

structure of the individual NPs in the Ag/Se-hybrid NP, 20 μL of the NP solution was deposited and dried on carbon-membrane-coated Cu grids in the air and investigated using a JEOL 1200 TEM operating at a 120 kV accelerating voltage.

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- [1] H. S. Nalwa, *Nanostructured Materials and Nanotechnology*, Academic Press, San Diego, CA **2002**.
- [2] V. Rotello, *Nanoparticles: Building Blocks for Nanotechnology*, Kluwer Academic/Plenum Publishers, New York **2004**.
- [3] F. X. Redl, K. S. Cho, C. B. Murray, S. O'Brien, *Nature* **2003**, 423, 968.
- [4] C. F. Landes, S. Link, M. B. Mohamed, B. Nikoobakht, M. A. El-Sayed, *Pure Appl. Chem.* **2002**, 74, 1675.
- [5] J. Panyam, V. Labhsetwar, *Mol. Pharm.* **2004**, 1, 77.
- [6] J. K. Jaiswal, H. Mattoussi, J. M. Mauro, S. M. Simon, *Nature Biotech.* **2002**, 21, 47.
- [7] B. Dubertret, P. Skourides, D. J. Norris, V. Noireaux, A. H. Brivanlou, A. Libchaber, *Science* **2002**, 298, 1759.
- [8] X. Wu, J. Liu, K. N. Haley, J. A. Treadway, J. P. Larson, N. Ge, F. Peale, M. P. Bruchez, *Nature Biotech.* **2003**, 21, 41.
- [9] W. J. Parak, R. Boudreau, M. L. Gros, D. Gerion, D. Zanchet, C. M. Micheel, S. C. Williams, A. P. Alivisatos, C. Larabell, *Adv. Mater.* **2002**, 14, 882.
- [10] C. Bergemann, D. Muller-Schulte, J. Oster, L. a Brassard, A. S. Lubbe, *J. Magn. Magn. Mater.* **1999**, 194, 45.
- [11] B. Gates, B. Mayers, B. Cattle, Y. Xia, *Adv. Funct. Mater.* **2002**, 12, 219.
- [12] I. T. Virlos, J. Mason, D. Schofield, R. F. McCloy, J. M. Eddleston, A. K. Siriwardena, *Scand. J. Gastroentero.* **2003**, 36, 1262.
- [13] X. Y. Gao, J. S. Zhang, L. Zhang, *Adv. Mater.* **2002**, 14, 290.
- [14] R. Shenhar, V. M. Rotello, *Acc. Chem. Res.* **2003**, 36, 549.
- [15] H. Hiramatsu, F. E. Osterloh, *Langmuir* **2003**, 19, 7003.
- [16] D. Ryan, L. Nagle, D. Fitzmaurice, *Nano Lett.* **2004**, 4, 573.
- [17] D. Wang, J. He, N. Rosenzweig, Z. Rosenzweig, *Nano Lett.* **2004**, 4, 409.
- [18] R. Djalali, J. Samson, H. Matsui, *J. Am. Chem. Soc.* **2004**, 126, 7935.
- [19] B. Sadler, A. Wei, *Chem. Commun.* **2002**, 1604.
- [20] J. M. Slocik, D. W. Wright, *Biomacromolecules* **2003**, 4, 1135.
- [21] J. G. Worden, A. W. Shaffer, Q. Huo, *Chem. Commun.* **2004**, 518.
- [22] C. J. Loweth, W. B. Caldwell, X. Peng, A. P. Alivisatos, P. G. Schultz, *Angew. Chem. Int. Ed.* **1999**, 38, 1808.
- [23] C. M. Niemeyer, *Angew. Chem. Int. Ed.* **2001**, 40, 4128.
- [24] D. Zanchet, C. M. Micheel, W. J. Parak, D. Gerion, S. C. Williams, A. P. Alivisatos, *J. Phys. Chem. B.* **2002**, 106, 11 758.
- [25] A. G. Kanaras, Z. X. Wang, A. D. Bates, R. Cosstick, M. Brust, *Angew. Chem. Int. Ed.* **2003**, 42, 191.
- [26] K. K. Caswell, J. N. Wilson, U. H. F. Bunz, C. J. Murphy, *J. Am. Chem. Soc.* **2003**, 125, 13 914.
- [27] K. Hamad-Schifferli, J. J. Schwartz, A. T. Santos, S. Zhang, J. M. Jacobson, *Nature* **2002**, 415, 152.
- [28] X. Y. Gao, T. Gao, L. D. Zhang, *J. Mater. Chem.* **2003**, 13, 6.
- [29] D. Timpel, K. Scheerschmidt, *Phys. Status Solidi A* **1995**, 150, 51.
- [30] K. R. Brown, L. A. Lyon, A. P. Fox, B. D. Reiss, M. J. Natan, *Chem. Mater.* **2000**, 12, 314.
- [31] L. Nagle, D. Fitzmaurice, *Adv. Mater.* **2003**, 15, 933.
- [32] J. H. He, T. Kunitake, A. Nakao, *Chem. Mater.* **2003**, 15, 4401.
- [33] I. Pastoriza-Santos, L. M. Liz-Marzan, *Pure Appl. Chem.* **2000**, 72, 83.

