materials, based on size-quantization effect and extremely large specific surface area.[1−5] In particular, nanosized nickel oxides, NiO, are of great interest because they exhibit particular catalytic,[6−8] and anomalous electronic[9−11] and magnetic[12−15] properties. The characteristic properties of nanosized NiO particles enable one to tailor materials for a variety of applications including catalysis,[6−8] electrochromic windows,[16] and sensors.[17] Because these properties can be enhanced with decreasing a particle's size, especially less than 10 nm, and are highly depend-

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(1) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555.

(2) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.

(3) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.

(4) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267.

(5) Kjabunde, K. J.; Stark, J.; Koper, O.; Mohs, C.; Dong, G. P.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. *J. Phys. Chem.* **1996**, *100*, 12142.

(6) Fievet, F.; Figlarz, M. *J. Catal.* **1975**, *39*, 350.

(7) Alejandre, A.; Medina, F.; Salagre, P.; Fabregat, A.; Sueiras, J. E. *Appl. Catal. B* **1998**, *18*, 307.

(8) Carnes, C. L.; Klabunde, K. J. *J. Mol. Catal.* in press.

(9) Roberts, M. W.; Smart, R. St. C. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2957.

(10) Soriano, L.; Abbate, M.; Vogel, J.; Fuggle, J. C. *Chem. Phys. Lett.* **1993**, *208*, 460.

(11) Biji, V.; Khadar, M. A. *Mater. Sci. Eng. A* **2001**, *304−306*, 814.

(12) Makhlouf, S. A.; Parker, F. T.; Spada, F. E.; Berkowitz, A. E. *J. Appl. Phys.* **1997**, *81*, 5561.

(13) Kodama, R. H.; Makhlouf, S. A.; Berkowitz, A. E. *Phys. Rev. Lett.* **1997**, *79*, 1393.

(14) Kodama, R. H. *J. Magn. Magn. Mater.* **1999**, *200*, 359.

(15) Bødker, F.; Hansen, M. F.; Koch, C. B.; Mørup, S. *J. Magn. Magn. Mater.* **2000**, *221*, 32.

(16) Boschloo, G.; Hagfeldt, A. *J. Phys. Chem. B* **2001**, *105*, 3039.

(17) Das, D.; Pal, M.; Bartolomeo, E. D.; Traversa, E.; Chakravorty, D. *J. Appl. Phys.* **2000**, *88*, 6856.

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ent on particle size, the precise control of the size and distribution in nm regime is required. In addition, a facile preparation process that allows convenient mass production of these particles at high concentration is necessarily for practical applications.

Many different methods have been intensively reported for the synthesis of nanosized metal or metal oxide particles, in which stabilizers such as polymers and surfactants with polar functional groups have often been used to prevent the particles from aggregating or coalescing.[18−22] However, there are only a few reports on preparation of nanosized NiO fulfilling the requests mentioned above.[23−26] For example, in the case of wet process for preparing metal colloids successfully via liquid-phase reduction of metal salts in the presence of stabilizer, posttreatment for complete oxidation of metal particles is often required, which may cause the degrading or decomposition of stabilizer, thus leading to aggregation of these nanosized particles.[23,24] Moreover, it is difficult to synthesize well-dispersed magnetic particles at high concentration in these systems because the particles have an intense tendency to aggregate, probably due to the magnetic interaction.[27,28]

Recently, we reported a simple route to prepare nanosized Au[29] or Cu_2O[30] particles dispersed uniformly in NH_2-terminated poly(ethylene oxide) ($PEO-NH_2$) film. These nanosized particles can be obtained by the vacuum evaporation of a metal on a molten $PEO-NH_2$ film followed by postheat treatment. The vacuum-evaporated atoms (or clusters) can diffuse into the molten matrix, and formation of nuclei proceeds continuously because the matrix is heated at 50 °C during metal deposition at which the molten $PEO-NH_2$ can behave as a viscous fluid, and hence nanosized particles are formed at high content. Because these particles are stabilized by the matrix molecules they can be dispersed uniformly with no evidence for aggregation.

