

Icosahedral FCC-Fe Nanoparticles: Facile Synthesis and Characterization with Aberration-Corrected TEM

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Methods

Preparation of PVP/Fe³⁺ Solution: 2 g of polyvinylpyrrolidone (PVP, Molecular weight=13000) was dissolved in 20 ml deionized water, followed by stirring for 4 h to ensure the dissolution of PVP. Afterwards, 2 g of ferric nitrate (Fe(NO₃)₃) was added into the solution with stirring for 1 h.

HRTEM Experiment and Simulation: High-resolution transmission electron microscopy investigation was carried out on a FEI Titan 80-300 microscope with an image Cs corrector. Our experiment was operated at a voltage of 300 kV and Cs was carefully adjusted to a range of -2 ~ 3 μm . Images were recorded by a Gatan UltraScan™ 1000 CCD. Image simulations were carried out using the commercial software package MacTempasX. Atom models were put into a supercell of dimension $10 \times 10 \text{ nm}^2$ for simulation. In the beam direction, the particle was sliced into different layers by the program. The simulation parameters we used were $Cc = 1.5 \text{ mm}$, $\Delta E \text{ (FWHM)} = 0.8 \text{ eV}$, $\Delta V/V = 0.25 \text{ ppm}$, $\Delta I/I = 0.5 \text{ ppm}$ and focal spread was about 2.3 nm. Series defocus images were calculated from -6 nm to +6 nm with 1 nm a step, using $Cs = 2 \mu\text{m}$ and objective aperture = 2 \AA^{-1} . Thermal diffuse scattering was not taken into account in the simulation.

Atomic Model of Icosahedral FCC-Fe Nanoparticle: Investigations suggest that icosahedral

nanoparticles and clusters possess shell periodicity and grow by the accretion of atomic layers. Since the atomic distribution of icosahedral particles does not possess long-range periodicity, HRTEM simulations of icosahedral Fe nanoparticles require all the atomic coordinates of each nanoparticle. Fig. S1 displays an icosahedral Fe nanoparticle consisting of 2 atomic layers, with each atom numbered. We index the 13 atomic coordinates of this icosahedron in Table S1. For larger icosahedra composed of more atomic layers, all the atom positions can be calculated using a computational programme. We constructed 18 and 20 layer atomic models to simulate the HRTEM images of icosahedral FCC-Fe nanoparticles situated in threefold and twofold, fivefold orientations, respectively.

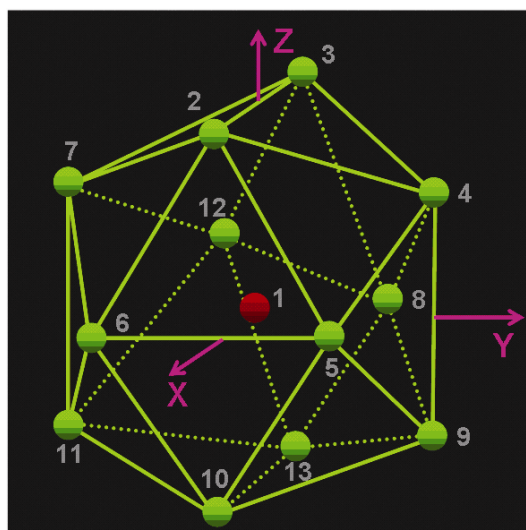


Figure S1. An icosahedron consists of two layers with 13 atoms.

Table S1. The coordinates of the atoms in the icosahedron shown in Fig. S1. The ratio $u/v = \tau - 1$, where $2v = 0.252 \text{ nm}$ is the interatomic distance and $\tau = (\sqrt{5} + 1)/2 = 1.618$ is the golden ratio.

