## **Supplementary Information**

# Ensemble averaged structure-function relationship for nanocrystals: effective superparamagnetic Fe clusters with catalytically active Pt skin

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## Methods:

## *i)* <u>Synthesis of Fe core-Pt skin NCs</u>

Three samples of Fe core-Pt skin nanocrystals (NCs) were synthesized by a one-step ultrasoundassisted polyol reaction involving Fe(III) acetylacetonate, Pt(II) acetylacetonate, Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> and Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>. In particular, mixtures of Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> and Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> were sonicated in ethylene glycol in the presence of fine carbon powder (Ketjen black), filtered, washed and then dried under vacuum. The size of Fe core and the thickness of Pt skin were fine-tuned through varying the Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> to Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> ratio so that the resulting NCs appeared with the same overall size of about 2.5 nm. In particular, mixtures wherein the ratio of Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> to Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> was close to 0.1 yielded NCs with a relatively large Fe core (~300 atoms) and a monolayer-thin Pt skin (~300 atoms). Mixtures wherein the ratio of Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> to Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> was close to 1.2 yielded NCs with a relatively small Fe core (~200 atoms) and Pt skin comprising two atomic layers (~400 atoms). Mixtures wherein the amount of Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> to Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> was nearly equal yielded NCs with an Fe core and Pt skin formed of approximately 300 atoms each, that is, the Pt skin appeared about 1.5 atomic layer thick. More details of the synthesis protocol can be found in ref. [S1].

## *ii)* Determining the overall chemical composition, size, shape and chemical pattern of Fe core-Pt skin NCs

The overall (bulk) chemical composition of Fe core-Pt skin samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Measurements were done on a Perkin Elmer 2000 DV ICP-AES instrument. The instrument was calibrated using standards dissolved in the same acid matrix as the unknowns. Several batches of the unknowns were analysed thus ensuring < 2 % experimental error. Data showed that, as desired, the three Fe core-Pt skin samples appeared with an overall chemical composition of approximately Fe<sub>0.4</sub>Pt (Fe<sub>166</sub>Pt<sub>421</sub>), Fe<sub>0.7</sub>Pt (Fe<sub>244</sub>Pt<sub>351</sub>) and Fe<sub>1.2</sub>Pt (Fe<sub>336</sub>Pt<sub>297</sub>).

The size, shape and chemical pattern of Fe<sub>x</sub>Pt (x=0.4, 0.7 and 1.2) NCs were determined by High-Angle Annular Dark-Field (HAADF)-Scanning Transmission Electron Microscopy (STEM). Standard Pt NCs were also measured. The measurements were done on a JEOL JEM 2100F instrument equipped with a CEOS hexapole probe. The instrument was operated at 200 keV. The lens settings combined with the corrector tuning ensured a spatial resolution of ~ 90 pm. Exemplary HAADF-STEM images of Fe<sub>x</sub>Pt (x=0, 0.4, 0.7 and 1.2) and standard Pt NCs are shown in Figure S1. Representative HAADF-STEM images of single Fe<sub>x</sub>Pt (x=0.4, 0.7 and 1.2) NCs are shown in Figure 1(*b*). As can be seen in the Figures, the NCs studied here are rather uniform in size and shape. To be more specific, the NCs appear with an average size of 2.5 ( $\pm$  0.3) nm, polyhedral shape and relatively well-defined facets. Furthermore, the NCs possess a good degree of crystallinity as evidenced by the lattice fringes in the respective images.

Energy-dispersive x-ray spectroscopy (EDS) maps of Fe<sub>x</sub>Pt (x=0.4. 07 and 1.2) NCs are shown in Figure 1(*d*, *e* and *f*). The maps indicate that the NCs are with a core@skin-type morphology. To evaluate the number of Pt layers on top of Fe cores, we carried out simplistic calculations using the experimental ICP-AES data for the chemical composition of the NCs, HAADF-STEM data for the size of the NCs (~2.5 nm) and the well-known size of Fe (2.52) Å and Pt (2.775 Å) atoms [S2]. In particular, Pt skin of Fe<sub>1.2</sub>Pt NCs, that is the difference between the radius of the NCs and the radius of Fe core, appeared approximately one monolayer thick. For Fe<sub>0.7</sub>Pt and Fe<sub>0.4</sub>Pt NCs the skin turned out to be about 1.5 and 2 Pt atomic layers thick, respectively. The so-obtained independent estimate of Pt skin thicknesses matched well the pre-desired number of Pt layers. Hence, hereafter, Fe<sub>x</sub>Pt (x=0.4, 0.7 and 1.2) NCs are referred to as Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs, respectively.

#### iii) <u>X-ray photoelectron spectroscopy (XPS) studies on Fe core-Pt skin NCs</u>

The electronic properties of Fe and Pt atoms forming the core and skin of Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs were studied by XPS. The measurements were done on a Kratos AXIS Ultra DLD spectrometer using a monochromatic Al source. The spectrometer was calibrated using the C *1s* Cu  $2p_{3/2}$ , and Au  $4f_{7/2}$  peaks at 284.8 eV, 932.7 eV and 83.96 eV, respectively, as internal standards. The pass energy was fixed at 20 eV for the detailed scans. Typical XPS Fe 2p and Pt 4f spectra are shown in Figure 1a and 1c, respectively. Shifts in the binding energy of Fe and Pt atoms with changes in their relative concentration in the NCs are also shown. The shifts are evaluated with respect to the Fe  $2p_{3/2}$  (706.9 eV) and Pt  $4f_{7/2}$  (71.0 eV) spectral lines characteristic to bulk Fe and Pt, respectively [S3, S4].

As data in Figure 1a show, the Fe  $2p_{3/2}$  core-level peak position in Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs is shifted by 0.59 eV, 0.79 eV and 1.19 eV, respectively, in comparison to the bulk value of 706.9 eV. The shift may not be due to oxidation of Fe cores because the Fe  $2p_{3/2}$  spectral line in common iron oxides involving Fe<sup>3+</sup> and Fe<sup>2+</sup> species, such as Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>x</sub>O, appear at 711 eV, 710.6 eV and 709.5 eV [S5]. Results of our independent resonant HE-XRD experiments also indicated that Fe cores in Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs are not oxidized (see Figure S7). The shift may not be due to alloying of Fe and Pt species at the Fe-core@Pt-skin interface either because prior studies have shown that Fe  $2p_{3/2}$  orbitals do not shift up in energy considerably when Fe and Pt atoms intermix at the nanoscale [S6, S7]. On the other hand, studies on Fe NCs and thin Fe layers have found that the Fe  $2p_{3/2}$  peak progressively shifts towards a higher binding energy with the diminishing of NC's size and layer's thickness. In particular, the shift has been found to amount to about (+) 1.2-1.5 eV for Fe monolayers and particles with a size less than 2-3 nm. Hence, the observed consistent shift of Fe  $2p_{3/2}$  core-level peak position towards

higher energy with the thickness of Pt skin may be associated with the respective decrease in the size of Fe cores covered by the skin. Furthermore, the concurrent broadening of the peak can be associated with the so-called "vacancy-cascade" mechanism evoked to explain the XPS spectra of nanosized Fe [S8, S9].