In this paper, we report on the preparation and characterization of well-dispersed NiO particles with not only small size (less than 10 nm) but also narrow size distribution at extremely high content by using the successful method. The important point to note is that the dispersion condition of nanosized NiO particles is unique in comparison with other systems such as Au and Cu_2O, i.e., main parts of the composite comprising NiO particles and $PEO-NH_2$ cannot be dissolved in polar solvents (Au and Cu_2O systems as well as $PEO-NH_2$ itself can be readily dissolved in ethanol). The insoluble composite was extracted from the Ni deposited matrix film by excluding excess $PEO-NH_2$, and hence the powder including well-dispersed NiO particles at extremely high content can be easily obtained. Furthermore, the extracted composite powder can be dissolved in propionic acid readily with no evidence for significant aggregation between NiO particles, which leads to the advantage of converting the powder into various forms such as thin film or uniform mixing with other functional materials. The characteristics of the particles are investigated by using transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), and thermogravimetry analysis (TGA). The microstructure of the composite is also discussed in terms of interaction between $PEO-NH_2$ and NiO particles as well as of structure of $PEO-NH_2$ by means of Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), XRD, and differential scanning calorimetry (DSC) analysis.

Experimental Section

Chemicals. Diamine-terminated poly(ethylene oxide) ($PEO-NH_2$, MW 2000) was purchased from Scientific Polymer Products. The metal source used was high-purity Ni plate (99.7%, Nilako Co.). All other reagents having a purity level higher than GR grade were used without further purification.

Synthesis. $PEO-NH_2$ was dissolved in ethanol and the solution was coated uniformly on a glass substrate by means of a spinning technique. The film thickness obtained was ca. 11 μm, which was determined directly from cross-sectional SEM observation. After heating the film at 110 °C for 30 min in air followed by drying in a vacuum for 30 min at room temperature to remove residual solvent, the film was set in a vacuum evaporating chamber. After holding the chamber at 50 °C for 10 min, metallic nickel was vacuum-evaporated at a pressure of ca. 5×10^{-4} Torr and a deposition rate of ca. 0.2 nm/sec monitored by means of a quartz oscillator. The thickness of deposited Ni ranged from 100 to 400 nm.

After the vacuum evaporation was completed, the films were retained in the chamber for 10 min until cooled to room temperature. Oxidation of Ni can occur during the vacuum evaporation process because of residual oxygen (as will be explained in the discussion section). The films were then heat treated at 110 °C for 30 min in air. This post heat treatment is essential for obtaining a homogeneous distribution of the particles throughout the depth of the Ni-deposited $PEO-NH_2$ film. As the initial amount of deposited Ni increases, the viscosity of the matrix increases, which arises from its thixotropic property.[31,32] The increase in the viscosity prevents the nuclei or atoms (cluster) formed on the $PEO-NH_2$ film from further diffusion into the matrix film. Therefore, upon deposition of a relatively high amount of Ni, some of the particles obtained may distribute near the surface region. The post heat treatment allows further diffusion of the localized particles because the temperature is higher than that during the vacuum evaporation process.

The films were then shaved from the glass substrate and immersed in ethanol at room temperature for 60 min. The supernatants were excluded by means of centrifugation at 6000 rpm for 10 min. The purification was performed several times repeatedly until the components soluble in ethanol were completely extracted (until the supernatant exhibited no color).

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(18) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. W. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

(19) Ramesh, S.; Koltypin, Y.; Prozorov, P.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 546.

(20) Sun, S.; Murray, C. B. *J. Appl. Phys.* **1999**, *85*, 4325.

(21) Castro, C.; Ramos, J.; Millán, A.; Calbet, J. G.; Palacio, F. *Chem. Mater.* **2000**, *12*, 3681.

(22) Thomas, K. G.; Zajicek, J.; Kamat, P. V. *Langmuir* **2002**, *18*, 3722.

(23) Cordente, N.; Toustou, B.; Collière, V.; Amiens, C.; Chaudret, B.; Verelst, M.; Respaud, M.; Broto, J. M. *C. R. Acad. Sci. Paris, Chimie/Chem.* **2001**, *4*, 143.

(24) Wan, Y.; Ma, C.; Sun, X.; Li, H. *Inorg. Chem. Commun.* **2002**, *5*, 751.

(25) Carnes, C. L.; Stipp, J.; Klabunde, J. *Langmuir* **2002**, *18*, 1352.

(26) Xia, B.; Lenggoro, W.; Okuyama, K. *Chem. Mater.* **2002**, *14*, 2623.

(27) Reddy, B. V.; Nayak, S. K.; Khanna, S. N.; Rao, B. K.; Jena, P. *J. Phys. Chem. A* **1998**, *102*, 1748.

(28) Gallezot, P.; Leclercq, C.; Fort, Y.; Caubère, P. *J. Mol. Catal.* **1994**, *93*, 79.

(29) Deki, S.; Sayo, K.; Yamada, A.; Akamatsu, K.; Hayashi, S. *J. Colloid Interface Sci.* **1999**, *214*, 123.

(30) Yanagimoto, H.; Akamatsu, K.; Gotoh, K.; Deki, S. *J. Mater. Chem.* **2001**, *11*, 2387.