Atomic Number	Coordinates		
1	0	0	0
2	v	0	u
3	-v	0	u
4	0	u	v
5	u	v	0
6	u	-v	0
7	0	-u	v
8	-u	v	0
9	0	u	-v
10	v	0	-u
11	0	-u	-v
12	-u	-v	0
13	-v	0	-u

Thermodynamic calculation for critical size of the icosahedral FCC-Fe nanoparticle

For FCC structural metal nanoparticles, theoretical and experimental investigations have suggested that, small sizes favor icosahedral nanoparticles; decahedral ones are favored at intermediate sizes, and single crystalline morphologies at large sizes. Here, we estimate the critical size distribution of icosahedral nanoparticles with reference to decahedral FCC-Fe nanoparticles. The total Gibbs free energy of Fe nanoparticles, for icosahedron (G_i) and decahedron (G_d) can express as

$$\begin{aligned}
G_i(r_i) &= U_c + U_s + U_e + U_t \\
&= V_i(r_i)E_c + S_i(r_i)\gamma_{111} + V_i(r_i)W_i + T_i(r_i)\gamma_t \\
&= \frac{5\sqrt{2}}{3}r_i^3E_c + 5\sqrt{3}r_i^2\gamma_{111} + \frac{5\sqrt{2}}{3}r_i^3W_i + \frac{15\sqrt{3}}{2}r_i^2\gamma_t
\end{aligned} \tag{S1}$$

$$\begin{aligned}
G_d(r_d) &= U_c + U_s + U_e + U_t \\
&= V_d(r_d)E_c + S_d(r_d)\gamma_{111} + V_d(r_d)W_d + T_d(r_d)\gamma_t \\
&= \frac{5\sqrt{2}}{12}r_d^3E_c + \frac{5\sqrt{3}}{2}r_d^2\gamma_{111} + \frac{5\sqrt{2}}{12}r_d^3W_d + \frac{5\sqrt{3}}{4}r_d^2\gamma_t
\end{aligned} \tag{S2}$$

where U_c , U_s , U_e and U_t are the cohesive energy, the surface energy, the elastic strain energy and the twin boundary energy, respectively; E_c , γ_{111} , W_i , W_d and γ_t are the cohesive energy per unit volume, the (111) surface energy per unit area, the elastic strain energy density for a icosahedron, the elastic strain energy density for a decahedron, and the twin boundary energy per unit area, respectively; V , S and T are the volume, the total (111) surface area and the twin boundary area, respectively; r_i and r_d are the edge length of the icosahedron and decahedron, respectively (Fig. S2). According to Ino,^{S1} the strain energy densities for icosahedral W_i and decahedral W_d Fe nanoparticle are taken as $4.609 \times 10^8 \text{ J/m}^3$ and $3.85 \times 10^7 \text{ J/m}^3$, respectively, and the twin boundary energy per unit area γ_t is 0.05 J/m^2 .

Due to the lack of experimental data we estimated the surface energy of FCC-Fe by applying the broken-bond rule,^{S2} using BCC-Fe as a reference. It has been reported that the experimental surface energy of BCC-Fe is 2.41 J/m^2 at $T = 0 \text{ K}$.^{S3} Guggenheim^{S4} has proposed the following relationship for the dependence of the surface energy on temperature: $\gamma = \gamma_0(1 - T/T_c)^n$, where γ_0 is the surface energy at $T = 0 \text{ K}$. For metal $n \sim 1$, and T_c is the critical temperature. Hence, it is easy to deduce $\gamma_{BCC} = 2.37 \text{ J/m}^2$ at $T = 300 \text{ K}$.

It is reasonable to assume that the surface of polycrystalline nanoparticle is composed of low index surfaces:

$$\gamma_{BCC} = \frac{1}{3}(\gamma_{BCC-111} + \gamma_{BCC-100} + \gamma_{BCC-110}) \tag{S3}$$

where $\gamma_{BCC-111}$, $\gamma_{BCC-100}$, $\gamma_{BCC-110}$ are the surface energy of the {111}, {100}, {110} planes of BCC-Fe, respectively. Using the surface energy of BCC-Fe for reference, we calculated the surface energy of FCC-Fe by,

$$\frac{\gamma_{hkl}}{\gamma_{BCC-110}} = \frac{N_{hkl} \cdot Z_{hkl} \cdot \frac{E_{FCC}}{2} / A_{hkl}}{N_{BCC-110} \cdot Z_{BCC-110} \cdot \frac{E_{BCC}}{2} / A_{BCC-110}} \quad (S4)$$