Monodisperse Nanoparticles of Ni and NiO: Synthesis, Characterization, Self-Assembled Superlattices, and Catalytic Applications in the Suzuki Coupling Reaction**

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The synthesis of discrete magnetic nanoparticles is of significant importance because of their applications in multi-terabit in⁻² (1 in = 2.54 cm) magnetic storage devices, ferrofluids, magnetic refrigeration systems, contrast enhancement in magnetic resonance imaging, magnetic carriers for drug targeting, and catalysis.^[1] There have been many attempts to synthesize monodisperse magnetic nanoparticles having controllable particle sizes because their magnetic properties are dependent on the particle size.^[2] Recently, intensive research has been conducted on the organization of nanoparticles to form two-dimensional (2D) and three-dimensional (3D) superlattice structures. These organized nanoparticles exhibit novel physical properties which are derived from their collective interaction,^[3] and are essential for their use in magnetic storage media and electronic devices. The synthesis of highly monodisperse nanoparticles is critical to the formation of large-area superlattices. Recently, there have been several reports on the synthesis of nickel nanoparticles, for example, by sonochemical or thermal decomposition of organometallic precursors,^[4,5]

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chemical reduction,^[6] and electrochemical reduction.^[7] Herein, we report on the synthesis of highly monodisperse nanoparticles of Ni and NiO and their self-assembly into 2D and 3D superlattice structures.

The current synthetic procedure is a modified version of the method developed by our group for the synthesis of monodisperse nanocrystals of metals, metal oxides, and metal sulfides that employs the thermal decomposition of metal-surfactant complexes.^[8] Unless otherwise noted, all reactions were carried out in a dry-argon atmosphere. The overall synthetic procedure is shown in Scheme 1.

In the synthesis, nickel-metal nanoparticles were prepared by the thermal decomposition of Ni-oleylamine complexes. The following procedure describes the synthesis of 7 nm sized nickel nanoparticles. First, the Ni-oleylamine complex was prepared by reacting 0.52 g of nickel(acetylacetonate)₂ [Ni(acac)₂, Aldrich Chemical Co., 95 %] and 2 mL of oleylamine (Aldrich Chemical Co., technical grade, 80 %) at 100 °C under an Ar atmosphere. The resulting metal-complex solution was injected into 5 g of triphenylphosphine (TPP, Aldrich Chemical Co., 99 %) at 215 °C. The color of the solution changed from green to black, indicating that colloidal nanoparticles were generated. The black solution was aged at 200 °C for 30 min, and was then cooled to room temperature. The nanoparticles were precipitated by adding excess ethanol to the solution. The precipitated nanoparticles were retrieved by centrifugation. The yield of the overall synthesis was 60 % based on the amount of Ni(acac)₂. The nanoparticles could easily be redispersed in non-polar organic solvents, such as hexane or toluene. The particle size of the nickel nanoparticles was controlled by using various types of phosphines, which acted as both the solvent and the surfactant. Bulky trioctylphosphine (TOP, 5 mL, Aldrich Chemical Co., 90 %) limited the growth of the particles, and led to the formation of 2 nm sized particles. 5 nm and 7 nm sized spherical nanoparticles were produced by using the less-bulky tributylphosphine (TBP, 5 mL, Aldrich Chemical Co., 97 %) and triphenylphosphine, respectively. As shown in Figure 1, transmission elec-

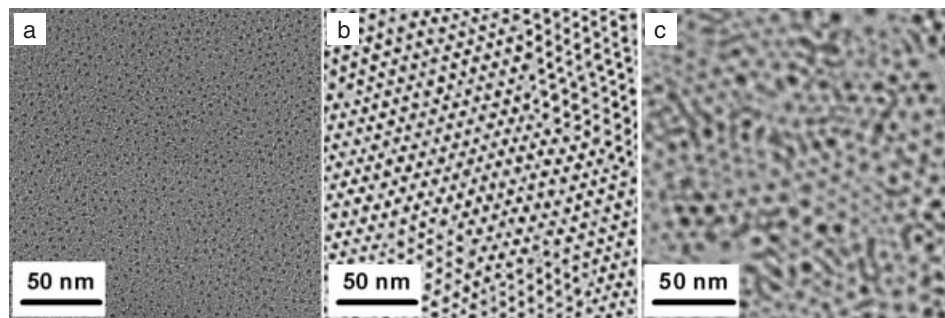


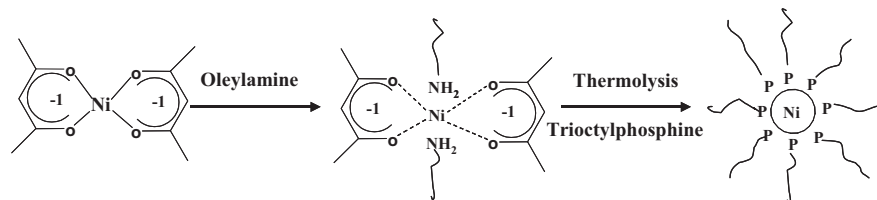
Figure 1. TEM images of a) 2 nm, b) 5 nm, and c) 7 nm sized Ni nanoparticles. The TEM images were obtained on a JEOL 2010 microscope.

tron microscopy (TEM) images reveal that these nickel nanoparticles possess highly monodisperse particle size distributions. These monodisperse nanoparticles were obtained without going through any size-selection process, which is very important for large-scale production.