(31) Mullins, L. *J. Phys. Colloid Chem.* **1950**, *54*, 239.

(32) Suetsugu, Y.; White, J. L. *J. Non-Newtonian Fluid Mech.* **1984**, *14*, 121.

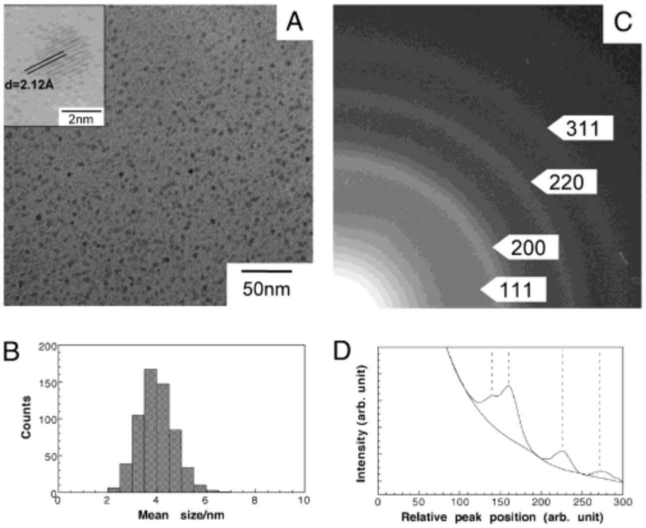

Figure 1. (A) TEM image and (B) corresponding size histogram of NiO particles dispersed in PEO−NH_2. The thickness of deposited Ni is 400 nm. TEM sample was prepared by mounting thin sections of the composite obtained by ultramicrotome technique onto carbon-coated TEM copper grid. Inset in A: high-resolution TEM image of NiO particle. (C) SAED pattern and (D) intensity distribution curve taken from SAED pattern of NiO particles dispersed in PEO−NH_2.

Finally, the residues were dried in vacuo for 30 min and the dark green powders were obtained as samples. Unless otherwise noted, all the measurements were performed for these purified samples.

Instruments. TEM examinations of samples were carried out on a JEOL JEM-2010 transmission electron microscope operating at 200 kV. Thin sections of the samples were obtained by the following procedure. The samples were immersed in an epoxy matrix, curied at 60 °C for 24 h, and sliced with a Leica Ultracut UCT ultramicrotome using a diamond knife. The thin sections were then mounted on a conventional carbon-coated copper grid.

X-ray diffraction studies of the samples were carried out on a Rigaku RINT-2100 diffractometer. Cu Kα radiation was used as the X-ray source with applied voltage of 40 kV and current of 40 mA. 2θ angles ranged from 15° to 80° with a rate of 4°/min by step scanning at intervals of 0.1°. The patterns obtained were calibrated using gold films deposited on a glass substrate. The gold (111) reflection was used as a standard for calculation of lattice spacing of NiO nanoparticles.

The crystallite size of NiO was calculated from the XRD spectra in accordance with Scherrer's formula. X-ray photoelectron spectra were obtained with a ESCA 3400 spectrometer (Shimazu) using an Mg Kα X-ray source. Calibration of the binding energy of the spectra was performed with the C 1s peak of the aliphatic carbons of the PEO−NH_2 matrix (284.6 eV). TGA (Rigaku TG 8120) was used to determine the content of NiO in the samples. To measure the weight loss, the samples were placed on a basket and heated at a rate of 10 °C/min from room temperature to 550 °C. IR spectra were measured using a FTIR spectrometer (FT/IR 615R, Japan Spectroscopic Co.) in diffuse reflectance mode. Thermal properties of the samples were analyzed by DSC (Rigaku, DSC 8230L) under nitrogen atmosphere.

Results and Discussion

Synthesis and Characterization of Nanosized NiO Particles. Typical TEM images and electron diffraction patterns of the sample with the deposited Ni thickness of 400 nm are shown in Figure 1. The small particles with a nearly spherical shape are considerably well-dispersed and uniform in size with an average diameter of 4.0 nm (Figure 1A and B). The corresponding selected area electron diffraction (SAED) pattern is indicated in Figure 2C, in which some broad Debye−Scherrer rings characteristic of nanocrystallite materials can be seen. To calculate plane distances correctly, the intensity distribution curve was obtained from the SAED pattern (Figure 1D). The reflection appearing around 150 of relative peak position was decomposed into two subcomponents using a Gaussian curve-fitting program with a nonlinear least-squares method. Four peaks correspond to plane distances of 0.242, 0.209, 0.154, and 0.128 nm which are approximately consistent with the indices (111), (200), (220), and (311) of face centered cubic (fcc) NiO, respectively. For further characterization of the nanosized particles, their lattice images were observed by using high-resolution TEM (inset in Figure 1A). The lattice spacing is estimated to be 0.212 nm which is also nearly consistent with (200) spacing of bulk fcc NiO ($d = 0.209$ nm), but the value is just slightly higher than that of bulk material, implying that the lattice expansion occurs. Similar results have been observed in other samples with different deposited Ni thicknesses. This is further evidenced from the X-ray analysis shown later.