As data in Figure 1c show, the Pt  $4f_{7/2}$  core-level peak position in Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs is shifted by -0.34 eV, -0.25 eV and -0.12 eV, respectively, in comparison with the bulk value of 71.0 eV. The shift may not be due to the presence of PtO<sub>x</sub> species because the respective Pt  $4f_{7/2}$  spectral line would have appeared at about 74.2 eV [S10]. The shift may not be due to alloying of Fe and Pt species at the Fe-core@Pt-skin interface in the NCs either because prior studies have shown that, due to Pt↔Fe charge exchange effects in the nanoalloys, Pt  $4f_{7/2}$  orbitals in Pt-Fe nanoalloys shift up in energy by about 0.5 eV [S6, S7, S11]. Generally, prior studies on Pt surfaces have suggested that the negative shift in the energy position of Pt  $4f_{7/2}$  corelevel peak is due to the inherently reduced coordination of surface Pt atoms as compared to atoms in bulk fcc Pt [S12, S13]. As discussed in the text, the observed here systematic shift of Fe  $2p_{3/2}$  and Pt  $4f_{7/2}$  core-level peak position towards higher and lower energy, respectively, is related to specific changes in the *d*-electron density distribution of atoms in Fe cores and Pt skin of the respective NCs.

#### iv) Electrochemical analyses of Fe core-Pt skin NCs

The catalytic activity of Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs for the oxygen reduction reaction (ORR) was studied using cyclic voltammetry (CV) and the rotating disk electrode (RDE) techniques in 0.1 M HClO<sub>4</sub> electrolyte at room temperature. Reference 2.5 nm Pt NCs were also studied. Exemplary CV curves are shown in Figure S2. The electrochemically active surface area (ECSA) of the NCs was estimated from the curves using the literature value of 210  $\mu$ C.cm<sup>-2</sup> for polycrystalline Pt. ECSA values ranged from 0.69 m<sup>2</sup>g<sup>-1</sup> for the reference Pt NCs to 0.59 m<sup>2</sup>g<sup>-1</sup>, 0.64 m<sup>2</sup>g<sup>-1</sup> and 0.63 m<sup>2</sup>g<sup>-1</sup> for the Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs, respectively. Voltammograms recorded at a sweep rate of 5 mV/s showed that the onset potential for Fe@1Pt is 1.02 V and that for Fe@1.5Pt and Fe@2Pt NPs is 1.00 V. The onset potential for pure Pt NCs was found to be 0.98 V. Tafel plots of the specific activity (SA) of Fe@Pt skin NCs for ORR are also shown in Figure S2. The plots demonstrate the largely improved kinetics of ORR over Fe core-Pt skin NCs in the higher potential range (0.88 V - 0.98 V) in comparison to pure Pt NCs. In particular, the mass activity (MA) for ORR, which is relevant to practical applications, was found to increase in the order Pt < Fe@2Pt < Fe@1.5Pt < Fe@1Pt NCs. Notably, the MA of Fe@1Pt NPs was found to exceed that of Pt NCs by a factor of ~ 6. The increase in the MA of Fe@Pt NCs is summarized in Figure 3(d). More details of the electrochemical analyses can be found in ref. [S1].

Without loss of generality, the mechanism of ORR over catalyst surfaces, including catalysts at the cathode of fuel cells, can be described by the following four major steps:

$* + O_2 + H^+ + e^- \rightarrow *OOH$	(S1)
$OOH + H^+ + e^- \rightarrow O + H_2O$	(S2)
$*O + H^+ + e^- \rightarrow *OH$	(S3)
$*OH + H^+ + e^- \rightarrow * + H_2O$	(S4),

where (\*) stands for catalytically active surface sites,  $H^+$  are protons resulting from splitting of  $H_2$  molecules at the cell's anode and  $O_2$  are oxygen molecules fed to the cell's cathode. It is considered that the likely ORR-rate determining steps are the dissociative adsorption and protonation of

molecular oxygen, i.e. step (S1) of ORR, and removal of reaction intermediates such as atomic oxygen and hydroxyl (OH) groups, in particular step (S4) of ORR. Hence, it is considered that an efficient catalyst for ORR should bind oxygen molecules with ample strength to allow the cleavage of O-O bonds but weakly enough to release the reaction intermediates and product when the reaction ends. In addition, it is considered that the binding energy of atomic oxygen can serve as an indicator for catalytic activity for ORR [S14-S16]. Here it may be added that pure Pt is the best monometallic catalyst for ORR, even though, according to theory, it binds oxygenated species a bit too strongly by about 0.2 eV [S14, S17]. Our prior work indicated that the superb catalytic activity of Fe@1Pt NCs for ORR can be related to the presence of particular terrace-type sites on the NC's surface that bind oxygen species weaker (by ~ 0.3 eV) as compared to corresponding surface sites in Fe@2Pt and pure Pt NCs [S1]. The particular (~6-fold) improvement of the ORR activity of the former (Fe@1Pt NCs) over that of the latter (reference Pt NCs), though, remained puzzling at the time. Here we find that, largely, the improvement is due to a counterintuitive increase in the CN<sub>eff</sub> of surface Pt atoms in the Fe@Pt NCs with the decrease in the thickness of Pt skin (see data in Figure 3d and related to it text).

#### v) Characterizing the magnetic properties of Fe core-Pt skin NCs

Magnetic properties of Fe@Pt NCs were characterized on a SQUID magnetometer from Quantum Design. Hysteresis curves for Fe@Pt NCs measured at 2 K are shown in Figure S3(left). Coercivity, H<sub>c</sub>, values for Fe@1Pt, <u>Fe@1.5Pt</u> and Fe@2Pt NCs determined from the curves are 2120 Oe, 2080 Oe and 2050 Oe, respectively. Zero field and field (100 Oe) cooled magnetization curves for Fe@Pt NCs are shown in Figure 4a. Note that to minimize the trapped magnetic field, the superconducting magnet was quenched and the shield was demagnetized prior to the zero-field cooling measurements. As can be seen in the Figure, the curves exhibit a clear "blocking effect", where the magnetic moment of Fe cores is pinned to a direction of easy magnetization. The effect is considered a hallmark of superparamagnetism [S18-S22]. The superparamagnetic behavior of Fe@Pt NCs is also documented by the frequency-dependent "cusp" in the measured AC susceptibly curves shown in Figure S3(right). The so-called "blocking temperature", T<sub>B</sub>, for Fe@1Pt, <u>Fe@1.5Pt</u> and Fe@2Pt NCs was determined from the DC magnetization curves (follow the arrows in Figure 4a) and found to be 15 K, 11 K and 8 K, respectively.

For an assembly of uniform in shape and well-separated from each other cluster-like Fe particles with a size < 2 nm, such as Fe cores in Fe@Pt NCs (see EDS maps in Figure 1 and Fe-Fe partial PDFs in Figure 2d), the magnetic anisotropy energy (MEA) may be defined as MEA =  $K_{eff}$ V, where  $K_{eff}$  and V are the NC's effective anisotropy constant and volume, respectively. In general, the MEA can involve contributions from magnetostatic anisotropy related to the NC's shape, magnetoelastic anisotropy related to atomic-level stresses, magneto-crystalline anisotropy intrinsic to bcc Fe and surface anisotropy arising from breaking of the 3D periodicity at the NC's surface. Also, studies have shown that for Fe particles < 2 nm the latter appears as a dominant contributor to the MEA [S18-S20]. Besides, it is related to the blocking temperature, T<sub>B</sub>, as follows [S21, S22, S23]:

$$K_{eff} * \mathbf{V} = 25k_B * \mathbf{T}_B \tag{S5}$$

where  $k_B$  is the Boltzman constant and the pre-factor 25 is chosen to account for the typical measuring time,  $\tau$ , in SQUID experiments ( $\tau \sim 100$  s). Using *eq*. S5 and experimental data for T<sub>B</sub> (see Figure 4a) and size of respective Fe cores, the effective magnetic anisotropy constant,  $K_{eff}$ , for Fe@1Pt, Fe@1.5Pt and Fe@2Pt NPs was found to be  $9.2 \times 10^5$  J/m<sup>3</sup>,  $9.09 \times 10^5$  J/m<sup>3</sup> and  $9.04 \times 10^5$ 

J/m<sup>3</sup>, respectively. The values appear considerably larger than the intrinsic anisotropy for of bcc Fe ( $5.5 \times 10^4 \text{ J/m^3}$ ) [S24]. The values though are consistent with  $K_{eff}$ = $3 \times 10^5 \text{ J/m^3}$  and  $K_{eff}$ = $5.4 \times 10^5 \text{ J/m^3}$  reported for 2.4 nm inert gas protected and 1.8 nm surfactant coated Fe clusters, respectively [S25, S26]. All in one, both the AC and DC experimental data clearly indicate that Fe@Pt NCs behave as superparamagnets above T<sub>B</sub>. Note that, due to uncertainties in the mass of magnetic component in the studied samples, no attempt was made to analyze the experimental DC magnetization data in terms of magnetic moment of Fe atoms constituting the cores of Fe@Pt NCs. The magnetic moment was derived from the respective 3D structures through a rigorous procedure instead, as described below.