The X-ray diffraction (XRD) patterns of the nanoparticle powders were collected with a M18XHF-SRA diffractometer equipped with a Cu K α radiation source. The XRD pattern of the 5 nm sized fresh nickel nanoparticles, shown in Figure 2a, shows the face-centered cubic (fcc) structure of nickel.^[9] The peaks are extremely broad, demonstrating that the nanoparticles are nearly amorphous. The electron diffraction pattern showed two diffuse rings, which were indexed as Ni (111) and (220). The XRD pattern after exposing the nanoparticles to air for more than 24 h showed a NiO structure (Fig. 2b), demonstrating that the initially synthesized metallic-nickel nanoparticles were readily oxidized to NiO nanoparticles. The X-ray photoelectron spectroscopy (XPS) spectrum of the nanoparticles after air exposure revealed the NiO electronic structure rather than the metallic-nickel structure, confirming the XRD data.

The self-organization of magnetic nanoparticles to generate 2D and 3D superlattices is very important, both from the viewpoint of fundamental interest in the collective interaction of magnetic particles, as well as for their possible applications in multi-terabit in⁻² magnetic storage media. In order to achieve large-area superlattice formation, the synthesis of highly uniform nanoparticles with a standard deviation of less than 5 % is critical.^[10] There have been several reports on the fabrication of superlattice structures of monodisperse nanoparticles

by slow solvent evaporation. In these processes, several experimental conditions need to be optimized, including the rate of solvent evaporation, the interaction between the nanoparticles, the interaction between the substrate surface and the nanoparticles, and the concentration of the nanoparticles.^[3,6b] In this report, we demonstrate the formation of superlattices using the 5 nm sized monodisperse nickel nanoparticles. As



Scheme 1. Synthesis of nickel-metal nanoparticles by the thermal decomposition of Ni-oleylamine complexes.

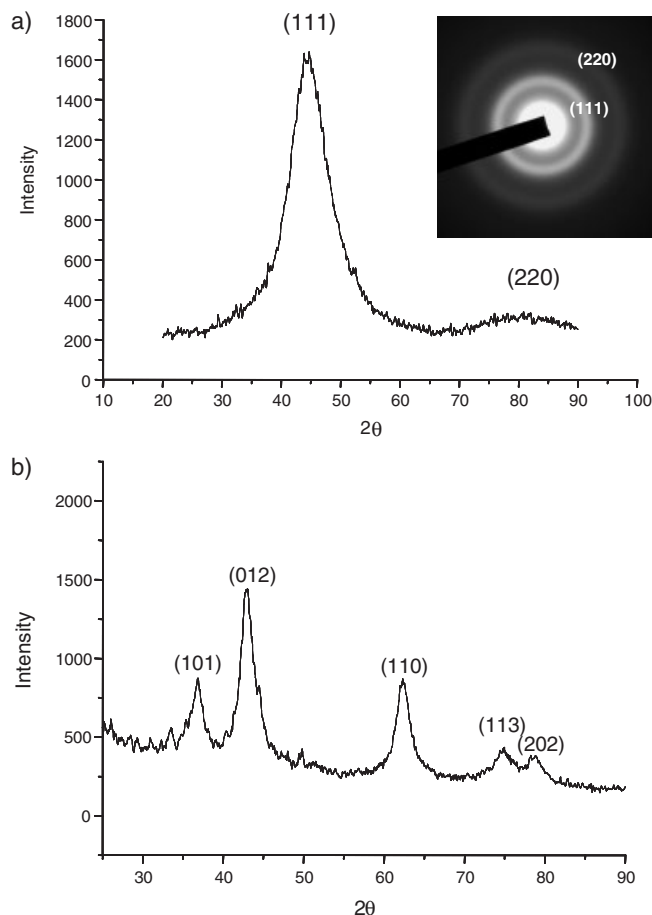


Figure 2. The powder X-ray diffraction (XRD) patterns of a) 5 nm sized fresh Ni nanoparticles and b) 5 nm sized nanoparticles after air exposure. The XRD patterns were obtained on a M18XHF-SRA diffractometer equipped with a Cu K α radiation source. Inset is the electron diffraction pattern obtained on a JEOL 2010 microscope.

shown in Figures 3a,b, we were able to fabricate two different kinds of superlattice structures by controlling the concentration of the 5 nm sized Ni nanoparticles dispersed in toluene. We used carbon-coated copper grids, which are the most frequently used TEM grids, as the substrates for superlattice formation. One drop of Ni nanoparticles dispersed in toluene was put on the grid, and the toluene solvent was slowly evaporated. As the particle concentration increased, the self-assembled structure changed from an initial locally ordered 2D hexagonal close-packed (hcp) structure to a 3D superlattice structure. Excess tributylphosphine was added to the solution in order to induce the formation of superlattice structures over a large area by increasing van der Waals' interactions between the nanoparticles and by decreasing the rates of evaporation of the solvent. This approach is similar to that used in the formation of gold-nanoparticle superlattices using excess dodecanethiol^[11] and the formation of iron oxide nanoparticle superlattices using excess oleic acid.^[8a] As expected, when the concentration of tributylphosphine was increased, multi-layered 3D superlattice structures were generated. Figure 3a