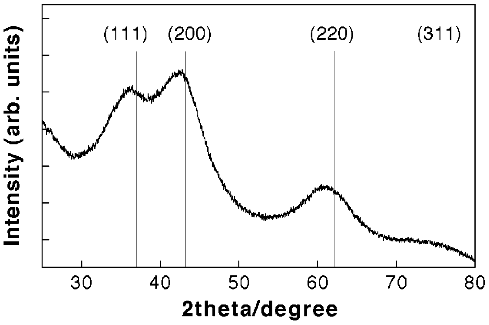

Figure 2. XRD pattern of NiO particles dispersed in PEO−NH_2. The thickness of deposited Ni is 400 nm. The solid lines show diffraction peak positions of bulk fcc NiO.

To obtain NiO particles using the present process, it is crucial to control vacuum pressure (5×10^{-4} Torr) in the chamber during vacuum evaporation of Ni. XRD study revealed that the NiO was found to be formed just after Ni deposition without post heat treatment in air. On the other hand, in the case that the Ni deposition was performed under 1×10^{-4} Torr, XRD measurement and TEM observation indicated that the structure of the obtained particles could be a metallic nickel surrounded by a NiO thin layer (results not shown). It is well-known that metallic nickel is readily oxidized and forms an oxide thin layer at its surface, which plays a role of passivate layer to prevent further interdiffusion of oxygen. Cordente et al. have reported that, even for Ni particles with average diameter of 4.5 nm (protected by polymer), the oxidation could not be completed by heat treatment at 100 °C for two weeks in air.[23] In fact, Ni/NiO particles obtained in this study are also stable without further oxidation proceeding for more than 3 months at ambient conditions. We believe that vacuum-evaporated Ni is completely oxidized to NiO during the vacuum evaporation step (at 5×10^{-4} Torr) due to residual oxygen.

In Figure 2, the XRD pattern shows remarkably broad reflections associated with the formation of small-sized particles. The (200) interplanar spacing ($d = 0.212$ nm

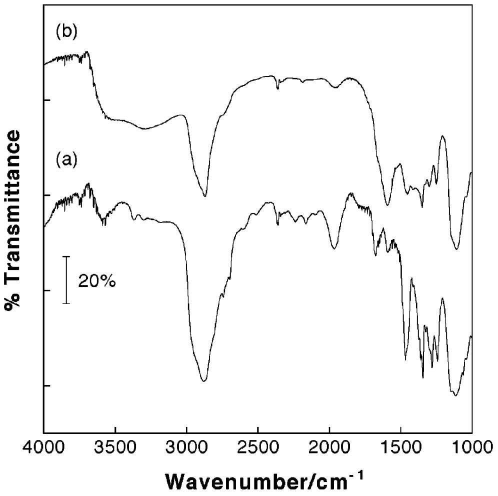

Figure 3. FTIR spectra of bare PEO$-NH_2$ (a) and composite with initial deposited Ni thickness of 100 nm (b).

at $2\theta = 42.55$ °) was consistent with that estimated from lattice images shown in the inset of Figure 1A. The crystallite size of NiO particles was determined from the full width at half-maximum of each reflection using Scherrer's formula; the value of which is 1.8 nm, much less than the average particle size (4.0 nm) estimated from TEM observation, indicating the polycrystalline nature of the NiO particles. It is noted that all the diffraction angles are found to be shifted toward lower values. From the diffraction angle, the lattice constant was estimated to be 0.4288 nm, which was 3% larger than that of bulk value (0.4177 nm). It is known that the nanosized metal oxide particles sometimes show an increase of their lattice constant with decreasing particle size in nm regime.[33-38] In our system, the dilation of the lattice constant may be considered to be due to a grain boundary effect or incorporation of oxygen vacancies in the lattice. However, further experimental study is necessarily to verify these assumptions and results will be reported elsewhere.

