# Electronic Supplementary Information

## Low Temperature Solventless Synthesis and Characterization of Ni and Fe Magnetic Nanoparticles

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## Synthesis of metal NPs

The reduction with $CaH_2$ was carried out following a method described elsewhere.[1] Briefly, nickel(II) acetylacetonate, ($Ni(acac)_2$, Nacalai Tesque, 99%), and one-weight excess of $CaH_2$ (Aldrich, 95%) were finely ground in a $N_2$-filled glove box and sealed in an evacuated Pyrex tube (length of ~15 cm and inner diameter of 8 mm). We inserted the sample tubes directly into a preheated furnace and kept them at constant reaction temperatures of 140 °C, 200 °C, 250 °C and 300 °C for 6 hours. In addition to these, various reaction temperatures and reaction times were used to study their influence on formation of NPs (see ESI Fig. S2). Byproducts such as CaO produced during the reduction and residual $CaH_2$ were removed by washing with a methanol solution of $NH_4Cl$ (0.3 M, Wako, 99,5%) under constant sonication for 15 minutes, followed by washing with methanol for several times in open air. The synthesis of metallic Fe NPs was carried out in the same way, starting with iron(III) acetylacetonate ($Fe(acac)_3$, Nacalai Tesque, 99%).

## Characterization Methods

Powder X-ray diffraction (XRD) measurements were performed with Bruker D8 operating with Cu Kα radiation (λ = 1.54 Å) with 40 kV beam voltage and 40 mA current. Patterns were collected in a $2\theta$ range from 30° to 80° with a step of 0.02° and the exposure time of 1 sec. To estimate the crystallite size of the NPs, we made a full-with-at-half-maximum (FWHM) peak fit for the (111) peak (with TOPAS),[2] and applied the Scherrer formula, where crystallite size (nm) = $K*\lambda/\beta*\cos\theta$, where $K$, $\lambda$, $\beta$ and $\theta$ represents shape factor, X-ray wavelength, line broadening at half the maximum intensity and the Bragg angle, respectively. Elemental mapping was performed by using a JEOL JEM 2200FS attached with an Energy Dispersive X-ray analyzer JED 2300T. TEM samples were prepared by dropping solution methanol suspension of the NPs on to a carbon-coated Cu grid. Magnetic properties were characterized by using a Physical Properties Measurement System (PPMS, Quantum Design PPMS-9RST) with a vibrating sample magnetometer (VSM) attachment. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center by using a Micro Coder JM-10.[3]

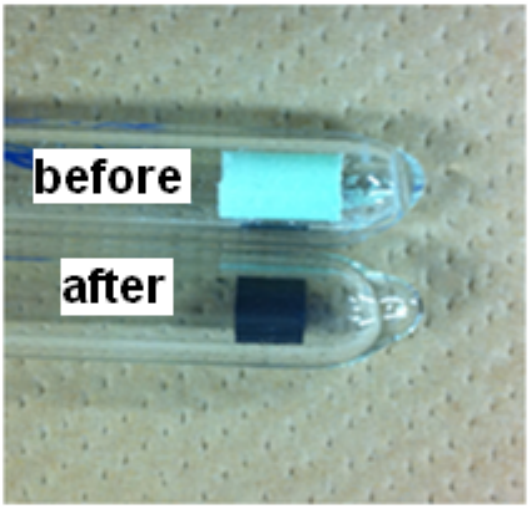


**Fig. S1** A photo of the samples before (light green) and after (black) reduction reaction of $Ni(acac)_2$ with $CaH_2$ at 300 °C for 6 hours. The aim of the photo is to show the color change upon reduction. Note that there is no apparent volume change; the lower sample after reduction was made from a different batch.

It is known that organic ligands have an ability to reduce transition metal ions at 800 °C.[4] In order to confirm that reduction without $CaH_2$ does not take place at 300 °C, which is the highest temperature used in this work, we carried out experiments only with $Ni(acac)_2$. After the heat treatment at 300 °C, we found that the sample color stayed light green indicating the existence of unreduced $Ni^{2+}$ ions and no hydrocarbon pyrolysis, signifying that $Ni(acac)_2$ is essentially left intact (see Fig. S2 in ESI). The result indicates that the use of $CaH_2$ is essential in order to synthesize metallic Ni NPs at lower temperatures than 300 °C.