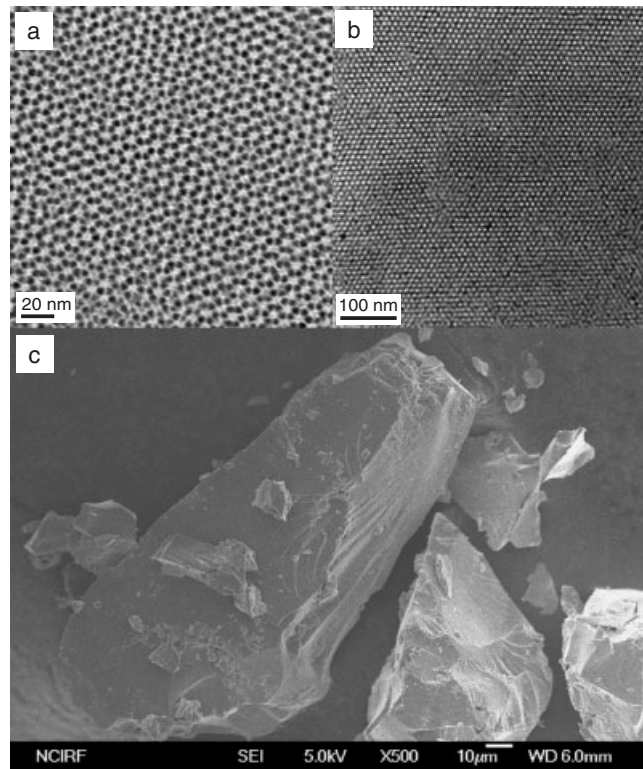


Figure 3. a,b) TEM images of superlattices of 5 nm sized monodisperse Ni nanoparticles. c) Scanning electron micrograph of colloidal crystals of 5 nm sized monodisperse Ni nanoparticles.

shows the TEM image of the superlattice structure having a hexagonal ring pattern, which is similar to the Moiré image obtained by twisting the second hexagonal layer with respect to the first layer.^[12] In this pattern, the nanoparticles in the second layer selectively occupy two-thirds of the interstitial sites generated by the first layer, resulting in a pattern consisting of interconnected six-membered rings. Figure 3b shows the regular 3D hcp structure. These organized self-assembled arrays cover the substrate on a micrometer scale. The 3D self-organization of monodisperse nickel nanoparticles was also observed in the powder form of the nanoparticles prepared by slow evaporation of the toluene solvent. Ordering of the nanoparticles in superlattice structures was characterized using small-angle X-ray scattering (SAXS) measurements. Synchrotron SAXS measurements were performed on the 4C2 beamline at the Pohang Light Source. The primary beam was monochromatized with a coupled Si(111) single crystal at a wavelength of 0.1608 nm (the photon energy of the X-ray was 7.78 keV, with a resolution $\Delta\lambda/\lambda \approx 0.0001$), and the beam was then focused on a detector plane by a bent cylindrical mirror. A 2D charge-coupled device (CCD) camera (Roper Scientific Inc., PI-SCX-2048) was used to collect the scattered X-rays. We used a styrene-ethylene-butylene-styrene (SEBS) block copolymer (with a d -spacing of 32.5 nm) as a periodic calibrant in order to calibrate the image from the 2D CCD camera. Figure 4 shows the SAXS spectra obtained from the Ni

nanoparticles with three different sizes, viz., 2 nm, 5 nm, and 7 nm. The q_{\max} values of the main peaks of (a), (b), and (c) shown in Figure 4 are 1.18 nm^{-1} , 0.93 nm^{-1} , and 0.50 nm^{-1} , corresponding to inter-planar spacings (d_{100}) of 5.76 nm, 6.75 nm, and 11.5 nm, respectively. This is in good agreement with the values obtained based on the particle–particle distances measured from the TEM micrograph shown in Figure 1.

For 2D cubic and hcp structures, the lattice spacing a corresponds to

$$a_{\text{cub}} = \left(\frac{2\pi \sqrt{(h^2+k^2)}}{q_{hk}} \right) \quad (1)$$

$$a_{\text{hex}} = \left(\frac{4\pi \sqrt{(h^2+hk+k^2)}}{\sqrt{3}+q_{hk}} \right) \quad (2)$$

The measured particle–particle distance and the lattice parameters obtained from the cubic and hexagonal close-packed structure models using Equations 1,2 are listed in Table 1. The lattice parameters calculated for the cubic close-packed structure are 5.32 nm/5.76 nm, 6.75 nm, and 11.63 nm for 2 nm, 5 nm, and 7 nm sized particles, respectively, and these

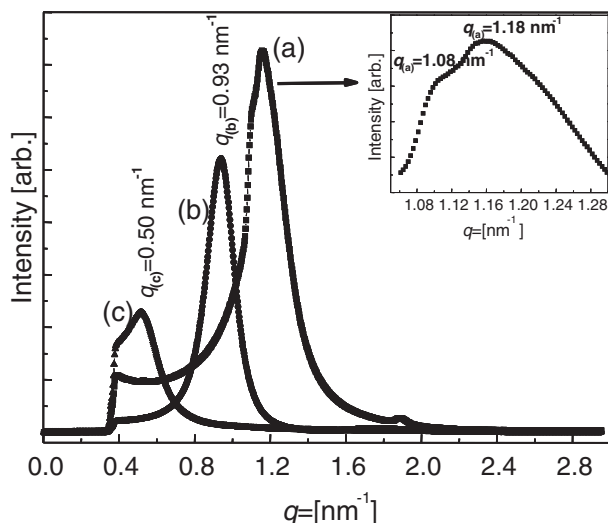


Figure 4. SAXS spectra obtained from a) 2 nm, b) 5 nm, and c) 7 nm NiO nanoparticles in powder form. SAXS measurements were performed at the 4C2 Beamline at the Pohang Light Source.