where N_{hkl} is the number of atoms for specific plane and Z_{hkl} is the number of broken bonds in the specific area of A_{hkl} . $E_{FCC} = 6.84 \times 10^{-19}$ J/atom and $E_{BCC} = 6.92 \times 10^{-19}$ J/atom are the cohesive energies for FCC-Fe and BCC-Fe, respectively.^{S5} Based on experimental surface energy measurement of BCC-Fe and numerical calculations using Eqs. (S3) and (S4), we can get $\gamma_{111} = 3.11$ J/m² and $\gamma_{100} = 3.59$ J/m².

The total energy of the icosahedron is compared with that of a decahedron. The precondition that the both particles contain the same number of atoms leads to

$$V_i(r_i) = V_d(r_d) \quad (S5)$$

The total free energy difference ΔG_{id} between the icosahedron and the decahedron can be written as

$$\begin{aligned} \Delta G_{id} &= G_i(r_i) - G_d(r_d) \\ &= \frac{5\sqrt{2}}{3}(W_i - W_d)r_i^3 + \left[\frac{5\sqrt{3}}{2}(2 - 4^{2/3})\gamma_{111} + \frac{5\sqrt{3}}{4}(6 - 4^{2/3})\gamma_t \right] r_i^2 \end{aligned} \quad (S6)$$

ΔG_{id} versus the particle size of icosahedron d_i is plotted in Fig. 4. By setting $\Delta G_{id} = 0$, the particle size of the icosahedron d_i^* is easily obtained as $d_i^* = 11$ nm. This value agrees well with our experimental observation of icosahedral particles ranging in size from 5-13 nm.

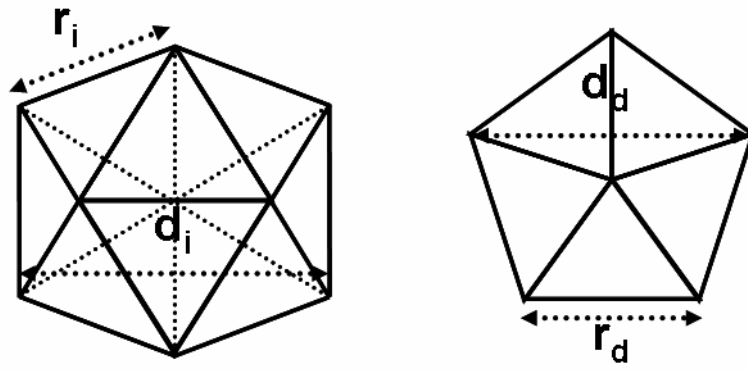


Figure S2. The schematic diagrams of icosahedron and decasahedron, with defined edge length (r) and size (d).

References:

- (S1) Ino, S. *J. Phys. Soc. Jpn.* **1969**, 27, 941.
- (S2) Pan, J.; Tong, J.; Tian, M. *The Basis of Material Science* (Tsinghua Univ. Press: Beijing, 1998).
- (S3) Tyson, W. R.; Miller, W. A. *Surf. Sci.* **1977**, 62, 267.
- (S4) Guggenheim, E. A. *J. Chem. Phys.* **1945**, 13, 253.
- (S5) Meng, Q.; Zhou, N.; Rong, Y.; Chen, S.; Hsu, T. Y.; Xu, Z. Y. *Acta Mater.* **2002**, 50, 4563.