Theoretical work based on a streamlined *d*-band model [S27, S28] has shown that the magnetic moment,  $\mu_i$ , of individual atoms in small transition metal clusters, in particular Fe clusters, is related to the coordination environment of the atoms as follows:

$$\mu_{i,} = (CN_{bulk}/CN_{eff}^{i})^{1/2} * \mu_{Fe (bulk)} \quad if \quad CN_{eff}^{i} \ge CN_{bulk} * (\mu_{(bulk)}/\mu_{Fe (dim)})^{2}$$
$$= \mu_{Fe}(dimer) \quad otherwise. \tag{S6}.$$

Here  $\mu_{Fe \text{ (bulk)}} = 2.22 \ \mu_B$  and  $\mu_{Fe} \text{ (dimer)} = 3.25 \ \mu_B$  are the magnetic moment of Fe atoms in bulk and Fe-Fe dimers, respectively,  $\text{CN}_{\text{bulk}}$  is the number of near neighbors in bulk Fe, and  $\text{CN}_{\text{eff}}^i$  is the effective coordination number for atom *i* in the considered cluster. Note, for reasons discussed in Section *x*) below,  $\text{CN}_{\text{bulk}}$  was set to 14 and  $\text{CN}_{\text{eff}}^i$  was computed according to *eq. S30*. The average magnetic moment,  $\langle \mu(N) \rangle$ , per atom for a cluster comprising N atoms was then computed from

$$<\mu(N)> = \frac{1}{N}\sum_{i=1}^{N}\mu_i$$
 (S7).

The so-obtained  $\langle \mu(N) \rangle$  values are summarized in Figure 4. As discussed in the text, the values are consistent with results from "Stern-Gerlach"-type experiments on Fe clusters [S19, S29].

## *vi)* <u>Resonant high-energy synchrotron XRD (HE-XRD) experiments and derivation of total</u> and element-specific atomic pair distribution functions (PDFs) for Fe@Pt NCs

Carbon supported pure Pu and Fe@Pt NCs were subjected to resonant high-energy synchrotron XRD experiments (HE-XRD) at the 1-ID beamline of the Advanced Photon Source, Argonne. Samples were sealed in thin-walled glass capillaries and measured in transmission geometry. An empty glass capillary, carbon powder alone, bulk fcc Pt and bcc Fe (polycrystalline powder) standards as well as 4.5 nm Fe particles, synthesized as described in [S26], were measured separately. The experimental set-up was calibrated with high-purity powder Si standard. Two sets of HE-XRD patterns for each of Fe@Pt NCs were obtained using x-rays of two different energies. One of the sets was obtained using x-rays with energy of 78.370 keV, which is 25 eV below the K absorption edge of Pt. The other set of patterns was obtained using x-rays of energy 78.070 keV, which is 325 eV below the K absorption edge of Pt. X-rays were delivered by a combination of a bent double-Laue monochromator, collimating refracting lenses and a four crystal high-energy resolution ( $\Delta E=8 \text{ eV}$ ) monochromator [S30]. Scattered x-rays intensities were collected by a solidstate Ge detector coupled to a multi-channel analyzer. A few energy windows, covering several neighboring channels, were set up to obtain x-ray intensities integrated over specific x-ray energy ranges during the data collection, as exemplified in Figure S4. The energy windows covered: the coherent intensities only; the coherent, Compton, and Pt  $K_{\beta}$  fluorescence intensities all together; the Pt  $K_{\alpha 1}$  and  $K_{\alpha 2}$  fluorescence; and the total intensities scattered into the Ge detector. HE-XRD patterns for the respective NCs were collected several times scanning up to wave vectors, q, of 25 Å<sup>-1</sup> and then averaged to improve the statistical accuracy. Exemplary HE-XRD patterns for pure Pt and Fe@Pt NCs obtained using x-rays with energy of 78.070 keV are shown in Figure S5(left). As can be seen in the Figure, the patterns show a few distinct Bragg-like peaks at low diffraction angles and several broad features at high diffraction angles. As demonstrated in Figure S5(right), the rather diffuse character of the experimental HE-XRD patterns rendered sharp-Bragg peak based techniques for determining the 3D atomic structure of bulk metals and alloys difficult to apply in the case of NCs studied here. Hence, HE-XRD patterns for pure Pt, Fe and Fe@Pt NCs were considered in terms of atomic pair distribution functions (PDFs) as described below. For consistency, HE-XRD patterns for bulk fcc Pt and bcc Fe polycrystalline powders were also considered in terms of atomic PDFs.

In particular, the experimental HE-XRD patterns obtained using x-rays with energy of 78.070 keV were corrected for experimental artifacts (e.g. background scattering) and then used to derive the so-called total structure factors defined as

$$S(q) = 1 + \left[ I^{coh.}(q) - \sum c_i |f_i(q)|^2 \right] / \left| \sum c_i f_i(q) |^2,$$
(S8)

where  $I^{coh.}(q)$  are the coherently scattered intensities extracted from the raw HE-XRD patterns,  $c_i$  and  $f_i(q)$  are the concentration and x-ray scattering factor, respectively, for atomic species of type *i* (*i*=Fe and Pt). The structure factors were Fourier transformed into the so-called total atomic PDFs, G(r), as follows:

$$G(r) = \frac{2}{\pi} \int_{q=0}^{q_{\text{max}}} [S(q) - 1] \sin(qr) dq , \qquad (S9)$$

where q is the magnitude of the wave vector  $(q=4\pi\sin\theta/\lambda)$ , 2 $\theta$  is the angle between the incoming and outgoing x-rays,  $\lambda$  is the wavelength of the x-rays used and r is the radial (real space) distance [S31, S32]. Total atomic PDFs for pure Pt and Fe@Pt NCs are shown in Figure 2a. Total atomic PDFs for bulk fcc Pt and bcc Fe are shown in Figure 2b. Total atomic PDF for 4.5 nm Fe particles is shown in Figure S6. Note that the Fourier transformation is a unitary operation and so does not alter in any way the atomic-structure relevant information contained in HE-XRD patterns.

By definition, total atomic PDFs reflect all atomic pair correlations in NCs. Hence, the total atomic PDF for Pt NCs shown in Figure 2a reflects correlations between pairs of Pt atoms alone. On the other hand, the total atomic PDFs for Fe@Pt NCs shown in the same Figure are a weighted sum of 3 partial atomic PDFs  $G_{ij}(r)$ , in particular  $G_{Fe-Fe}(r)$ ,  $G_{Fe-Pt}(r)$  and  $G_{Pt-Pt}(r)$  partial PDFs, as follows:

$$G(\mathbf{r}) = \sum_{i,j} w_{ij} G_{ij}(r),$$
(S10).

where  $c_i$ , and  $f_i(q)$  are the concentration and x-ray scattering factor of the particular atomic species, and the weighting factors  $w_{ij}$  are defined as:

$$w_{ij} = c_i c_j f_i(q) f_j(q) / [\sum_{i} c_i f_i(q)]^2$$
(S11).