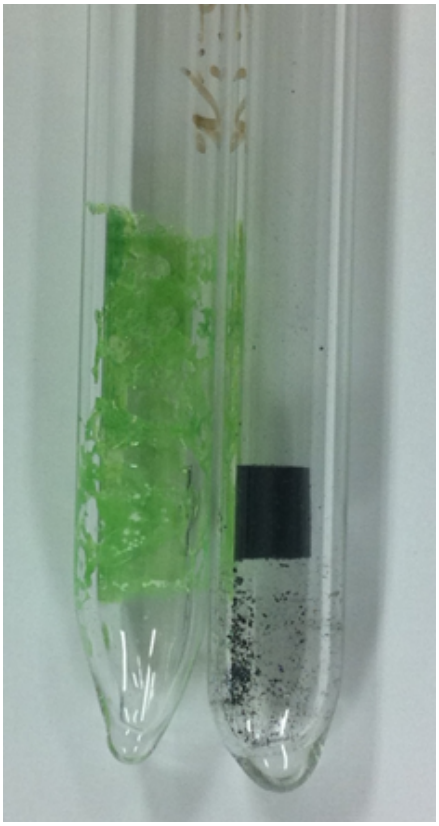

**Fig. S2** A photo of nickel salt without (left) and with (right) $CaH_2$ after a heat-treatment at 300 °C for a few hours. Light green color and black color indicate presence of $Ni^{2+}$ and $Ni^0$, respectively.

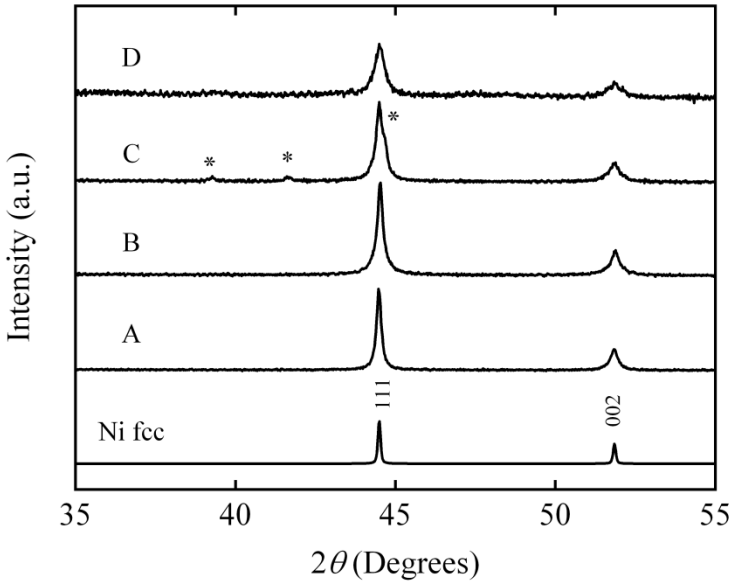


**Fig. S3** Enlargement of powder XRD patterns; A, B, C and D represent the samples prepared with heat-treatment for 6 hours at 140 °C, 200 °C, 250 °C and 300 °C, respectively. Reference XRD pattern of bulk Ni with fcc lattice structure is also shown for comparison (bottom).[5] Asterisk(*) represents hcp lattice structure peaks position.

Shown in Fig. S3 is the enlarged plot of (111) and (002) reflections, the peak width of which shows a significant reaction time dependence. To estimate the crystallite size, the (111) diffraction peak was fitted with a Pseudo-Voigt function by the TOPAS[2] program and then the crystallite size calculated using the Scherrer formula. The resulting crystallite sizes are plotted in Fig. 1(b). This tendency was also confirmed by additional experiments with different reaction temperatures and time as shown in ESI on Fig. S4 ESI. At 250 °C, we observed weak additional diffraction peaks that could be assigned to nickel's hexagonal close packed (hcp) structure with lattice constants of a = 2.540(5) Å and c = 4.222(1) Å. Consistently, it has been reported that in a temperature range of 240 °C to 260 °C, both hcp/fcc phases yield.[6] These lattice constants differ from the bulk values, but are close to those of the previously reported hcp NPs (a = 2.649(1) Å c = 4.335(7) Å) obtained by thermal decomposition of $Ni(acac)_2$ in alkylamines[6] and to those of the evaporated films of hcp-Ni (a = 2.622 Å and c = 4.321 Å).[7] Another explanation for the presence of the hcp phase is formation of nickel carbide ($Ni_3C$) at reaction conditions of 250°C under flowing hydrogen gas for 85 hours with lattice constance of a = 2.6449 Å and c = 4.3296 Å.[8] Although $Ni_3C$ forms an ordered superstructure of interstitial carbon in an hcp-Ni lattice and its structure can be

approximated by a hexagonal subcell, that is nearly identical in size to hcp-Ni. But currently the lattice parameters are closer to hcp Ni phase.