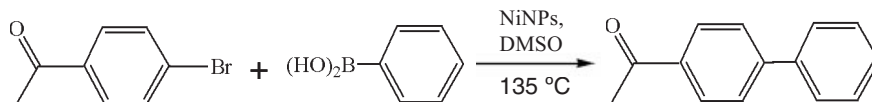
Table 1. The measured particle–particle distances and the calculated lattice parameters obtained from cubic and hexagonal symmetry models.

Particle size [nm]	Measured particle-particle distance [nm]	Calculated lattice parameters [nm]	
		cubic	hexagonal
2	5.7	5.32/5.76	6.14
5	6.8	6.75	7.8
7	11.5	11.63	13.4

calculated values match very well with the measured ones. From these results, it can be concluded that the long-range ordering of the Ni nanoparticle superlattice is as a cubic closed-packed structure. We grew colloidal crystals of 5 nm sized nickel nanoparticles using the three-layer technique developed by Shevchenko et al.^[10f] In brief, 0.6 mL of a colloidal toluene solution of 5 nm sized Ni nanoparticles (2 mg mL^{-1}) was added to a vertically positioned glass tube 20 cm in length and 0.5 cm in diameter, and 3.5 mL of a solvent mixture composed of 1:1 (vol./vol.) of 2-propanol and methanol was added on top of the colloidal solution. The resulting glass tube was kept under static conditions at room temperature for 15 days, and crystallization occurred at the interface. The scanning electron micrograph of the colloidal crystals are shown in Figure 3c.

Colloidal metal nanoparticles have attracted a lot of attention as catalysts for many organic reactions, because they have a characteristic high surface-to-volume ratio and, consequently, a large fraction of the metal atoms are located at the surface and thus available for catalysis.^[13] The palladium-catalyzed cross-coupling reaction of aryl halides with arylboronic acids, often referred to as the Suzuki coupling reaction, is a versatile method for synthesizing unsymmetrical biaryls.^[14] Recently, different colloidal palladium nanoparticles have been employed as catalysts for these coupling reactions.^[15] Very recently, nickel supported on charcoal was used as a catalyst for several coupling reactions, including Suzuki coupling reactions.^[16] We investigated the catalytic activity of the 7 nm sized Ni nanoparticles for the Suzuki cross-coupling reaction shown in Scheme 2. The coupling reaction was carried out using 4-bromoacetophenone and 4-iodoacetophenone as substrates in dimethylsulfoxide (DMSO) at 135°C (Scheme 2). The results of the catalytic reactions revealed that fresh Ni nanoparticles had such good reactivity that even reactions conducted using aryl bromides proceeded with 98 % yield. In contrast, when we tried to reuse the nanoparticles for the catalytic reaction, the yield decreased significantly, to 47 %. We presume that the Ni nanoparticles were significantly oxidized during the reaction.

In order to identify the oxidation state of nickel, X-ray absorption spectroscopy (XAS) measurements at the Ni $L_{2,3}$ -edges were carried out at the Dragon beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Figure 5 shows the Ni $L_{2,3}$ -edge XAS spectra obtained from 2 nm and 5 nm Ni nanoparticles. The spectra are dominated by the large 2p core–hole spin-orbit coupling energy, which divides them into the L_3 and L_2 regions at low and high photon energies, respectively. In contrast to the metallic spectral lineshape of the Ni metal, the spectra of the nanoparticles display an ionic multiplet structure, indicating that the Ni state of the nanoparticles is an ionic Ni oxide state rather than a pure metallic state. The spectrum of the 2 nm particles is nearly identical to that of bulk NiO,^[17] and the ionic multiplet becomes somewhat smeared out in the case of the larger 5 nm sized nanoparticles. This result indicates that Ni is oxidized to form NiO at the surface of the nanoparticles.



Scheme 2. Suzuki cross-coupling reaction of an aryl halide and an arylboronic acid in dimethylsulfoxide.

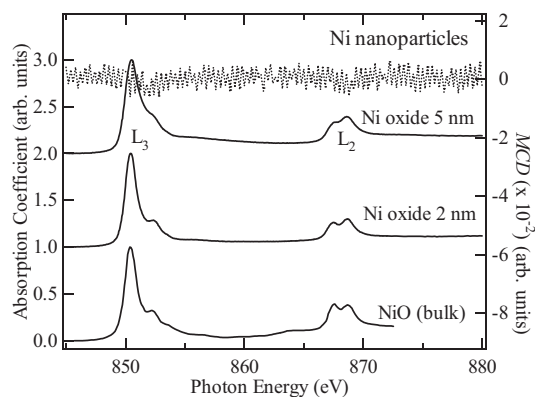


Figure 5. Ni $L_{2,3}$ -edge XAS spectra (solid lines, left axis) of 2 nm and 5 nm NiO nanoparticles compared with that of bulk NiO. The corresponding magnetic circular dichroism (MCD) spectrum (dotted line, right axis) is also presented. The measurements were performed at 100 K. XAS measurements at the Ni $L_{2,3}$ -edges were carried out at the Dragon beamline at the NSRRC in Taiwan.

