Supporting Information

Size-induced Structural Phase Transition at ~6.0 nm from Mixed fcc-hcp to Purely fcc Structure in Monodispersed Nickel Nanoparticles

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**Synthesis of nickel nanoparticles** Thermal decomposition method was used to synthesize the nanoparticles as detailed in ref. [16]. Briefly, 1 ml (i.e. 2.24 mM) of preheated (215 °C) trioctylphosphine (TOP) (90% Aldrich) was added in the already degassed (at 100 °C for 30 min) solution of 1.02 g nickel acetylacetonate (95% Aldrich) and 8 ml oleylamine (70% Aldrich). The resulting solution was further heated at 220 °C for 2 h under argon atmosphere. This led to black precipitate of nickel nanoparticles (NPs). Solution was then cooled to 27 °C, and centrifuged by adding ethanol (99.9% Jiangsu Huaxi) to extract and wash the nanoparticles. Washing was done four times. Similar procedures were followed for 2 ml, 3 ml, 5 ml, 8 ml, 10 ml and 12 ml of TOP at fixed (8 ml) OAm; their TEM size 10.1 nm, 9.0 nm, 7.1 nm, 6.0 nm, 4.0 nm and 3.8 nm, respectively, denoted these samples.

**X-ray Diffraction (XRD)** The Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (0.154 nm) in the angle range 30-90° was used for laboratory method of XRD measurements of the samples in powder form; X-rays were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector).

**Transmission electron microscopy (TEM)** Nanoparticle images were recorded using transmission electron microscopy (TECHNAI-20-G²) by drop-casting the well-sonicated solution of a few milligrams of nanoparticles dispersed in about 5 ml ethanol on carbon-coated TEM grids. TEM was operated at 120 keV. At least 200 particles were analyzed per sample to obtain a representative size distribution.

**Sample preparation for X-ray absorption (XAS) experiment** The monodispersed Ni NP samples of appropriate weight, estimated to obtain a reasonable edge jump were taken in powder form. Each of them was mixed thoroughly with cellulose powder to obtain total weight of approximately 100 mg to make 2.5 mm thick homogenous pellets of 12.5 mm diameter using an automated hydraulic press. This is to avoid thickness effects (i.e., self-
absorption\textsuperscript{50} and satisfaction of the condition $\Delta \mu x \leq 1$ for the good absorption edge steps, where $\Delta \mu$ is the step in the absorption coefficient $\mu(E)$ value at the absorption edge and $x$ is thickness of the sample pellet.

**XAS experiment** X-ray absorption measurements for Ni K edge of the monodispersed NC Ni samples in the above pellet forms were carried out at the scanning extended X-ray absorption fine structure (EXAFS) beamline (BL-9) at the INDUS-2 synchrotron radiation source (2.5 GeV, 100 mA) of the Raja Ramanna Centre for Advanced Technology, Indore, India\textsuperscript{51}. The beamline covers a photon energy range of 4-25 KeV and has a resolution of 10,000 at 10 KeV. The data collection uses a double crystal monochromator (DCM) with a Rh/Pt coated cylindrical pre-mirror for vertical collimation of the beam and a similar post-mirror placed upside down for horizontal focusing of the beam. Second crystal of the DCM, which is a sagittal cylinder with radius of curvature in range of 1.28 - 12.91 meter, provides horizontal focusing to the beam. For measurements in transmission mode, sample was placed between two ionization chamber detectors. First detector measures the incident flux ($I_0$) and second detector measures the transmitted intensity ($I_t$). From these intensities the absorbance of the sample was determined as a function of energy. The X-ray absorption spectra of the samples for Ni K edge were recorded in the energy range 8280 - 8900 eV to cover both the X-ray absorption near-edge structure (XANES) and EXAFS regions. Five scans were obtained per sample using 15 minute scans at a step size of 1.0 eV.