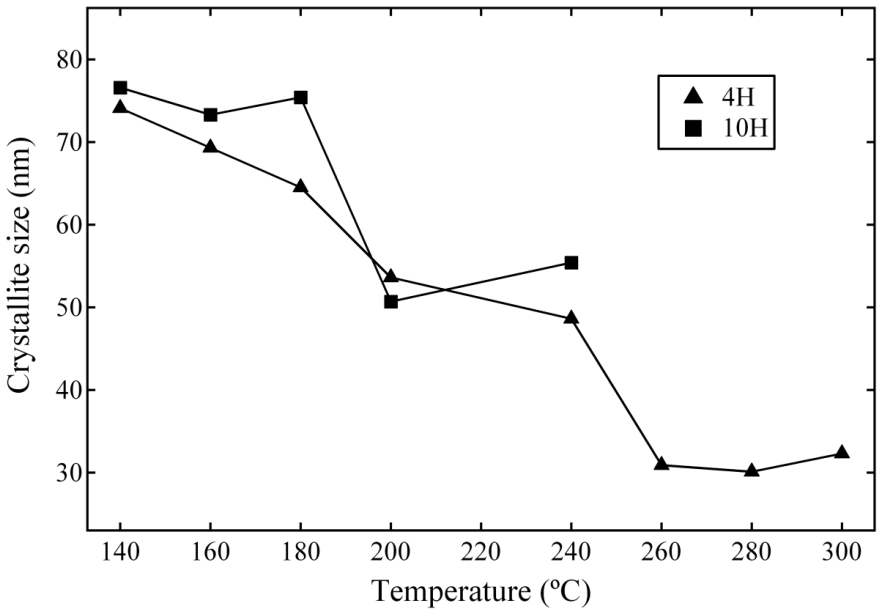


**Fig. S4** Plot of crystallite sizes of Ni NPs synthesized under various conditions.

We placed all samples, before heating with $CaH_2$, into a preheated furnace in order to allow fast heating of the sample, which is the main reason for smaller particle sizes at higher reaction temperatures. Heating at slower rates should result in crystal growth and Otswald ripening competeing with nucleation, but fast heating to a higher temperature results in more nucleation sites to compete with growth.

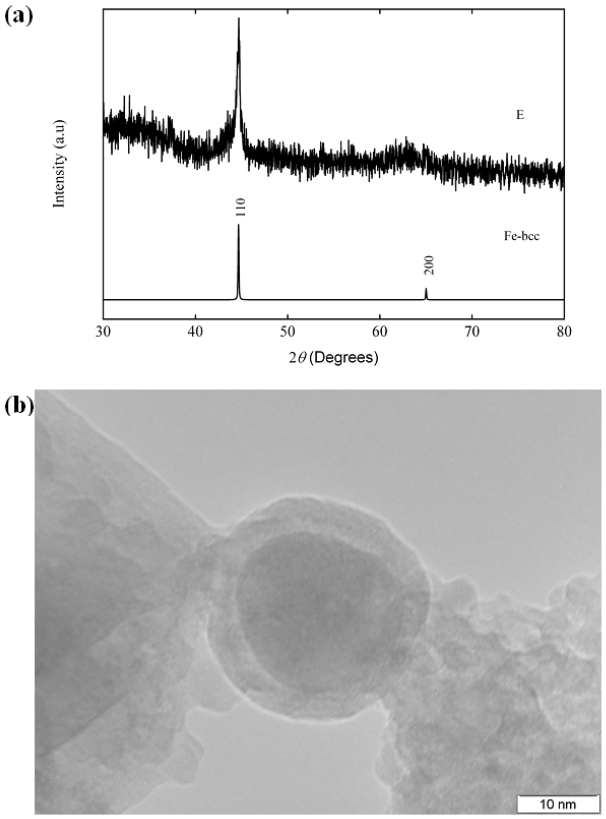


**Fig. S5** (a) XRD pattern of the sample prepared by the reaction with $Fe(acac)_3$ and $CaH_2$ at 300 °C for 6 hours. Reference XRD pattern of iron with bcc lattice structure[5] is also shown for comparison. (b) TEM image of the same sample.