Structural Analysis of the Composite. Although TEM analysis has confirmed that nanosized NiO particles disperse uniformly and are isolated individually in the sample, the composite is insoluble in polar solvents. The reason for this insoluble nature of the composite, which can be related to the interaction between the nanoparticles and the matrix molecules, should be demonstrated. Figure 3 shows FTIR spectra for the PEO$-NH_2$ matrix and the sample with the lowest amount of deposited Ni (100-nm Ni thickness). The spectrum of the matrix (Figure 4a) is well characterized by bands attributed to the backbone modes of PEO together with the amine end groups. After incorporation of NiO particles, no significant change can be seen in the spectrum (Figure 4b), suggesting no major structural decomposition or transformation of backbone chains. On the other hand, in the XPS spectra shown in Figure 4, the N 1s peak of amine end groups for this composite is found to slightly shift toward higher binding energy (399.8 eV, Figure 4b) as compared with that for bare PEO$-NH_2$ matrix, which is centered at 399.0 eV.[39] This indicates that the amine end groups in the composite are in different environments, presumably due to chemisorption to the surface of the NiO particles.

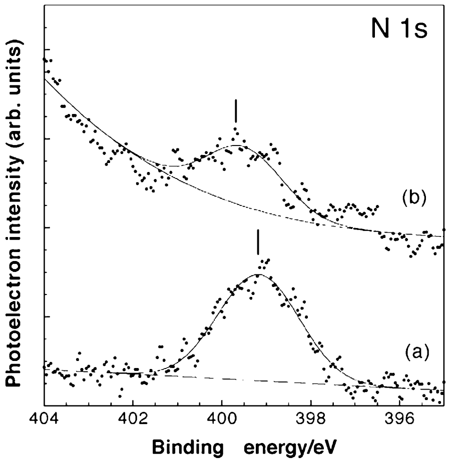

Figure 4. N 1s X-ray photoelectron spectra of bare PEO$-NH_2$ (a) and composite with initial deposited Ni thickness of 100 nm (b).

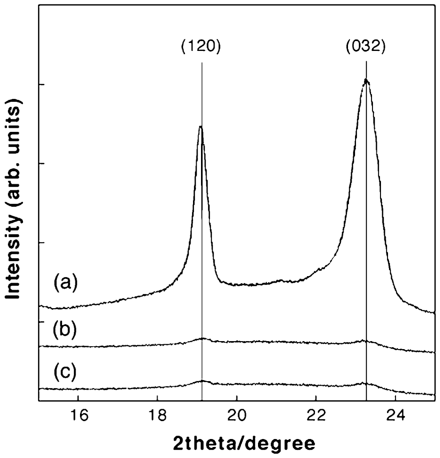

Figure 5. XRD patterns of bare PEO$-NH_2$ (a) and composite with initial deposited Ni thickness of 100 nm (b) and 400 nm (c). The solid lines show diffraction peak positions of bulk PEO.

To elucidate the structure of the matrix component in the sample, we also examined it using the XRD and DSC techniques that are useful for characterizing the crystallinity and thermal property of polymeric matrix, respectively. Figure 5 shows XRD patterns of PEO$-NH_2$ and the samples with the lowest (100 nm) and highest (400 nm) initial amount of deposited Ni. The diffraction peaks for PEO containing NiO particles (Figure 5b and c) are found to be much less intense in samples compared to those of the pure PEO$-NH_2$ (Figure 5a), indicating that the incorporation of NiO particles causes a significant decrease in the crystallinity of PEO$-NH_2$. There is no difference in profiles of Figure 5b and c, despite the major difference of NiO content in these

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(33) Tsunekawa, S.; Sahara, R.; Kawazoe, Y.; Ishikawa, K. *Appl. Surf. Sci.* **1999**, *152*, 53.

(34) Zhang, F.; Chan, S.-W.; Spanier, J. E.; Apak, E.; Jin, Q.; Robinson, R. D.; Herman, I. P. *Appl. Phys. Lett.* **2002**, *80*, 127.

(35) Tsunekawa, S.; Ito, S.; Mori, T.; Ishikawa, K.; Li, Z. Q.; Kawazoe, Y. *Phys. Rev. B* **2000**, *62*, 3065.

(36) Ayyub, P.; Palkar, V. R.; Chattopadhyay, S.; Multani, M. *Phys. Rev. B* **1995**, *51*, 6135.

(37) Mitsuhashi, T.; Ichihara, M.; Tatsuke, U. *J. Am. Ceram. Soc.* **1974**, *57*, 97.

(38) Edelstein, A. S.; Cammarata, R. C. *Nanomaterials: Synthesis, Properties and Applications*; IOP Publishing: London, 1996.

(39) Xu, Z.; Liu, Q.; Finch, J. A. *Appl. Surf. Sci.* **1997**, *120*, 269.