Thus, the 2 nm Ni nanoparticles are closer to NiO than Ni metal, and the NiO phase dominates in the case of the 5 nm nanoparticles. X-ray magnetic circular dichroism (MCD) measurements using circularly polarized light was performed for the 5 nm particles in order to test the possibility of ferromagnetic ordering. As shown in the figure, there is no observable MCD signal, showing that the nanoparticles have no ferromagnetic ordering, and thus indicating that their oxidation is severe and that even the core is not a pure metallic phase. Magnetic studies of the nanoparticles using a superconducting quantum interference device (SQUID) also confirmed the XAS and MCD results, indicating that the nickel nanoparticles were severely oxidized.

Magnetic studies using a SQUID were performed on the 2 nm and 7 nm sized NiO nanoparticles. The magnetization data obtained for the 2 nm sample during zero-field cooling show paramagnetic behavior at high temperatures before showing a peak at 2 K, which indicates that the 2 nm sample has a blocking temperature of 2 K. For the 7 nm sample, this blocking temperature increases to 5 K (Fig. 6a). The estimated magnetic anisotropy constants are $2.5 \times 10^6 \text{ erg cm}^{-3}$ and $1.0 \times 10^5 \text{ erg cm}^{-3}$ for the 2 nm and

7 nm samples, respectively ($1 \text{ erg} = 1 \times 10^{-7} \text{ J}$). For the sake of comparison, the magnetic anisotropy constant of NiO is $5.0 \times 10^6 \text{ erg cm}^{-3}$.^[18] The blocking temperature behavior is also confirmed by the field dependence of magnetization for the 7 nm sample (Fig. 6b), for which the magnetic hysteresis disappears at temperatures higher than the blocking temperature. Similar behavior is also seen for the 2 nm sample. Before discussing the origin of the superparamagnetic behavior seen in the magnetization data, we note that bulk NiO has an antiferromagnetic transition at 520 K.^[19] Although a pure antiferromagnetic material cannot possibly show superparamagnetic behavior, at least in the bulk form, it is now well known that nanoparticles of antiferromagnetic materials can exhibit such unusual behavior because of the so-called finite size effects, or the modifications of the bulk state due to surface effects.^[20] When we measured the magnetization of the 7 nm sized sample at 2 K, after field cooling from 320 K with a magnetic field of 1 kOe ($1 \text{ Oe} = 79.58 \text{ A m}^{-1}$), the observed magnetization was almost identical to that measured after zero-field cooling (Fig 6b).

In conclusion, we have synthesized monodisperse nanoparticles of Ni and NiO with particle sizes of 2 nm, 5 nm, and 7 nm from the thermal decomposition of Ni-alkylamine complexes, and these nanoparticles subsequently self-assembled to form superlattices with long-range ordering via controlled solvent evaporation. The nanoparticles were successfully used as the catalyst for a Suzuki-coupling reaction. XAS, MCD, and SQUID studies revealed that the initially formed nickel nanoparticles were oxidized to form NiO nanoparticles.

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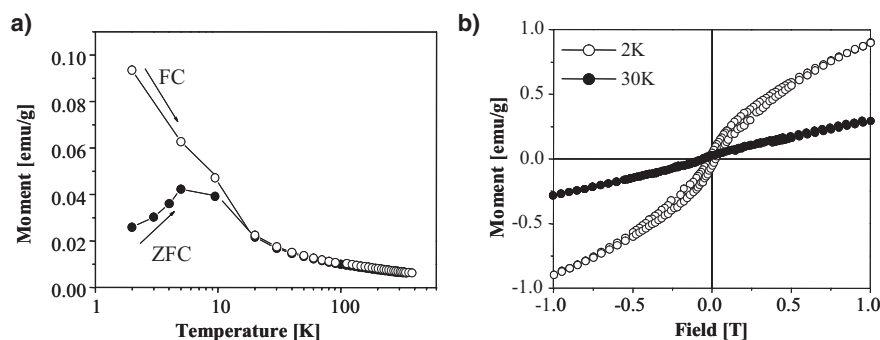


Figure 6. a) Temperature dependence of magnetization measured with 100 Oe ($1 \text{ Oe} = 79.58 \text{ A m}^{-1}$) for 7 nm NiO nanoparticles after zero-field cooling (●) and field cooling (○). b) Field dependence of the magnetization at 2 K and 30 K. Magnetic measurements were performed on a MPMS 5XL Quantum Design SQUID magnetometer.