In order to investigate if our method is applicable also to other transition metal salts, we carried out reduction reactions with iron(III) acetylacetonate as a precursor. After treatment at 300 °C for 6 hours the sample colour changed from dark red ($Fe^{3+}$) to black again, again suggestive of metallic iron ($Fe^0$). Fig. S6(a) shows a powder XRD pattern of the sample together with that of a bulk iron reference.[5] The observed peaks could be assigned to {220} and {200} planes of body-centered cubic (bcc)-iron[5] with a lattice constant of a = 2.8665(4) Å. Fig. S6(b) shows a TEM image of the same sample. We can see that a spherical Fe NP (dark core) is surrounded by a light gray shell. The gray shell is expected to be a carbon coated since metallic Fe is known to have similar

catalytic activities like Ni.[9] This carbon layer probably accounts for the Fe metal NP's stability in air against oxidation.

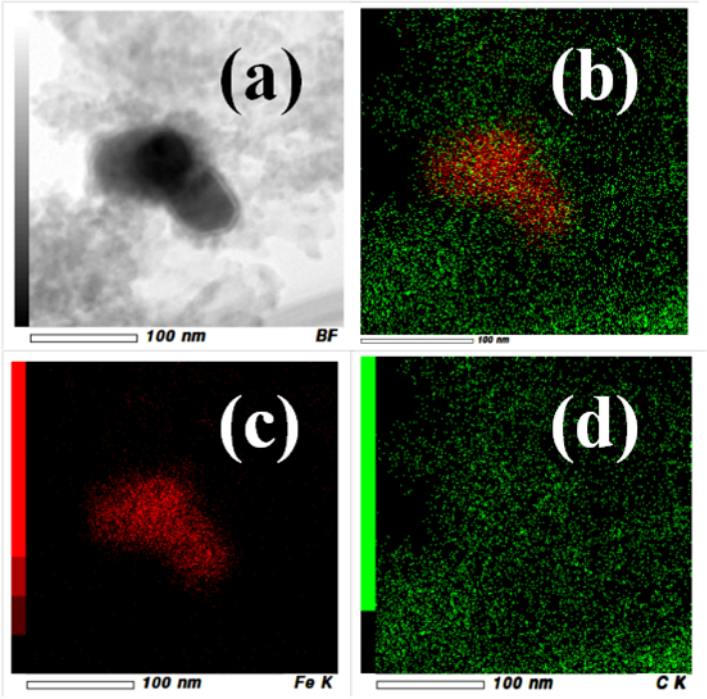


**Fig. S6** (a) TEM image of the sample, (b)Elemental mapping overlay of the sample, where Fe NPs core (red) are surrounded with carbon shell (green), (c) Fe mapping and (d) C mapping of the same position.

**Table S1. Lattice parameter (a) (fcc phase), crystallite size, $M_s$ and of $H_c$ at 300 K of the samples and reference; A, B, C and D represent the samples heat-treated for 6 hours at 140 °C, 200 °C, 250 °C and 300 °C, respectively.**

| Sample code | a (Å) | Crystallite size (nm) | $M_s$ (emu/g) | $H_c$ (Oe) |
|---|---|---|---|---|
| A | 3.526(5) | 61.4(5) | 54 | 142 |
| B | 3.520(15) | 41.7(6) | 50 | 127 |
| C | 3.520(16) | 37.5(8) | 41 | 129 |
| D | 3.510(6) | 32.5(6) | 19 | 100 |
| Bulk Ni[a)] | 3.523 | – | – | – |

[a)]Lattice parameter of bulk nickel with the fcc structure.[5]

**Table S2. Elemental analysis of the samples; A, B, C, and D represents the samples heat-treated for 6 hours at 140 °C, 200 °C, 250 °C and 300 °C, respectively. H (%), C (%) and N (%) stands for mass percentage of hydrogen, carbon and nitrogen, respectively.**

| Sample code | H (%) | C (%) | N (%) |
|---|---|---|---|
| A | 0.46 | 0.49 | 0 |
| B | 0.32 | 0.76 | 0 |
| C | 0.25 | 1.79 | 0 |
| D | 1.16 | 8.61 | 0.18 |

**References for Electronic Supplementary Information**

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