Supplemental Information
for
Shapes of Fe nanocrystals encapsulated at the graphite surface

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S1. DFT Calculations of Surface Energy: Details.

Figure S1 shows surface energies of freestanding bcc Fe(100) slabs versus slab thickness \( L_{Fe} \) from PBE and optB88 functionals. The curve from PBE functional was obtained previously.\(^1\) The values of surface energies for bulk bcc Fe(100) film (\( L_{Fe} \to \infty \)) from PBE and optB88-vdW functionals are \( \gamma_{Fe(100)} = 2.495 \) and 2.810 J/m\(^2\), respectively, estimated as an average over \( L_{Fe} = 14 \) to 31 for relaxed slabs. In calculations for Fig. S1, we use the lateral supercell size of 1 × 1 (in units of \( a \)) with the \( k \) mesh of 51 × 51 × 1 and \( E_{cut} = 268 \) (400) eV for PBE (optB88-vdW) functional.
Figure S1. Surface energies of freestanding bcc Fe(100) slabs from PBE and optB88-vdW functionals versus thickness \( L \). Circled and dotted curves are for unrelaxed and relaxed slabs, respectively.

Figure S2 shows surface energies of freestanding bcc Fe(110) slabs versus slab thickness \( L_{Fe} \) from PBE and optB88 functionals. The values of surface energies for bulk bcc Fe(110) film (\( L_{Fe} \to \infty \)) from PBE and optB88-vdW functionals are \( \gamma_{Fe(110)} = 2.432 \) and \( 2.669 \text{ J/m}^2 \), respectively, estimated as an average over \( L_{Fe} = 14 \) to 31 for relaxed slabs. In calculations for Fig. S2, we use the lateral supercell size of \( \sqrt{2} \times 1 \) (in units of \( a \)) with the \( k \) mesh of \( 41 \times 51 \times 1 \) and \( E_{\text{cut}} = 268 \) (400) eV for PBE (optB88-vdW) functional.
Figure S2. Surface energies of freestanding bcc Fe(110) slabs from PBE and optB88-vdW functionals versus thickness $L$. Circled and dotted curves are for unrelaxed and relaxed slabs, respectively.

Figure S3 shows surface energies of freestanding hcp Fe(0001) slabs versus slab thickness $L_{Fe}$ from PBE and optB88 functionals. The values of surface energies for bulk bcc Fe(0001) film ($L_{Fe} \rightarrow \infty$) from PBE and optB88-vdW functionals are $\gamma_{Fe(0001)} = 2.664$ and 3.025 J/m$^2$, respectively, estimated as an average over $L_{Fe} = 14$ to 31 for relaxed slabs. In calculations for Fig. S3, we use the lateral supercell size of $1 \times 1$ (in units of $a$) with the $k$ mesh of $51 \times 51 \times 1$ and $E_{cut} = 400$ eV for both PBE and optB88-vdW functionals.
Electronic properties of a metal slab can oscillate as a function of the slab thickness.\textsuperscript{2} Such oscillation behavior is associated with quantum size effects (QSEs). Analysis based on a noninteracting electron-gas model (EGM)\textsuperscript{3-5} shows that this behavior is controlled by the relationship between the interlayer spacing \(d\) of a metal film and the half Fermi wavelength \(\lambda_F/2\) of the metal. Specifically, if one has

\[ jd \approx m \frac{\lambda_F}{2}, \]  

where both \(j > 1\) and \(m\) are the smallest possible positive integers with no common factor, then surface energy as a function of film thickness will display damped oscillations with a period of \(jd\). If \(m \lambda_F/2\) is sufficiently close but not exactly equal to \(jd\), then oscillations with a period of \(jd\) will be modulated into a beating pattern with a beat period of \(\Lambda d\), where

\[ \Lambda = \frac{1}{|m - 2jd/\lambda_F|}. \]  

If we consider the six 3d electrons of Fe as noninteracting free electrons, then the Fermi wavelengths of bcc and hcp Fe are \(\lambda_F = 0.2542\) and 0.2498 nm, obtained from their experimental lattice constants (see Table 1 in Reference\textsuperscript{6}), respectively. The corresponding interlayer spacings of bcc Fe(100), bcc Fe(110), and hcp Fe(0001) are 0.1433, 0.2027, and 0.2023 nm, respectively.

**Figure S3.** Surface energies of freestanding hcp Fe(0001) slabs from PBE and optB88-vdW functionals versus thickness \(L_{Fe}\). Circled and dotted curves are for unrelaxed and relaxed slabs, respectively.
For bcc Fe(100), the integers satisfying Eq. (S2) are $m = 8$ and $j = 7$ with $\Lambda \approx 9.2$, or $m = 9$ and $j = 8$ with $\Lambda \approx 55.5$. It is indeed that the curves (especially for the PBE curves) in Fig. S1 have the weak oscillation profiles with a period of 7 or 8 monolayers, while the beating is too weak to be observed. For bcc Fe(110), the integers satisfying Eq. (S2) are $m = 8$ and $j = 5$ with $\Lambda \approx 34.3$. Again, the curves in Fig. S2 have the weak oscillation profiles with a period of 5 monolayers, while the beating is too weak with a too long period to be observed. The strong oscillations or irregularities for small $L_{Fe}$ in Fig. S1 and Fig. S2 are expected to be from the contributions of electron-electron and electron-core interactions, which lead to the non-sphericalness of the Fermi surface. For hcp Fe(0001), the integers satisfying Eq. (S2) are $m = 5$ and $j = 3$ with $\Lambda \approx 5.2$ to 7.1. In fact, the 3-monolayer oscillations in Fig. S3 are very clear (the beating period of about 6 monolayers is coincident with the 3-monolayer oscillations). Thus, the noninteracting EGM can still reproduce the overall oscillation feature in the QSEs of Fe nanofilms, besides previously-studied films of metals (including Ag, Au, Cu, Pb, Mg, and Al).3, 5, 7, 8

2. DFT Treatment of Different High-Symmetry Interfaces between hcp-Fe(0001) and Graphite or Graphene.

In this work, we only calculate the configurations with high-symmetry lattice match and expect that the interfaces with low-symmetry lattice match are less favorable energetically.