To determine the contributions of  $G_{Fe-Fe}(r)$  partial PDFs to the total PDFs for Fe@Pt NCs, the socalled Pt-differential atomic PDFs were obtained at first as follows [S33, S34]:

$$DS(q)_{Pt} = \frac{I^{coh}(q, E_1) - I^{coh}(q, E_2) - [\langle f^2(E_1) \rangle - \langle f^2(E_2) \rangle]}{\langle f(E_1) \rangle^2 - \langle f(E_2) \rangle^2} + 1$$
(S12)

where  $E_1$  and  $E_2$  denote the data sets collected using x-rays with energy of 78.070 keV and 78.370 keV, respectively, the atomic scattering factors  $f(E) = f_0(q) + f'(q, E) + if''(q, E)$ , and f' and f' are the so-called dispersion corrections. Then, Pt-differential atomic PDFs,  $DG(r)_{Pt}$ , were obtained via a Fourier transformation as given below:

$$DG(r)_{Pt} = \frac{2}{\pi} \int_{q=0}^{q_{\text{max}}} q[DS(q)_{Pt} - 1]\sin(qr)dq$$
(S13).

Note that the Pt-differential atomic PDFs comprise contributions from Pt-Pt and Pt-Fe atomic pairs because only the scattering factor of Pt species changes significantly when resonant HE-XRD experiments are done at the Pt K edge, *i.e.* 

$$DG(r)_{Pt} = \sum_{i} \Delta w_{Pt-i} G_{Pt-i}(r)$$
(S14)

where

$$\Delta w_{P_{t-i}} = \frac{c_{P_t}c_i \operatorname{Re}[f_i(f_{P_t}^*(E_1) - f_{P_t}^*(E_2)]}{\langle f(E_1) \rangle^2 - \langle f(E_2) \rangle^2} , \qquad (S15).$$

Here  $c_i$  is the concentration of atomic species of type *i* and  $f^*(E)$  is the complex conjugate of f(E). Finally, by using the so-called MIXSCAT approach, the Fe-Fe partial PDFs for Fe@Pt, Fe@1.5Pt and Fe@2Pt were obtained from the respective total and Pt-differential PDFs as follows [S35]:

Fe-Fe partial PDF = [respective Total 
$$G(r)/w_{ij}$$
 – [respective DG(r)<sub>Pt</sub>]/ $\Delta w_{Pt-i}$  (S16).

Here  $w_{ij}$  and  $\Delta w_{Pt-i}$  are the weighting factors of Pt-Pt and Pt-Fe atomic pairs computed using *eqs.* (*S11*) and (*S15*), respectively. The resulting partial G<sub>Fe-Fe</sub>(r)s for Fe@Pt NCs are shown in Figure 2d. More details of resonant HE-XRD experiments and derivation of element-specific atomic PDFs can be found in ref. [S36]. Evidence for the sensitivity of resonant HE-XRD to the distribution of chemical species in metallic NCs can be found in refs. [S37, S38]

### vii) Crystal-structure Constrained Modeling

To ascertain the quality of HE-XRD experiments and atomic PDFs derivation, the total PDFs for bulk Fe and Pt powder standards were fit with models constrained to the bcc- and fcc-type crystal structure adopted by bulk Fe and Pt, respectively [S39]. The initial models featured perfectly 3D periodic, infinite lattices of the respective structure type. The  $\delta$ -functions-like peaks in the atomic PDFs derived from the models were broadened by convolution with Gaussian functions as to mimic the usual broadening of the atomic coordination spheres in metallic NCs at ambient conditions. The unit cell parameters of the model lattices were adjusted such that model-derived atomic PDFs approached the corresponding experimental ones as closely as possible. The computations were done with the help of the program PDFgui [S40]. Resulting fits are shown in Figure 2b. As can be seen in the Figure, the experimental PDF data are fit very well by the respective 3D model lattices. The refined lattice parameters, a=2.869 Å for bcc Fe, and a= 3.921 Å for fcc Pt, compare very well with literature data (a=2.867 Å for bulk Fe and 3.923 Å for bulk Pt) [S39]. Results attest to the very good quality of synchrotron HE-XRD experiments conducted here.

To ascertain the phase state of Fe cores, the experimental Fe-Fe partial PDFs for Fe@Pt NCs were approached with models based on the atomic structure of common iron oxides containing Fe<sup>+2</sup> and Fe<sup>+3</sup> species, including wustite, hematite and magnetite. The models made sense since Fe is known to be highly reactive towards oxygen under ambient conditions. Modeling was done with the help of the program PDFgui. Models were based on crystal structure data for wustite, hematite and magnetite obtained from literature sources [S41]. Results of the modeling, which may be looked at as a "nanophase-analysis" by HE-XRD, are shown in Figure S7. As can be seen in the Figure, experimental Fe-Fe partial PDFs do not show features characteristic to the considered common Fe oxides. Thus, in line with the findings of XPS experiments, HE-XRD experiments indicated that Pt skin of Fe@Pt NCs largely protects Fe cores from oxidation.

#### viii) Molecular Dynamics simulations

3D atomic models for Fe (4.5 nm), Pt( 2.5 nm) and Fe@Pt (2.5 nm) NCs were built by classical Molecular Dynamics (MD) simulations based on the quantum-corrected Sutton-Chen (Q-SC) potential [S42-S44]. It considers the energy of atomic-level models, *E*, as a sum of an atomic pair potential *P*( $r_{ij}$ ) term and a local electron density ( $\rho_i$ ) term defined as follows:

$$E = \sum_{i} \left[ \sum_{j \neq i} \frac{1}{2} h_i * \epsilon_{ij} * P(r_{ij}) - s_i * \epsilon_{ij} * (\rho_i)^{\frac{1}{2}} \right]$$
(S17)

where

$$P(r_{ij}) = \left(\frac{a_{ij}}{r_{ij}}\right)^{n_{ij}} \text{ and } \rho_i = \sum_{j \neq i} \left(\frac{a_{ij}}{r_{ij}}\right)^{m_{ij}}$$
(S18).

The so-called "energy" parameter  $\epsilon_{ij}(meV)$  and the dimensionless parameter  $s_i$  are used to scale appropriately the strength of repulsive  $P(r_{ij})$  and attractive ( $\rho_i$ ) metal-to-metal atom interactions, respectively. Parameters  $m_{ii}$  and  $n_{ii}$  are positive integers such that  $n_{ii} < m_{ii}$ . The parameter  $a_{ij}$  is a quantity used to scale distances  $r_{ij}$  between *i* and *j* type atoms in the structure models. Typically, values of  $a_{ij}$  are calibrated against the lattice parameter for the respective bulk metals. SC parameters for Fe and Pt were taken from literature sources [S44, S45].

In general, the realism of MD simulations depends both on the type of structure models chosen and conditions under which the simulations are run. Hence, to be as realistic as possible, the initial model atomic configurations for pure Pt and Fe@Pt NCs reflected the average size (~ 2.5 nm), shape (polyhedral) and chemical composition (Fe<sub>x</sub>Pt, where x=0, 0.4. 07 and 1.2) of the NCs modeled. Accounting for the diffraction features of experimental HE-XRD patterns and phase diagrams of bulk Fe, Pt and Fe-Pt alloys, several types of structure models were considered. In particular, models based on a fcc-type structure alone and models wherein Fe and Pt atoms maintain the structure type of their bulk counterparts, that is bcc for Fe and fcc for Pt, we generated in the case of Fe@Pt NCs. An fcc-type model (2.5 nm in size) for pure Pt NCs and a bcc-type model (4.5 nm in size) for pure Fe particles were also generated. All initial atomic configurations were optimized in terms of energy, i.e. stabilized at atomic level, with the help of the computer program DL-POLY [S46]. The optimization was performed under canonical NVT ensemble in the absence of periodic boundary conditions. Velocity Verlet algorithm with a time step of 2 fs was used.