- [1] a) *Nanoparticles: From Theory to Application* (Ed: G. Schmid), Wiley-VCH, Weinheim, Germany **2004**. b) T. Hyeon, *Chem. Commun.* **2003**, 927. c) *Nanoscale Materials in Chemistry* (Ed: K. J. Klabunde), Wiley, New York **2001**. d) T. Sugimoto, *Monodispersed Particles*, Elsevier, Amsterdam, The Netherlands **2001**. e) R. C. O'Handley, *Modern Magnetic Materials: Principles and Applications*, Wiley, New York **2000**. f) V. E. Fertman, *Magnetic Fluids Guidebook: Properties and Applications*, Hemisphere, New York **1990**. g) S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* **2000**, 287, 1989. h) F. V. Mikulec, M. Kuno, M. Bennati, D. A. Hall, R. G. Griffin, M. G. Bawendi, *J. Am. Chem. Soc.* **2000**, 122, 2532. i) S.-W. Kim, S. U. Son, S. S. Lee, T. Hyeon, Y. K. Chung, *Chem. Commun.* **2001**, 2212.
- [2] a) S. Sun, C. B. Murray, *J. Appl. Phys.* **1999**, 85, 4325. b) S. Sun, S. Anders, T. Thomson, J. E. E. Baglin, M. F. Toney, H. F. Hamann, C. B. Murray, B. D. Terris, *J. Phys. Chem. B* **2003**, 107, 6831. c) S. Sun, H. Zeng, *J. Am. Chem. Soc.* **2002**, 124, 8204. d) S.-J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char, T. Hyeon, *J. Am. Chem. Soc.* **2000**, 122, 8581. e) F. Dumestre, B. Chaudret, C. Amiens, P. Renaud, P. Fejes, *Science* **2004**, 303, 821. f) F. Dumestre, B. Chaudret, C. Amiens, M. Respaud, P. Fejes, P. Renaud, P. Zurcher, *Angew. Chem. Int. Ed.* **2003**, 42, 5213. g) F. Dumestre, B. Chaudret, C. Amiens, M.-C. Fromen, M.-J. Casanove, M. Respaud, P. Zurcher, *Angew. Chem. Int. Ed.* **2002**, 41, 4286. h) J. Park, B. Koo, Y. Hwang, C. Bae, K. An, J.-G. Park, H. M. Park, T. Hyeon, *Angew. Chem. Int. Ed.* **2004**, 43, 2282. i) H. D. Jang, D. W. Hwang, D. P. Kim, H. C. Kim, B. Y. Lee, I. B. Jeong, *J. Ind. Eng. Chem. (Seoul, Repub. Korea)* **2003**, 9, 407.
- [3] a) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Annu. Rev. Mater. Sci.* **2000**, 30, 545. b) C. P. Collier, T. Vossmeier, J. R. Heath, *Annu. Rev. Phys. Chem.* **1998**, 49, 371. c) S. Sun, S. Anders, H. F. Hamann, J.-U. Thiele, J. E. E. Baglin, T. Thomson, E. E. Fullerton, C. B. Murray, B. D. Terris, *J. Am. Chem. Soc.* **2002**, 124, 2884. d) F. X. Redl, K.-S. Cho, C. B. Murray, S. O'Brien, *Nature* **2003**, 423, 968. e) F. Dumestre, B. Chaudret, C. Amiens, P. Renaud, P. Fejes, *Science* **2004**, 303, 821. f) Y. Lalatonne, J. Richardi, M. P. Pileni, *Nat. Mater.* **2004**, 3, 121. g) N. Feltin, M. P. Pileni, *Langmuir* **1997**, 13, 3927. h) A. T. Ngo, M. P. Pileni, *Adv. Mater.* **2000**, 12, 276. i) A. T. Ngo, M. P. Pileni, *J. Phys. Chem. B* **2001**, 105, 53. j) N. Moumen, M. P. Pileni, *Chem. Mater.* **1996**, 8, 1128. k) I. Lisiecki, P.-A. Albouy, M. P. Pileni, *Adv. Mater.* **2003**, 15, 712. l) E. V. Shevchenko, D. V. Talapin, H. Schnabegger, A. Kornowski, O. Festin, P. Svedlindh, M. Haase, H. Weller, *J. Am. Chem. Soc.* **2003**, 125, 9090. m) E. V. Shevchenko, D. V. Talapin, A. Kornowski, F. Wiekhorst, J. Kötztler, M. Haase, A. L. Rogach, H. Weller, *Adv. Mater.* **2002**, 14, 287.
- [4] Y. Koltypin, A. Fernandez, T. C. Rojas, J. Campora, P. Palma, R. Prozorov, A. Gedanken, *Chem. Mater.* **1999**, 11, 1331.
- [5] a) T. O. Ely, C. Amiens, B. Chaudret, *Chem. Mater.* **1999**, 11, 526. b) N. Cordente, M. Respaud, F. Senocq, M.-J. Casanove, C. Amiens, B. Chaudret, *Nano Lett.* **2001**, 1, 565. c) D. de Caro, J. S. Bradley, *Langmuir* **1997**, 13, 3067.
- [6] a) Y.-P. Sun, H. W. Rollins, R. Guduru, *Chem. Mater.* **1999**, 11, 7. b) C. B. Murray, S. Sun, H. Doyle, T. Betley, *MRS Bull.* **2001**, 985.
- [7] M. P. Zach, R. M. Penner, *Adv. Mater.* **2000**, 12, 878.
- [8] a) T. Hyeon, S. S. Lee, J. Park, Y. Chung, H. B. Na, *J. Am. Chem. Soc.* **2001**, 123, 12798. b) T. Hyeon, Y. Chung, J. Park, S. S. Lee, Y.-W. Kim, B. H. Park, *J. Phys. Chem. B* **2002**, 106, 6831. c) S.-W. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang, T. Hyeon, Y. W. Kim, *Nano Lett.* **2003**, 3, 1289. d) J. Joo, T. Yu, Y.-W. Kim, H. M. Park, F. Wu, J. Z. Zhang, T. Hyeon, *J. Am. Chem. Soc.* **2003**, 125, 6553.