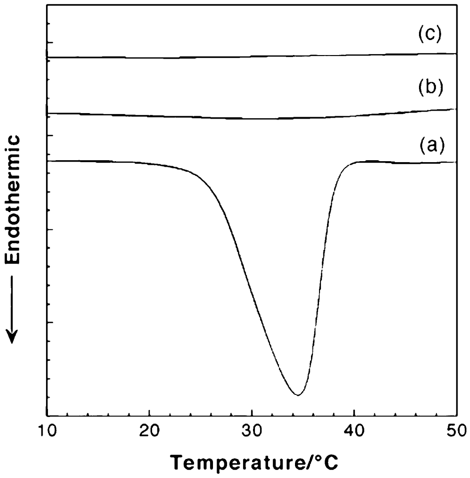

Figure 6. DSC curves of bare PEO−NH_2 (a) and composite with initial deposited Ni thickness of 100 nm (b) and 400 nm (c).

samples. Effect of incorporation of NiO particles is also observed in the thermal property of the sample. Figure 6 shows the DSC curves of these three samples. As expected, bulk PEO−NH_2 (Figure 6a) exhibits the definite endothermic peak that is attributed to the melting point of PEO−NH_2. On the other hand, for the samples containing NiO particles (Figure 6b and 6c), no peaks can be seen in the range of 10−50 °C. It should be noted that the endothermic band could not be detected over the wide range of temperature examined (from −90 °C to 70 °C), indicating that the amorphous structure of the matrix is thermodynamically stable.

These results obtained by FTIR, XRD, and DSC demonstrate that most of the amine end groups in the matrix molecules have relatively strong chemical interaction with NiO particles, and therefore the mobility of the matrix molecule is highly restricted, resulting in the amorphous structure of the matrix. We believe that this effect causes the insoluble nature of the composite in polar solvents.

Dispersibility of NiO Particles in Solvent. Upon practical application, it is crucial to obtain a stable solution in which nanosized particles are dispersed uniformly without aggregation, because such a solution enables us not only to form a uniform film on a variety of substrates but also to mix nanosized NiO particles homogeneously with other components. It was found that the composite was readily soluble in propionic acid instead of ethanol. The solutions are very stable at room temperature with no indication of aggregation or coalescence of the NiO particles occurring over several weeks. This stability is because the amine end groups bound to NiO particles can be oxidized in part by the acid, presumably due to protonation of amine end groups,[40] and hence chemical bonding between the NiO particle and PEO−NH_2 may be isolated. The solutions were dropped on a carbon thin film supported on a copper grid, and then TEM observation was performed. Figure 7 presents a representative TEM image and size distribution of the sample (thickness of deposited Ni 400 nm), showing uniform dispersion of NiO particles (average diameter 4.7 nm, standard deviation 0.59 nm). The average diameter slightly increased as compared with that of the sample before being dissolved in propionic acid, while the standard deviation decreased (see Figure 1). This suggests that relatively small NiO particles can aggregate with larger NiO particles or with each other, because most of the protective matrix molecules may be isolated for these smaller particles.

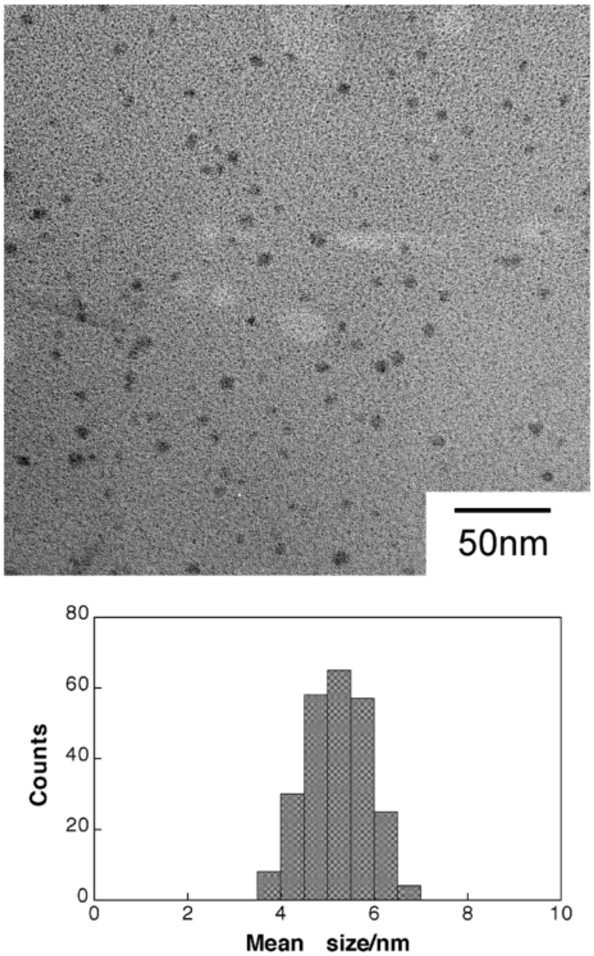

Figure 7. TEM image and corresponding size histogram of NiO particles stabilized with PEO−NH_2 after dissolving the composite in propionic acid.