Typically, MD simulations on metallic systems involve quenching of atomic configurations equilibrated at very high temperature. However, as it is the common practice in nanotechnology, pure Pt and Fe@Pt NCs were synthesized in solution, i.e. they were not obtained by rapid

quenching from a melt. Hence, the initial atomic configurations used in the MD simulations were not melted but equilibrated for 150 ps at 400 °C, cooled down to room temperature in steps of 50 K and again equilibrated for 150 ps. Results from MD simulations of 4.5 nm Fe particles and 2.5 nm Pt NCs are shown in Figure S8. Results from MD simulations featuring Fe@Pt NCs with an overall fcc-type atomic structure are presented in Figures 2a and S9. Results from MD simulations featuring Fe@Pt NCs with a bcc-type Fe core nested inside a tight fcc Pt shell are shown in Figure S10. Data in Figure S8 indicate that the atomic ordering in pure Fe and Pt particles is bcc- and fcclike, respectively. However, as can be seen in Figures 2a and S9, models based on a structurally coherent fcc Fe core and fcc Pt shell do not reproduce the experimental PDF data for Fe@Pt NCs well, in particular the intensities of several major PDF peaks. The observation indicates that, though exhibiting HE-XRD patterns similar to that of fcc Pt NCs (see Figure S3), Fe@Pt NCs may not be described as stacks of close packed atomic layers known to occur with bulk fcc Pt and FexPt alloys, where x is in the range from 0.4 to 1.2 [S39, S47]. On the other hand, as data in Figure S10 show, models based on a bcc Fe core and a fcc Pt skin, that are incommensurate in terms of atomic packing efficiency and near neighbor coordination, reproduce the experimental PDF data reasonably well. For reference, contrary to the fcc-type structure which involves both close packed (111)<sub>fcc</sub> atomic layers and <110><sub>fcc</sub> directions, the bcc-type structure does not involve close packed atomic layers but close packed <111><sub>bcc</sub> directions alone [S39]. Accordingly, the atomic packing fraction (68 % vs 74 %) and near-neighbor coordination (8 + 6 vs 12; see Figure 2b) in bcc-and fcc-type structure are significantly different. The advantage of bcc Fe@fcc Pt structure model over the fcc Fe@fcc Pt one becomes even more evident when Fe-Fe partial PDFs derived from the models are compared with the respective experimental data sets, as demonstrated n Figure S11. Hence, the former model was considered as a plausible 3D atomic structure of Fe@Pt NCs studied here and refined further against the experimental total and Fe-Fe partial PDFs by reverse Monte Carlo (RMC). The bcc- and fcc-type structure models for pure Fe particles and Pt NCs, respectively, were also refined by RMC, as described below.

#### ix) Reverse Monte Carlo Refinement of the MD models

Best MD models for Fe (4.5 nm), Pt2.5 nm) and Fe@Pt (2.5 nm) NCs were refined further by RMC guided by the respective total and partial Fe-Fe atomic PDFs [S48]. The refinement was necessary since actual metallic NCs exhibit local structural distortions, in particular close to their surface, and chemical patterns which may not be captured by MD alone, i.e. without experimental input. Note, as demonstrated in Figures 2c, 2d, S7, S9, S10, S11 and work of others [S49-S52], atomic PDFs are sensitive to the size and phase composition (e.g. oxidized vs metallic, bcc vs fcc type structure) of metallic NCs. Details of the RMC refinement are described below:

i) It is well-known that atoms in metallic materials can experience both random atomic displacements, also known as (Debye-Waller type) thermal vibrations, and static displacements, i.e. relax. Hence, to decouple the latter from the former, peaks in the total and partial PDFs computed from the RMC-refined models were convoluted with a Gaussian broadening function,

$$\mathbf{F}(r) = \frac{1}{\sigma_T \sqrt{2\pi}} * \exp\left(-\frac{r^2}{2\sigma_T^2}\right) \tag{S19}$$

where *r* is the radial distance and  $\sigma_T$  is the thermal root-mean-square (rms) displacement of either Fe or Pt atoms at room temperature. The respective values of  $\sigma_T$  were taken from literature sources [S39, S41].

ii) During the refinement, positions of atoms in the MD-optimized atomic configurations were adjusted as to minimize the difference between the RMC-computed and experimental total and partial atomic PDFs. Normalized distribution of Pt-Pt bonding distances in pure Pt and Fe@Pt NCs, computed from the adjusted atomic positions, are shown in Figure 3b.

iii) Simultaneously, the RMC refinement was frequently switched between two modes of operation exemplified in Figure S12. That is, the experimental atomic PDF data were represented either in terms of G(r) or  $r^*G(r)$  so that the distinctive atomic-level features of both the interior and near-surface region of the modeled NCs were captured in due detail.

iv) In addition, atoms in the refined 3D structures were required (i.e. restrained but not constrained) not to come much closer than pre-selected distances of closest approach, thereby taking into account the fact that individual atoms in metallic materials may share valence electrons but remain distinct entities.

v) Last but not least, the energy of the refined models was minimized further, i.e. beyond the level already achieved by MD, using pair-wise potentials taken from literature sources [S53].

Altogether, RMC refinements aimed at minimizing a residuals function  $\chi^2$  involving two major terms,  $\chi^2_{\Omega}$  and  $\chi^2_{\Theta}$ , defined as as follows [S54]:

$$\chi_{\Omega}^{2} = \frac{\sum [G(tot)_{i}^{exp} - G(tot)_{i}^{calc}]^{2}}{\varepsilon_{G(r)}^{2}} + \frac{\sum [G(Fe - Fe)_{i}^{exp} - G(Fe - Fe)_{i}^{calc}]^{2}}{\varepsilon_{G(r)}^{2}} + \frac{\sum [R_{ij}^{des} - R_{ij}^{calc}]^{2}}{\varepsilon_{R_{i}}^{2}}$$
(S20)

$$\chi_{\Theta}^2 = \frac{\Delta U}{\varepsilon_{AU}^2}$$
(S21)

where  $G(tot)_i^{exp}$  and  $G(tot)_i^{cal}$ ,  $G(Fe-Fe)_i^{exp}$  and  $G(Fe-Fe)_i^{exp}$  are model-derived and experimental total and Fe-Fe partial atomic PDFs for a given value of the real space distance  $r_i$ , respectively, and  $R_{ij}^{des}$  and  $R_{ij}^{cal}$  are preset plausible (see above) and model calculated *ij* atomic pair distances of closest approach, respectively. Understandably, both total and Fe-Fe partial atomic PDFs participated in *eq. S24* in the case of Fe@Pt NCs whereas total PDFs alone were fit in the case of pure Fe and Pt NCs. The term  $\Delta U$  reflects changes in model's energy as described by pair-wise potentials (see above). The  $\varepsilon$ 's in the denominators of *eqs. S20* and *S21* are weighting factors allowing controlling the relative importance of the individual terms in the residuals function  $\chi^2$ 

being minimized. In the course of refinements the values of  $\varepsilon$ 's and rate of switching between the two modes of RMC operation exemplified in Figure S12 were changed several times to increase the chances of finding the global minimum of the residuals function  $\chi^2$ , instead of a local minimum. Note that using constraints, restraints, penalty functions etc. is a common practice in refining 3D structure models against diffraction data [S53-S58]. The former though are used to guide the latter and not to pre-determine its outcome. To be more specific, the major goal of the refinement is to find a 3D structure that not only reproduces the experimental diffraction/PDF data in very good detail but also is consistent with any other available piece of structure-relevant information (e.g. overall chemical composition, morphology, structure type as optimized by MD, etc.) for the NCs under study. Hence, the RMC refinements were considered complete when their major goal was achieved, including the minimization of the residuals function  $\chi^2$ . Computations

were done with the help of a newer version of the program RMC++ allowing refining full-scale models for metallic NPs of any size and shape under non-periodic boundary conditions [S54].