**Fullprof Rietveld fitting of XRD**

The nearest-neighbor NN bond distance of 2.665 Å in hcp and 2.5095 Å in fcc nickel of literature value in bulk form comes to near 2.60 - 2.64 Å and 2.49 - 2.51 Å on nanostructuring in the present samples, showing significant change in the (local) crystal structure. Coordination number for both fcc and hcp is 12.
Figure S1 XRD patterns of (a) 4 nm (Ni37), (b) 6.0 nm (Ni38), (c) 7.1 nm (Ni36), (d) 9.0 nm (Ni35) and (e) 10.1 nm (Ni34) nickel nanoparticle samples along with Rietveld fitted (red) curve, difference (blue) curve and Bragg peak positions (vertical lines) of fcc and hcp structure of nickel.
Theory of XAS When an x-ray is absorbed by a core-level electron with a binding energy, a photoelectron with wave number $k$ is created and knocks out of the absorbing atom. Absorption takes place only when the photoelectron state, with a quantum state at exactly the right energy, and also with the right angular momentum, is available. When there is no available state, there will be no absorption from that core level. Since the absorbing atom has its neighbors in the lattice, the photoelectron is scattered from the electrons of this neighboring atom, and the scattered photoelectron can return to the absorbing atom. While the absorption coefficient depends on whether there is an available electronic state at the right energy and momentum, presence of the photoelectron scattered back from the neighboring atom will alter the absorption coefficient.

X-ray absorption is thus a transition between two states: an initial state $\langle i \mid$ (having an X-ray photon, a core electron and no photoelectron) to a final state $\mid f \rangle$ (of no X-ray photon, a core hole and a photoelectron), and its coefficient $\mu(E)$ is described by the Fermi’s Golden rule

$$\mu(E) \propto |\langle i \mid \mathbf{H} \mid f \rangle|^2,$$

where $\mathbf{H}$ is the interaction term that comprises the quantized vector potential $\mathbf{A}$ of the theory of radiation. This can be reduced to a term that is proportional to $e^{ikr}$, where $k$ is the magnitude of wave vector and $r$ is the magnitude of position vector in real space of the photoelectron. The initial state is a tightly bound core-level that can be approximated by delta function, say a 1s level for atomic number $Z$ extends to around $a_0/Z$, where $a_0$ is the Bohr radius (~0.529 Å). The change in final state is just the wave-function of the scattered photoelectron, $\Psi_{\text{scat}}(r)$.

Scattering-path amplitude $f_i^{\text{eff}}(k)$ and phase $\delta_i(k)$ of the photoelectron are dependent on $Z$ of the neighboring atom, where $i$ stands for $i^{th}$ shell. As a result, EXAFS is proportional to the amplitude of the scattered photoelectron at the absorbing atom. This consideration for one pair of absorbing atom and scattering atom is summed up in the total EXAFS from a sample.
to average over millions of atom pairs. Now, even if neighboring atoms are of the same type as absorbing atoms, the thermal and static disorder in the bond distances give a range of distances that will affect the EXAFS. This gives rise to the factor, \( e^{-2k^2\sigma_i^2} \), where \( \sigma_i^2 \) is the mean-square deviation in the position of the \( i \)th atom at an effective half-path-length or the interatomic distance for single-scattering paths, \( r_i \). In addition, other conduction electrons, phonons, and so on also scatter the outgoing photoelectron inelastically. This is described by \( e^{-2r/\lambda_i(k)} \) with \( \lambda_i(k) \) as mean free path of the photoelectron.