Formation Process of the Composite in PEO−NH_2 Film. To investigate the spatial distribution of the particles in the PEO−NH_2 matrix film before purification, cross-sectional TEM observation was carried out. A representative TEM image of the matrix film after vacuum evaporation of Ni is shown in Figure 8.[41] The image shows that nanosized NiO particles are localized within some parts of the PEO−NH_2 film but isolated individually. The localization is probably due to the magnetic property of Ni.[27,28] Both average diameter and standard deviation of the particles, which are estimated from the cross-sectional TEM image, are nearly consistent with those of the composite obtained after purification (Figure 1), suggesting that the parts containing the localized NiO particles in the PEO−NH_2 film correspond

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(40) Guo, H. F.; Lin, H. Z.; Yu, T. L. *J. Macromol. Sci., Pure Appl. Chem.* **2002**, *A39*, 837.

(41) This sample was prepared as follows: poly (vinyl alcohol) (PVA) film was adhered to a glass substrate with tape, and PEO−NH_2 films were formed on the PVA film by spinning technique. Then metallic nickel was vacuum-evaporated on the substrate (Ni thickness 400 nm) under the same conditions as other samples. Finally, after the Ni/PEO−NH_2/PVA film was exfoliated from the glass substrate, a thin cross-section was obtained with conventional ultramicrotome technique.

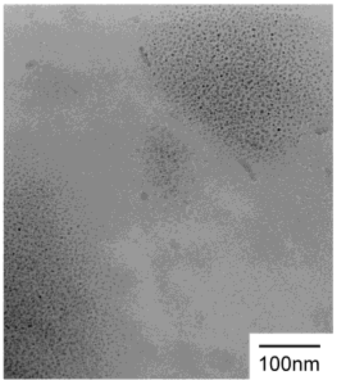

Figure 8. TEM image for thin section of as-prepared NiO particles dispersed in PEO−NH_2 film.

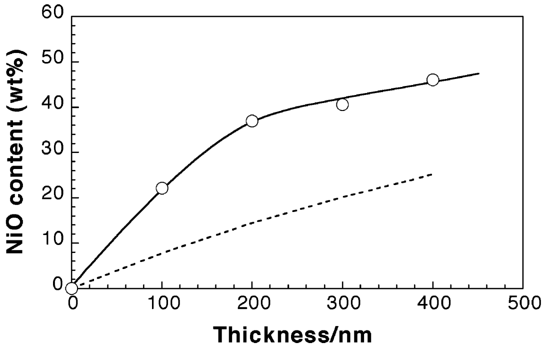

Figure 9. Variation of NiO content calculated from TGA analysis (solid line and open circle) and from initial amount of deposited Ni and the thickness of PEO−NH_2 film (dotted line) with the thickness of vacuum-evaporated Ni. The value of PEO−NH_2 density is employed as 1.1 g/cm^3.

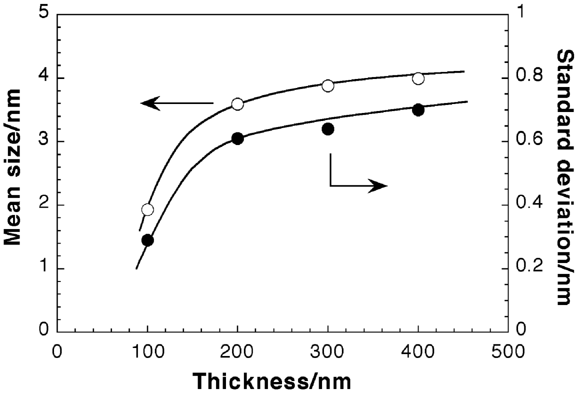

Figure 10. Plots of average diameter (open circle) and standard deviation (closed circle) of NiO particles dispersed in PEO−NH_2 as a function of the thickness of deposited Ni.

to the final composite. Figure 9 shows the correlation between NiO content as measured by TGA and the initial amount of deposited Ni. The dashed line represents the values calculated from an initial amount of deposited Ni and a thickness of the matrix film under the assumption that NiO particles are uniformly dispersed spatially throughout the PEO−NH_2 film.[42] The significant increase in NiO content is observed for the composite as compared with calculated ones. This increase results from purification of the samples, during which the part of the composite soluble in ethanol (free PEO−NH_2 containing no NiO particles) is removed.