MD-optimized models for pure Pt and Fe@Pt NCs converged to the atomic configurations shown in Figure 3a. The MD-optimized MD model for 4.5 nm Fe converged to the atomic configuration shown in Figure S6(see the inset). As can be seen in the Figures 2c, 2d, and S6, atomic PDFs derived from the refined configurations reproduce the respective experimental data sets in very good detail. The overall quality of the configurations was quantified by computing a goodness-of-RMC-fit indicator defined as

$$R_{w} = \left\{ \frac{\sum w_{i} (G_{i}^{\exp.} - G_{i}^{calc.})^{2}}{\sum w_{i} (G_{i}^{\exp.})^{2}} \right\}^{1/2}$$
(S22)

where Gexp. and G<sup>calc.</sup> are the experimental and RMC-fit atomic (total and Fe-Fe) PDFs, respectively, and  $w_i$  are weighting factors reflecting the experimental uncertainty of individual experimental data points. Here  $w_i$  were considered to be uniform which, as predicted by theory [S55] and corroborated by experiment [S56], is a reasonable approximation. The  $R_w$  values of about 7 ( $\pm$  3) % for the RMC-fits shown in Figures 2c, 2d and S6 certify the high quality of the respective 3D atomic configurations. Here it is to be underlined that the configurations are generated by MD, refined by RMC and evaluated (see eq. S22) strictly following the successful practices of determining the 3D atomic structure of metallic materials, including fine polycrystalline powders, by x-ray scattering techniques [S57, S58]. The comparison with the latter is particularly fair since determining the 3D structure both of polycrystalline and nanocrystalline metallic particles rely on diffraction datasets obtained from ensembles of entities with a fairly close chemical composition, size and shape. As such, within the limits of the experimental accuracy, the RMC refined 3D atomic configurations shown in Figures 3a and S6 can be considered as the most likely 3D atomic structure of the respective NCs, and so are fit for their purpose. That is, the structures can provide a sound basis for assessing the structure-function relationship for Fe@Pt NCs, as done in Figures 3d and 4c.

## ix) Assessing the local atomic structure in Fe cores and Pt skin in terms of effective coordination numbers $CN_{eff}$

It is well established that the reactivity of Pt surfaces and magnetic properties of Fe clusters are largely determined by the width,  $w_d$ , and energy position,  $\varepsilon_d$ , of surface *d*-electron bands with respect to the Fermi energy, degree of hybridization of valence *s*, *p* and *d* electrons of surface atoms and the resulting number and character of valence electrons at the Fermi level. The latter are often represented in terms of electron density of states (DOS) near the Fermi energy. In general, according to electronic structure theory of metals,  $w_d$  depends on the local coordination of atoms, in particular on their first coordination number (CN), as follows:

$$w_d = \operatorname{CN}_* \cdot \sqrt{\beta(r_{ij})^2},\tag{S23}$$

Here  $\beta$  represents the average hopping probability of a *d*-electron from one metal atom to another, assuming only the near neighbor hopping. The CN of surface atoms, CN(surf), in NCs though is greatly reduced as compared to that of atoms in the respective bulk, CN(bulk). Hence, the *d*-band width,  $w_d^s$ , of surface atoms narrows considerably. As shown by theory [S16, S28],

$$W_d^s \sim W_{d(bulk)*} \sqrt{\frac{CN(suf)}{CN(bulk)}}$$
 (S24).

Furthermore, the energy position of the *d*-band for surface atoms,  $\varepsilon_d^s$ , also changes considerably as follows

$$\varepsilon_d^s = \varepsilon_{d(bulk)} + \frac{\varepsilon(coh)}{2\theta_d} * \left(\frac{cN(surf)}{cN(bulk)} - 1\right),$$
(S25)

where E(coh.) is the cohesive energy of a bulk atom and  $\Theta_d$  is the degree of filling of the *d*-band for that atom. Evidently, changes in the coordination of surface atoms would modify greatly the reactivity of noble metal surfaces and magnetism of transition metals clusters, where the surface to volume ratio is very high. Therefore, as shown in work of others [S27, S59-S61], the former (atomic coordination) may be used to evaluate the latter (reactivity and magnetism of NCs). To capture the dependence of physicochemical properties of surfaces and clusters on the coordination of surface atoms in better detail, the use of so-called effective CN, CN<sub>eff</sub>, has proven very useful. It is defined as

$$CN_{eff}(i) = \sum_{i=1}^{n} \frac{CN(j)}{CN_{max}},$$
(S26)

where the sum includes all *j* near-neighbors of a surface atom *i*, and the division by the maximum coordination number,  $CN_{max}$ , for the respective structure gives a weight of the contribution of nearby atoms to the coordination of the surface atom under consideration. Note that computing and using  $CN_{eff}$  is similar to the embedded atom method (EAM) in a sense that the charge density at a surface site is approximated by a superposition of charge densities of the nearest neighbors which, in turn, depend on the charge densities of their near neighbors. In the EAM and other models based on the "atom in jellium" concept, the superposing contributions from neighboring atoms have an exponential form and are averaged over a sphere at the surface sites so that a local charge balance (continuity of the Fermi level) is achieved. Often, the sphere coincides with the so-called Wigner-Seitz sphere associated with the "size" of the atom occupying the surface site under consideration [S62-S64].

In computing the  $CN_{eff}$  for Pt atoms forming the thin skin of Fe@Pt NCs, the first physical minimum in the experimental PDF for pure Pt NCs at 3.2 Å was used as a maximum near neighbor distance. Also, the  $CN_{max}$  was set to 6, which is the maximum possible CN for Pt atoms occupying a close-packed (111)<sub>fcc</sub> monolayer. The distribution of near-neighbor distances for surface Pt atoms in Fe@Pt NCs, as normalized against the bulk Pt-Pt value of 2.775 Å, is shown in Figure 3b. The evolution of  $CN_{eff}$  for surface Pt sites in Fe@Pt NCs with the skin thickness is shown in Figure 3c using pure Pt and Fe@1Pt NCs as an example. The respective changes in the surface  $CN_{eff}$  are quantified in Figure 3d (see the respective bars).

In computing the CN<sub>eff</sub> for Fe atoms in Fe@Pt NCs, the first physical minimum in the experimental Fe-Fe partial PDFs at 3.20 Å was used as a maximum near neighbor distance. Thus we accounted for the observed relaxation of bcc Fe cores leading to near merging of the first (8 neighbors) and second (six neighbors) coordination spheres of the constituent atoms (see vertical broken lines in Figure 2d). Accordingly,  $CN_{max}$  was set to 14. Note that contrary to the case of fcc metals such as Pt, the radius of the first, R<sub>1</sub>, and second, R<sub>2</sub>, coordination spheres in bcc Fe are rather close to each other (R<sub>2</sub> = 1.15 R<sub>1</sub> for bcc Fe vs R<sub>2</sub> = 1.41 R<sub>1</sub> for fcc Pt). Hence, the spheres are likely to come even closer together in Fe clusters comprising a few hundreds of atoms alone. Arrows in Figure 4b represent magnetic moments for Fe atoms in Fe@Pt NCs, as computed from *eq. S6* using CN<sub>eff</sub> extracted from the respective 3D structures. The evolution of CN<sub>eff</sub> and so the

magnetic moment for Fe atoms with the radial distance, R, from the center of Fe@Pt NCs is shown in Figure 4c. Contrary to the finding of others [S65], the magnetic moment is seen to converge smoothly toward the bulk value of 2.22  $\mu_B$  with diminishing R.