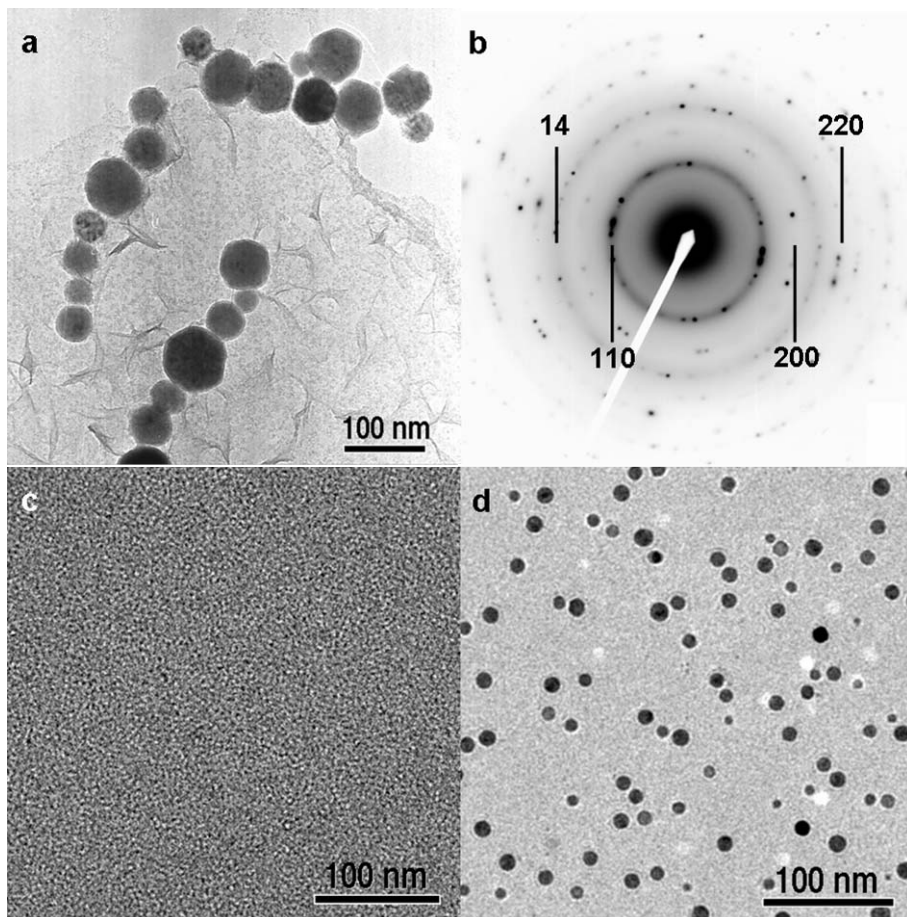


Figure S3. The process controlling of icosahedral FCC-Fe nanoparticles growth. A mild reducing agent is essential for the Fe^{3+} reduction. Strong reduction agents, such as NaBH_4 , results in the formation of spherical Fe nanoparticles in strings (a) of BCC structure (b). Moreover, growth in thermodynamic equilibrium condition is quite requisite for the synthetic procedure. (c) A TEM image of carbon film attached Fe^{3+} /PVP solution before heating, which is amorphous. During the heating procedure in vacuum, Fe ions formed energetically favorable icosahedral structure (d).