As shown in Figure 10, both the average diameters and standard deviations of NiO particles increase with increasing thickness of deposited Ni, indicating that the sizes of NiO particles with relatively narrow distribution are controllable on a nanometer scale by varying the initial amount of deposited Ni. For the sample with initial deposited Ni thickness of 100 nm, the average particle size is very small, while the increase in NiO content is observed after purification (Figure 9). This demonstrates that the localization of NiO particles to form aggregates in the matrix (Figure 8) can occur during early stages of the Ni deposition.

From the above results, the proposed process of formation of the composite into the matrix film is illustrated in Figure 11. Because the vacuum evaporation of Ni was performed at 50 °C, at which the matrix film melts and behaves as a viscous fluid, deposited Ni atoms or clusters (nucleus) can diffuse into bulk phase of the PEO−NH_2 matrix and form nanometer-sized NiO particles through oxidation by residual oxygen. Then, these particles concentrate in some parts of the matrix to form aggregates, presumably due to magnetic effect, during which the amine end groups of the matrix molecule may form a strong coordination bond with NiO particles and have a strong ability to protect the NiO particles from coalescence. When both end groups of one PEO−NH_2 molecule bind to neighboring NiO particles, the mobility of the molecule is highly restricted. This may cause the characteristic nature of the composite, i.e., insolubility in ethanol, and hence the present processes enable us to obtain the composite including well-dispersed NiO particles at high content.

Conclusions

The composites consisting of NiO particles dispersed uniformly in the PEO−NH_2 matrix were obtained by vacuum evaporation of Ni on a molten PEO−NH_2 matrix film followed by purification. The results have shown that the particles have average particle size below 5 nm with relatively narrow size distribution, and the particle size can be controlled by varying the initial amount of deposited Ni. HRTEM observation and XRD analysis indicate an expansion of lattice spacing, which may be due to an increase of oxygen vacancies or distortion in polycrystalline NiO structure with decreas-

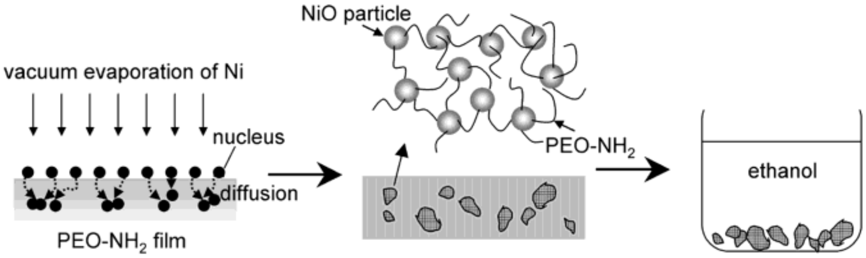

Figure 11. Schematic representation of the formation process of the composites.

ing particle size. It is confirmed by XPS measurements that NiO particles have an interaction with amine end groups of the matrix molecule, which is related to isolation and well-dispercity of NiO particles in the composite. The structure of the matrix molecules in the composite is found to be amorphous, which is thermally stable because the mobility of the molecules is highly restricted due to interaction between the amine end groups and the NiO particles. The composite is soluble in propionic acid to form a clear solution with no evidence for significant aggregation, and the solution is very stable. Cross-sectional TEM observation shows that the dispersed NiO particles localize into some parts of the PEO$-$NH$_2$ film before purification. The anomalous dispersion behavior enables us to obtain the composite involving extensively high content of NiO particles (maximum content: ca. 50 wt %). Thus, the present composite containing nanosized NiO particles will be a potential material for not only providing a favorable system for fundamental investigation of the unique physical properties based on quantum size effect, but also utilizing nanosized NiO particles for various technological applications.

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(42) Calculated line was obtained using following equation: $x = 100\ W_{\mathrm{NiO}}/(W_{\mathrm{NiO}} + t_{\mathrm{PEO}}\ d_{\mathrm{PEO}})$, where x is the NiO contents in the composite (wt %), W_{NiO} is the weight of NiO per unit area (cm^2) calculated using deposited Ni thickness and bulk density (under the assumption that all the deposited Ni was oxidized to NiO), t_{PEO} is the thickness of the PEO$-$NH$_2$ matrix (11 μm), and d_{PEO} is the bulk density of the PEO$-$NH$_2$ matrix (1.1 g cm^{-2}).