#### x) Evaluating the cluster-size dependence of $\langle \mu(N) \rangle$ for Fe cores in Fe@Pt NCs

By adopting a spherical cluster model, it may be conjectured that for a cluster comprising N atoms, the ratio of surface to total number of atoms is about  $3N^{-1/3}$ . Hence, the cluster-size dependence of the average magnetic moment for Fe atoms in clusters,  $\langle \mu(N) \rangle$ , would be

$$\langle \mu(N) \rangle = \mu_{Fe} + (\mu_{surf} - \mu_{Fe}) * 3N^{-1/3}$$
 (S27).

Here  $\mu_{Fe}$  and  $\mu_{surf}$  are the magnetic moment of Fe atoms in bulk (2.22  $\mu_B$ ) and at the open surface of Fe clusters, respectively. Furthermore, based on experimental findings [S29, S66], it may be conjectured that surface Fe atoms are in  $3d^74s^1$  state and have their majority *d*-band entirely below the Fermi level, thus occupied by five 3d-electrons in spin up state. Accordingly, the minority *d*band is occupied by two 3d-electrons in spin down state. Then,  $\mu_{surf} = 3 \mu_B$ . Values for  $\langle \mu(N) \rangle$ computed according to eq. S27 are shown in Figure S4. Also shown in the Figure are experimental  $\langle \mu(N)^{exp} \rangle$  data obtained by "Stern-Gerlach"-type studies [S19, S67]. Note that in deriving  $\langle \mu(N)^{exp} \rangle$  data, it has been assumed that the dependence of magnetization, *M*, for a superparamagnetic sample on the applied external magnetic field, *H*, and temperature, *T*, may be well described as follows:

$$M/(\underline{n}^{*} < \mu(N)^{exp} >) = L(<\mu(N)^{exp} > *H/(k_{B}*T).$$
(S28)

Here *n* is the number of superparamagnetic clusters of N atoms in the sample,  $k_B$  is the Botlzmann constant and L(x) = 1/tanh(x)-1/x is the so-called Langevin function with an argument  $x = \langle \mu(N)^{exp} \rangle * H/(k_B * T)$ . A comparison between  $\langle \mu(N)^{exp} \rangle$  data and computed  $\langle \mu(N) \rangle$  values shows that the convergence of the average magnetic moment for Fe atoms in clusters to the bulk value with increasing N is not as uniform and slow as predicted by eq. S27. Evidently, a model based on common considerations expressed by eq. S27 is too simple to account for the observed cluster-size dependence of  $\langle \mu(N) \rangle$ . Somewhat more specific models envisioning that Fe clusters comprising a particular number of atoms ought to appear as a particular polyhedron or some of its derivatives, including truncated decahedron, cuboctahedron, rhombic dodecahedron and others, fail in describing the observed dependence of  $\langle \mu(N) \rangle$  on N either [S65, S68, S69]. Largely, the failure of foregoing models is due to ignoring the ensemble-average nature of  $\langle \mu(N)^{exp} \rangle$  data [S70]. In particular, such models ignore the fact that, due to their intrinsic non-periodicity, transition metal clusters with the same size (number of atoms N) may co-exist as various isomers wherein corresponding atoms, in particular surface atoms, may have somewhat different coordination environment, including somewhat different CN<sub>eff</sub>, and so carry a somewhat different magnetic moment [S71-S73]. A more realistic approach is to take into account the ensemble-average nature of  $\langle \mu(N)^{exp} \rangle$  and describe its functional dependence on N with a generic equation as follows:

$$\langle \mu(N) \rangle = \mu_{Fe} + \left( \mu_{Fe(\text{dimer})} - \mu_{Fe} \right) / \left( 1 + e^{\left( \frac{N - N_0}{\Delta N} \right)} \right)$$
(S29).

-

Here  $\mu_{Fe} = 2.22 \,\mu_B$  and  $\mu_{Fe(\text{dimer})=} 3.2 \,\mu_B$  is the magnetic moment of Fe atoms in bulk (corresponding to large values of N) and Fe-Fe dimers (N=2), respectively,  $N_o$  is the so-called point of symmetry where  $\langle \mu(N) \rangle = \mu_{Fe+} (\mu_{dim} - \mu_{Fe})/2$ , and the empirical parameter  $\Delta N$  is the rate of change of  $\langle \mu(N) \rangle$  with N. As can be seen in Figure 4c, the experimental data of Billas et al. [S19, S67] can

be fit well (R<sup>2</sup>=0.92) with the function described by eq. S29. The fit returns  $\mu_{dim} = 2.98(8) \mu_{B}$ ,  $\mu_{Fe}$ = 2.26(6)  $\mu_B$ , and  $N_o = 283(2)$  [S19, S66]. The values of  $\langle \mu(N) \rangle$  for Fe@Pt NCs derived here on the basis of experimental structure data (see eqs. S6, S7 and S26) can also be fit well ( $R^2 = 0.89$ ) with the function described by *eq. S33*. The fit returns  $\mu_{Fe(\text{dimer})} = 3.22(1) \mu_B$ ,  $\mu_{Fe} = 2.25(1) \mu_B$ , and  $N_o = 350(3)$ . Here it is to be noted that both the  $(\frac{1}{1+\exp(-x)})$ -type function used to describe the dependence of  $\langle \mu(N) \rangle$  on N (second term in eq. S29) and Langevin function 1/tanh(x)-1/x used to describe the dependence of  $M/(\underline{n}^* < \mu(N)^{exp} >)$  on the external magnetic field and temperature (see eq. S28) have a sigmoid-type shape. Indeed the two functions are strongly interrelated since  $\left(\frac{1}{1+\exp(-x)}\right) - \frac{1}{2} = \frac{1}{2} * tanh(x/2)$ . Moreover, the relationship is the formal definition for the cumulative distribution function of the so-called logistic distribution, also known as the Boltzmann sigmoidal model. Thus, eq. S29 is also strongly related to the Boltzmann distribution that may well describe the statistical distribution of non-interacting NCs comprising N atoms over possible structure states. The states may range from a dimer for N=2 ( $\mu_{Fe(dimer)=}$  3.2  $\mu_B$ ) to an entirely bcctype configuration for N  $\geq$  800 (bulk  $\mu_{Fe} = 2.22 \,\mu_B$ ) [S75-S78]. That is, when the ensemble-average nature of  $\langle \mu(N)^{exp} \rangle$  data resulted from "Stern-Gerlach" type experiments and  $\langle \mu(N) \rangle$  derived from ensemble-averaged 3D atomic structure data is accounted for properly, not only the latter appear a true representation of the former but also the cluster-size (N) dependence of both quantities can be described by statistical theory for non-interacting superparamagnetic clusters, such as Fe@Pt NCs studied here. It is to be underlined that, according to eq. S29,  $\langle \mu(N) \rangle$  would evolve pretty regularly with N. However, such an evolution does not preclude the occasional presence of noticeable statistical fluctuations of  $\langle \mu(N)^{exp} \rangle$  when N is small. The fluctuations may be due to particular details in the preparation conditions of the particular sample of small Fe clusters favoring a particular structure type and so a particular  $\langle \mu(N)^{exp} \rangle$  value, or others. In any event, the notion of the consistent presence of  $\langle \mu(N)^{exp} \rangle$  oscillations for particular values of N, e.g. N=13 and N=55, is still debatable and, perhaps for that reason, the respective N values are referred to as "magic numbers" [S79-S81].



**Figure S1.** Representative HAADF-STEM images of pure Pt, Fe@1Pt, Fe@1.5 Pt and Fe@2Pt NCs. The NCs appear with an average size of approximately  $2.5(\pm 0.3)$  nm and exhibit lattice fringes evidencing their true (nano)crystalline nature.