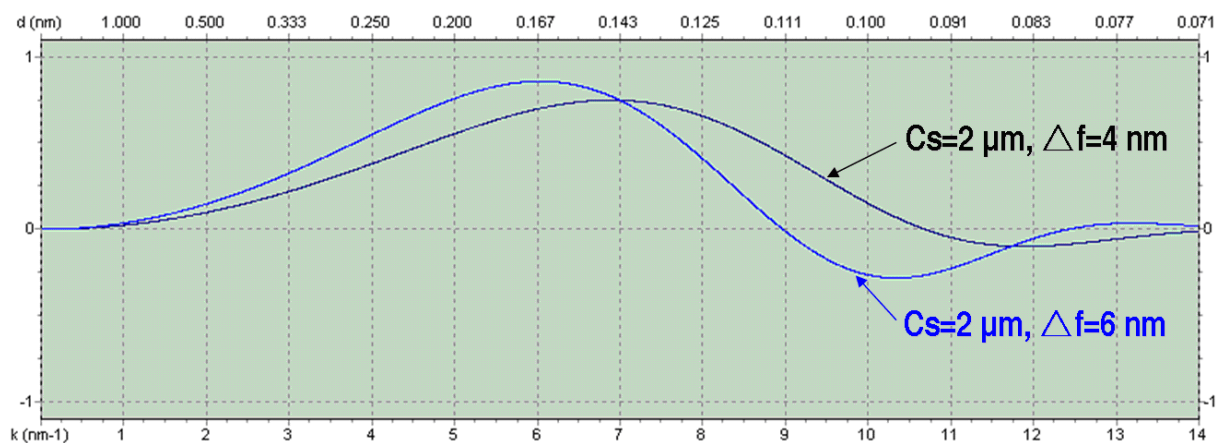


Figure S4. Contrast transfer function of the 300-kV FEI Titan 80-300 Cs corrected TEM with which the HRTEM images were taken (spherical aberration coefficient C_s : 2 μm). The upper and lower x-axes indicate the spatial frequency (k) and plane distance (d), respectively. Under these experimental conditions, spatial frequencies in the band between 4.85 and 7.94 nm^{-1} representing FCC-Fe (111) and (220) plane distances of 0.206 and 0.126 nm are transferred with the same contrast.

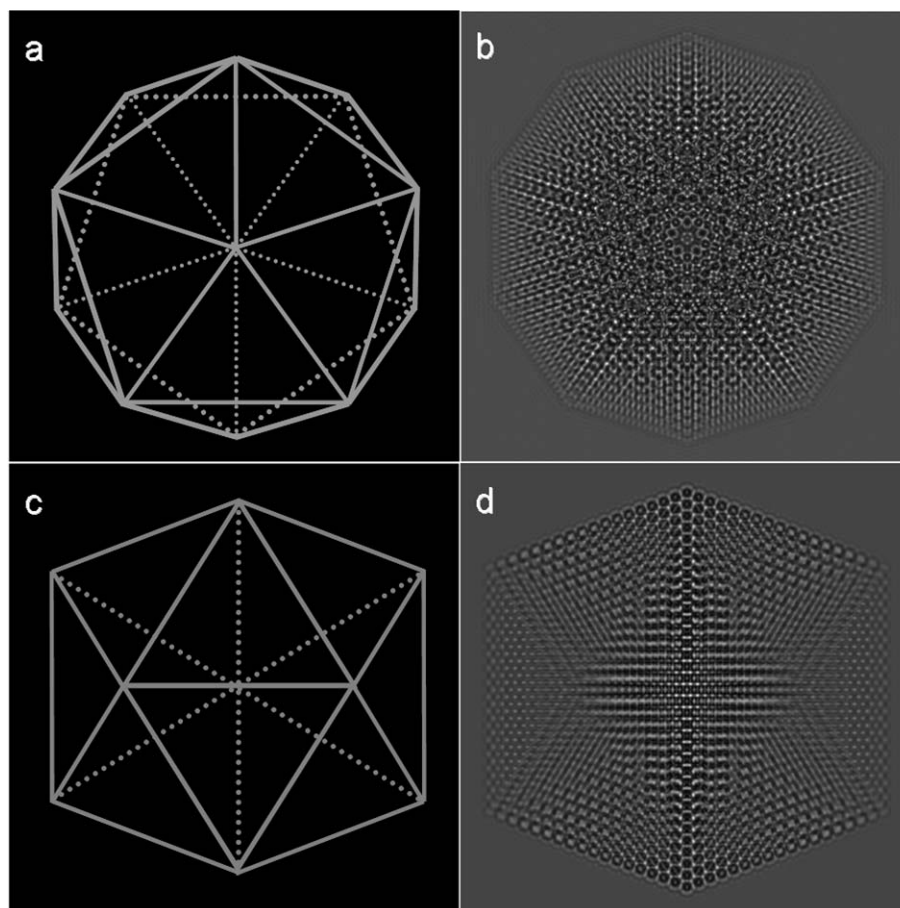


Figure S5. Structure diagrams (a and c) and simulated HRTEM image (b and d) of icosahedral FCC-Fe nanoparticle situated in exact fivefold and twofold orientations. The simulation was taken at spherical aberration coefficient: 2 μm ; defocus: +6 nm for fivefold axis and +4 nm for twofold axis; semi-angle of beam convergence: 0.1 mrad; defocus spread: 2.3 nm.