**Table S1** Lattice parameters obtained from Fullprof Rietveld fittings of XRD of samples

| Sample Name (Phase) | Wyckoff Position (x, y, z) | Thermal factor (\( \beta \)) | Occupancy | Phase Fraction | Lattice Parameter (Å) | Volume of unit cell (Å\(^3\)) | Bond length (Å) |
|--------------------|----------------------------|-----------------------------|-----------|----------------|----------------------|-------------------------------|----------------|
| Ni31 [3.8 nm] (FCC) | 0, 0, 0                    | 0                           | 1         | 3.48%          | a = b = c = 3.5330     | 44.099                        | 2.498          |
| Ni31 (HCP)         | 1/3,2/3,1/4                | 0                           | 1         | 96.52%         | a = b = 2.64, c = 4.22 | 25.471                        | 2.640          |
| Ni37 [4.0 nm] (FCC) | 0, 0, 0                    | 0                           | 1         | 11.98%         | a = b = c = 3.5390    | 44.324                        | 2.502          |
| Ni37 (HCP)         | 1/3,2/3,1/4                | 0                           | 1         | 88.02%         | a = b = 2.6, c = 4.0  | 23.417                        | 2.600          |
| Ni38 [6.0 nm] (FCC) | 0, 0, 0                    | 1.222                       | 1         | 100%           | a = b = c = 3.5413    | 44.411                        | 2.504          |
| Ni36 [7.1 nm] (FCC) | 0, 0, 0                    | 0.9                         | 1         | 100%           | a = b = c = 3.5400    | 44.362                        | 2.503          |
| Ni35 [9.0 nm] (FCC) | 0, 0, 0                    | 09                          | 1         | 100%           | a = b = c = 3.5400    | 44.362                        | 2.503          |
| Ni34 [10.1 nm] (FCC)| 0, 0, 0                    | 1.5                         | 1         | 100%           | a = b = c = 3.5500    | 44.739                        | 2.510          |
Thus, EXAFS, $\chi(k)$, with some algebra in the Fermi’s Golden rule after taking into accounts of the factors described above turns out to be the sum of all contributions, $\chi(k)$, from groups of atoms that lie at approximately same distances from the absorbing atom at the $i$th shell, and is given by:

$$\chi(k) = \sum_i S_0^2 N_i \left| f_{\text{eff}}(k) \right| \sin \left[ 2kr_i - \frac{4}{3} \sigma_i^{(3)} k^3 + \delta_i(k) \right] e^{-2\sigma_i^2 k^2} e^{-2r/\lambda_i(k)} \ldots \ (1)$$

where $S_0^2$ is the passive electron reduction factor, $N_i$ is the coordination number, and $\sigma_i^{(3)}$ is the third cumulant. Equation 1 indicates that EXAFS is an inherently local probe due to $\lambda_i(k)$ term and $R^{-2}$ term, restricting within 5 Å or so from the absorbing atom. Second, EXAFS oscillations will consist of different frequencies that correspond to different lengths for each coordination shell.

**EXAFS analysis** The data processing was done using the IFEFFIT software package. The AUTOBK code in IFEFFIT is used first to normalize the absorption coefficient, $\mu(E)$, and separation of the EXAFS signal, $\chi(E)$, from the isolated atom absorption background, $\mu_0(E)$ for each measured X-ray absorption spectrum. This gives the desired oscillations in the absorption spectra, whereby the energy dependent absorption coefficient $\mu(E)$ is converted to EXAFS function $\chi(E)$ or $\chi(k)$ defined as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

or

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\Delta\mu_0(k_0)}$$

where $E_0$ is energy at the absorption edge (chosen at the middle of the absorption edge jump), $k=\sqrt{2m(E-E_0)/\hbar^2}$ and $m$ is the electron mass. Minimization of the signal in the low-$r$ region of the Fourier transformed $\chi(k)$ data was used to choose the background absorption function,
\( \mu_0(k) \). Then, the theoretical photoelectron scattering amplitudes and phase shifts were computed by fitting the experimental data with the theoretical spectra through the FEFF 6.0 code using a model structure. Finally, the theoretical EXAFS data was fitted to the experimental EXAFS data in \( r \)-space by Fourier transforming both the theoretical and experimental data.