**Figure S2**. (*left*) Tafel plots for pure Pt and Fe@Pt NCs measured in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte [S1]. Note that data in the plot are normalized by the respective experimental ECSA values and amount (mass) of Pt, for better comparison. (*right*) Cyclic voltammograms (CVs) for Fe@Pt NCs. ECSA values used in deriving the Tafel plots shown on the left are estimated from the CV curves between 0.0 and 0.4 V, using the literature value of 210  $\mu$ C.cm<sup>-2</sup> for Pt. The CV curves exhibit peaks at about 0.7 V that are characteristic to surface oxidation and reduction. Broken line emphasizes the shift of the peaks to higher potentials with the relative Fe content in Fe@Pt NCs. Evidently, the thinner the Pt shell, the less oxophilic (prone to oxidation) the respective NCs. According to numerous studies, dissociation of oxygenated species (e.g. O and OH) is the rate-limiting step of ORR over catalyst surfaces [S1, S7, S14, S16 and S17]. Thus, less oxophilic NCs, such as Fe@1Pt NCs, can be expected to release ORR intermediates and product more easily than NCs with higher Pt content, resulting in an improved activity for ORR, as observed here.



**Figure S3.** (*left*) Hysteresis curves for Fe@Pt NCs measured at 2 K. Coercivity,  $H_c$ , is given for each data set. (*right.*) Temperature dependence of the real component of the AC susceptibility (in relative units) for Fe@Pt NCs measured at different frequencies.



**Figure S4.** X-ray energy sensitive spectra for Fe@1Pt NCs for a fixed diffraction (Bragg) angle of 35 deg. Spectra are obtained using x-rays with energy of 78.070 keV (red line) and 78.370 keV (blue line). The first energy is 325 eV below and the second energy is 25 eV below the K absorption edge of Pt (78.395 keV). Elastically and inelastically (Compton) scattered intensities as well as Pt (K $\alpha_1$  + K $\alpha_2$ ) fluorescent lines are marked with arrows. The difference between two XRD patterns including the elastically scattered intensities falling into the "x-ray energy window" outlined with a broken line, was used to derive (see *eq. S15*) the Pt-differential structure factors for Fe@Pt NCs.



Figure S5. (left) Experimental HE-XRD patterns for 2.5 nm Pt, Fe@1Pt, Fe@1.5Pt and Fe@2Pt NCs obtained using x-rays with energy of 78.070 keV. (right) Experimental (symbols) HE-XRD pattern for Fe@1Pt NCs compared to computed (solid line) HE-XRD patterns for hypothetical (a) bcc Fe and (b) fcc Pt NCs. Peaks in the computed patterns are broadened as to mimic the finite size (2.5 nm) of Fe@1Pt NCs. The computed HE-XRD pattern for fcc Pt NCs approaches whereas that for bcc Fe NCs largely disagrees with the experimental data. Nevertheless, an unambiguous conclusion for the structure type of Fe@1Pt NCs is difficult to achieve due the rapid fall off of experimental HE-XRD intensities with the wave vector, q. The respective atomic PDF data are much more informative in this respect due to the specific properties of Fourier transformation as demonstrated in Figures S9, S10 and S12(a). Note that experimental HE-XRD patterns and so their Fourier counterparts, the atomic PDFs, reflect ensemble averaged structural features of all NCs sampled by the x-ray beam in a way traditional powder XRD patterns reflect ensemble averaged structural features of all polycrystallites sampled by the x-ray beam in those experiments. Using NC ensemble-averaged 3D atomic positions to understand and explain NC ensemble-averaged functional properties, including catalytic, magnetic and optical properties, puts the NC atomic structure- functionality exploration on the same footing.



**Figure S6.** Experimental (symbols) and RMC fit (red line) atomic PDF for 4.5 nm pure Fe particles. The computed PDF is derived from the 3D structure shown in the inset. The structure comprises about 6000 Fe atoms and is refined against experimental PDF data through RMC as described in the text.



**Figure S7.** Experimental (symbols) Fe-Fe partial PDF for Fe@2Pt NCs and computed PDFs for common Fe oxides involving Fe<sup>+2</sup> and Fe<sup>+3</sup> species, including wustite, hematite and magnetite. Experimental and computed PDF data disagree testifying to the metallic character of Fe atomic in Fe@2Pt NCs.



**Figure S8.** (a) Experimental (symbols) and computed (red line) total atomic PDFs for 4.5 nm Fe particles. The bcc-type model captures the essential structural features of the particles such as, for example, the nearly split first peak in the PDF data. The model though is well too ordered structurally, i.e. shows a sequence of very well defined atomic coordination spheres (PDF peaks), as compared to the actual Fe particles it describes. (b) Experimental (symbols) and computed (red line) total PDFs for 2.5 nm Pt NCs. The fcc-type model reproduces the experimental data in very good detail, except in the region of higher-r values.



**Figure S9.** Experimental (symbols) and computed (red line) total atomic PDFs for Fe@Pt NCs. Computed PDFs are derived from structure models featuring a continuous fcc-type ordering throughout the NCs. The models are shown for each data set. Iron atoms are in brown and Pt atoms are in gray. Peaks in the experimental and model PDFs line up in position but disagree in intensity.



**Figure S10.** Experimental (symbols) and computed (red line) total atomic PDFs for Fe@Pt NCs. Computed PDFs are derived from structure models featuring a bcc Fe core nested inside a fcc Pt shell. The models are shown for each data set. Iron atoms are in brown and Pt atoms are in gray. Peaks in the experimental and model PDFs agree reasonably well in both position and intensity.



**Figure S11.** Experimental (symbols) and computed (red line) Fe-Fe partial atomic PDFs for Fe@1Pt NCs. Computed PDFs are derived from structure models featuring Fe(fcc)@Pt(fcc) NCs, wherein both Fe and Pt atoms are ordered fcc-like, and Fe(bcc)@Pt(fcc) NCs, wherein a bcc Fe core is nested inside a fcc Pt shell. The PDF derived from the latter model approaches the experimental data much closer than the PDF derived from the former model does it.



**Figure S12**. (*a*) Experimental (symbols) and RMC-fit (red line) total PDFs for 2.5 nm Fe@1Pt NCs. Data are presented as G(r) and G(r)\**r*, where *r* is the radial distance. (*b*) Experimental (symbols) and RMC-fit (red line) Fe-Fe partial PDFs for Fe@1Pt NCs. Data are presented as  $G_{Fe-Fe}(r)$  and  $G_{Fe-Fe}(r)*r$ . As can be seen, RMC fits to the experimental PDF data represented in terms of G(r) are very sensitive to the short-range (lower-r PDF peaks) and not so to the longer range (higher-r PDF peaks) interatomic correlations in Fe@1Pt NCs. On the other hand, RMC fits to the experimental PDF data represented as G(r)\**r* are very sensitive to the short-range (> 10 Å) and not so to the short-range (< 10 Å) interatomic correlations in Fe@1Pt NCs. Alternating the RMC computations between fitting the same experimental PDF data represented as G(r) and G(r)\**r* ensures that the refined 3D structure describes truly the interatomic correlations (atomic structure) across the studied NCs, including their bcc Fe core and fcc Pt skin. Note that the RMC fits in (a) and (b) reflect the respective 3D atomic structure shown in Figure 3a.



**Figure S13.** Distribution of bond angles in bulk bcc Fe (bars) and Fe cores of Fe@Pt NCs (solid line in the respective color). Distribution of bond angles in heavily disordered, nearly amorphous 4.5 nm Fe particles is also shown for comparison.

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**Figure S14.** Distribution of bond angles in bulk fcc Pt (bars) and Pt skin of Fe@Pt NCs (broken line in the respective color).

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