- [9] B. D. Cullity, S. R. Stock, *Elements of X-ray Diffraction*, 3rd ed., Prentice Hall, Englewood Cliffs, NJ **2001**.
- [10] a) S. Stoeva, K. J. Klabunde, C. M. Sorensen, I. Dragieva, *J. Am. Chem. Soc.* **2002**, 124, 2305. b) S. Stoeva, B. L. V. Prasad, S. Uma, P. K. Stoimenov, V. Zaikovski, C. M. Sorensen, *J. Phys. Chem. B* **2003**, 107, 7441. c) M. Chen, D. E. Nikles, *Nano Lett.* **2002**, 2, 211. d) Z. L. Wang, *Adv. Mater.* **1998**, 10, 18. e) A. L. Rogach, D. V. Talapin, E. V. Shevchenko, A. Kornowski, M. Haase, H. Weller, *Adv. Funct. Mater.* **2002**, 12, 653. f) E. Shevchenko, D. Talapin, A. Kornowski, F. Wiekhorst, J. Kötztler, M. Haase, A. L. Rogach, H. Weller, *Adv. Mater.* **2002**, 14, 287. g) H. Weller, *Philos. Trans. R. Soc. London, Ser. A* **2003**, 361, 229. h) E. V. Shevchenko, D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, H. Weller, *J. Am. Chem. Soc.* **2002**, 124, 11480.
- [11] X. M. Lin, H. M. Jaeger, C. M. Sorensen, K. J. Klabunde, *J. Phys. Chem. B* **2001**, 105, 3353.
- [12] G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fiévet-Vincent, F. Fiévet, *Chem. Mater.* **2003**, 15, 486.
- [13] a) Special issue on "Recoverable Catalysts and Reagents", *Chem. Rev.* **2002**, 102, 3215. b) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, 102, 3757. c) B. F. G. Johnson, *Coord. Chem. Rev.* **1999**, 190-192, 1269. d) S. U. Son, S. I. Lee, Y. K. Chung, S.-W. Kim, T. Hyeon, *Org. Lett.* **2002**, 4, 277. e) K. S. Weddle, J. D. Aikin, R. G. Finkel, *J. Am. Chem. Soc.* **1998**, 120, 5653. f) Y. Li, X. M. Hong, D. M. Collard, M. A. El-Sayed, *Org. Lett.* **2000**, 2, 2385. g) M. Zhao, R. M. Crooks, *Angew. Chem. Int. Ed.* **1999**, 38, 364. h) H. Bönemann, W. Brijoux, K. Siepen, J. Hormes, R. Franke, J. Pollmann, J. Rothe, *Appl. Organomet. Chem.* **1997**, 11, 783. i) Y. Shiraishi, N. Toshiya, *J. Mol. Catal. A: Chem.* **1999**, 141, 187. j) M. Beller, H. Fischer, K. Kühlein, C.-P. Reisinger, W. A. Herrmann, *J. Organomet. Chem.* **1996**, 520, 257. k) M. T. Reetz, R. Breinbauer, K. Wanninger, *Tetrahedron Lett.* **1996**, 37, 4499. l) M. T. Reetz, E. Westermann, *Angew. Chem. Int. Ed.* **2000**, 39, 165. m) N. Toshiyama, Y. Shiraishi, T. Teranishi, M. Miyake, T. Tominaga, H. Watanabe, W. Brijoux, H. Bönemann, G. Schmid, *Appl. Organomet. Chem.* **2001**, 15, 178.
- [14] a) N. Miyaoura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457. b) A. Suzuki, *J. Organomet. Chem.* **1999**, 576, 147. c) B. I. Alo, A. Kandil, P. A. Patil, M. J. Sharp, M. A. Siddiqui, V. Snieckus, P. D. Josephy, *J. Org. Chem.* **1991**, 56, 3763. d) J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, 122, 4020. e) J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, 121, 9550. f) J. P. Wolfe, S. L. Buchwald, *Angew. Chem. Int. Ed.* **1999**, 38, 2413. g) D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, 120, 9722. h) C. Zhang, J. Huang, M. T. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, 64, 3804. i) G. A. Grasa, A. C. Hillier, S. P. Nolan, *Org. Lett.* **2001**, 3, 1077.
- [15] a) M. T. Reetz, E. Westermann, *Angew. Chem. Int. Ed.* **2000**, 39, 165. b) Y. Li, M. A. El-Sayed, *J. Phys. Chem. B* **2001**, 105, 8938. c) M. T. Reetz, G. Lohmer, *Chem. Commun.* **1996**, 1921. d) M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed.* **1998**, 37, 481. e) S. Klingelhöfer, W. Heitz, A. Greiner, S. Oestreich, S. Förster, M. Antonietti, *J. Am. Chem. Soc.* **1997**, 119, 10116.
- [16] B. H. Lipshutz, S. Tasler, W. Chrisman, B. Spliethoff, B. Tesche, *J. Org. Chem.* **2003**, 68, 1177.
- [17] M. A. van Veenendaal, S. W. Sawatsky, *Phys. Rev. B: Condens. Matter Phys.* **1994**, 50, 11326.
- [18] H. Kondo, *J. Phys. Soc. Jpn.* **1960**, 15, 1970.
- [19] S. Chikazumi, *Physics of Ferromagnetism*, 2nd ed., Oxford University Press, Oxford, UK **1997**.
- [20] R. H. Kodama, S. A. Makhlof, A. E. Berkowitz, *Phys. Rev. Lett.* **1997**, 79, 1393.