We have carried out the EXAFS analysis following a model of fcc Ni for samples with larger particle size and mixture of fcc and hcp Ni for samples with smaller particle size along with NiO Ni hcp structure. Thus, the first path is assumed to consist of a path from fcc and a path from hcp structures each having coordination of 6 leading to a total coordination of 12. The final bond lengths are given in Table S2. The main peak in the FT-EXAFS spectra for the samples with larger crystallites appears at 2 Å. This matches Ni-Ni distance of 2.4-2.5 Å of bulk Ni. In case of samples with small crystallites, main peak appears at much lower value of 1.7 Å with broadening in larger values. To take care of this, we have taken Ni-Ni bulk distance along with a Ni-O path to represent any other compounds of Ni due to the ligands also\(^{16}\).

The fast decaying weak oscillations with \( k \) of \( \chi(k) \), derived from observed EXAFS data was weighted by \( k \) or \( k^2 \) to amplify them at high values of \( k \). The \( \chi(k)k^2 \) functions were then Fourier-transformed in \( r \)-space to generate the \( |\chi(r)| \) versus \( r \) (or FT-EXAFS) plots of the real space distances with respect to the absorbing atom. Since \( \chi(k) \) is dependent on the coordination numbers \( N \), bond distances \( r_i \) and mean square deviations \( \sigma_i^2 \), we determined these parameters from the above analysis and studied various aspects related to the local structure of these monodispersed Ni NPs. X-ray absorption near-edge structure (XANES) was investigated to understand the type of bonding, type of ligand/charge and symmetry of these NPs.
### Table S2 EXAFS Fitted parameters

| R Factor | Theoretical | 3.8 nm | 4.0 nm | 6.0 nm |
|----------|-------------|--------|--------|--------|
|          |             | 0.003  | 0.002  | 0.003  |
| r (Å) N  | r (Å) N τ  | r (Å) N τ  | r (Å) N τ  | r (Å) N τ  |
| Ni-O     | 2.08 6      | 2.01(1) 3.1(6) 0.003(1) 1.99(1) 3.2(2) 0.004(1) 2.00(1) 3.1(2) 0.003(1) |
| Ni-Ni (fcc Ni) | 2.31 6 | 2.41(1) 2.1(3) 0.006(1) 2.40(2) 2.0(1) 0.005(1) 2.40(1) 2.1(2) 0.005(1) |
| Ni-Ni (hec Ni) | 2.47 6 | 2.56(1) 1.9(3) 0.006(1) 2.55(1) 1.8(3) 0.005(1) 2.55(1) 2.0(3) 0.005(1) |

### Table S2 EXAFS Fitted parameters continued….

| R Factor | Theoretical | 10.1 nm | 9.0 nm | 7.1 nm |
|----------|-------------|---------|--------|--------|
|          |             | 0.004   | 0.001  | 0.002  |
| r (Å) N  | r (Å) N τ  | r (Å) N τ  | r (Å) N τ  | r (Å) N τ  |
| Ni-O     | 2.08 6      | - - - - | 2.02(1) | 2.4(3) 0.003(2) |
| Ni-Ni (fcc Ni) | 2.5 | 12 | 2.43(1) | 9.5(5) 0.006(1) 2.44(1) 8.3(3) 0.006(1) 2.44(3) 6.7(3) 0.007(1) |

### Table S3 Theoretical Coordination Numbers derived by the method developed by Calvin et al.45.

| Samples | Ni-Ni Co-ordination Number (N) |
|---------|--------------------------------|
| 10.1 nm | 11.78                          |
| 9.0 nm  | 11.75                          |
| 7.1 nm  | 11.69                          |

| Samples | Coordination no. of 1st shell | Coordination no. of 2nd shell | Total Coordination |
|---------|--------------------------------|-------------------------------|--------------------|
| 6.0 nm  | 5.78                           | 5.77                          | 11.55              |
| 4.0 nm  | 5.64                           | 5.62                          | 11.26              |
| 3.8 nm  | 5.05                           | 4.99                          | 10.04              |

Note: All references are given in the end of main manuscript.