For the FeGn interface, there are three types of high-symmetry lattice match, denoted as T-hcp_T-fcc, T-hcp_T-top, and T-fcc_T-top, which are defined in Fig. S4 and its caption, below. From Table S1, T-hcp_T-top and T-fcc_T-top are almost degenerate and are more favorable than T-hcp_T-fcc.

**Figure S4.** Three types of high-symmetry lattice match of a GML on an hcp Fe(0001) surface. T-hcp, T-fcc, and T-top denote that C atoms of the GML are in hcp, fcc, and on-top sites of the hcp Fe(0001) surface, respectively. The capital letter “T” indicates that the carbon atom in the GML is considered to be on top of the Fe(0001) surface, and closest to the viewer. The lowercase letters (fcc, hcp, and top) denote three high-symmetry sites with respect to the hcp (0001) surface. Gray circles are C atoms in the GML, and blue circles are Fe atoms in the AB-stacked Fe slab.
Table S1. The optB88-vdW energies (in eV) per cell of three types of high-symmetry lattice match for a GML on a Fe(0001) slab with thickness $L$. For a given $L$, the lowest of the three energies is taken to be the energy reference point.

| $L$ | T-hcp T-fcc | T-fcc T-top | T-hcp T-top |
|-----|-------------|-------------|-------------|
| 1   | 0.013       | 0.000       | 0.001       |
| 2   | 0.018       | 0.000       | 0.000       |
| 3   | 0.019       | 0.000       | 0.000       |
| 4   | 0.019       | 0.000       | 0.001       |
| 5   | 0.018       | 0.000       | 0.004       |
| 6   | 0.017       | 0.000       | 0.003       |
| 7   | 0.018       | 0.001       | 0.000       |
| 8   | 0.018       | 0.000       | 0.003       |
| 9   | 0.018       | 0.000       | 0.003       |
| 10  | 0.018       | 0.000       | 0.006       |

For FeGt systems, where the carbon can be considered as AB-stacked GMLs, there are two types of top T sites; they will be subdivided into TT and TH for top-top and top-hollow. These are illustrated in Fig. S4. In TT or TH, the first letter T refers to the “top” carbon atom closest to the viewer (farthest from the interface), and the second letter to the nature of the site directly beneath that carbon atom, in the plane of the GML that is closest to the interface. More specifically, the first letter, denoting the first carbon atom, is always T. If the second letter is also T (top), that means the first carbon atom sits directly above a lower carbon atom. If the second letter is H (hollow), that means the first carbon atom sits directly above an empty, hollow site in the second graphene sheet. The remainder of the name, e.g. fcc, refers to the adsorption site of the first carbon atom with respect to the Fe lattice, in the manner of Fig. S5. Thus there are six types of high-symmetry lattice match, denoted as TT-hcp_TH-fcc, TT-fcc_TH-hcp, TT-top_TH-hcp, TT-hcp_TH-top, TT-top_TH-fcc, and TT-fcc_TH-top, respectively. We note that elsewhere\(^6\) the same nomenclature has been used but the names were preceded by a lower letter “t” or “i”, which was meaningful in that context but not in the present discussion.\(^6\)
Figure S5. Illustration of six high-symmetry configurations possible at the hcp Fe(0001) interface with graphite. Large blue circles represent Fe atoms with AB stacking. Gray circles are carbon atoms in the graphene layer directly adjacent to the metal. White circles with black outlines are carbon atoms one layer removed from the interface and nearest to the viewer; the carbon layers also have AB stacking. The nomenclature is explained in the SI text.

For an Fe(0001) film or slab interfaced with graphite, TT-fcc_TH-top, TT-fcc_TH-fcc, TT-top_TH-fcc, TT-top_TH-hcp, and TT-hcp_TH-top are almost degenerate, and more favorable than TT-hcp_TH-fcc and TT-fcc_TH-hcp, which are also almost degenerate. The energies of systems with these six interface configurations are listed in Table S2.

Table S2. The optB88-vdW energies (in eV) per cell of six types of high-symmetry lattice match for an Fe(0001) film with thickness \( L \), interfaced with graphite. For a given \( L \), the lowest of the six energies is taken to be the energy reference point.

| \( L \) | TT-hcp_TH-fcc | TT-fcc_TH-top | TT-top_TH-hcp | TT-fcc_TH-hcp | TT-hcp_TH-top | TT-top_TH-fcc |
|--------|----------------|--------------|---------------|---------------|---------------|--------------|
| 1      | 0.014          | 0.001        | 0.001         | 0.013         | 0.000         | 0.001        |
| 2      | 0.024          | 0.001        | 0.001         | 0.020         | 0.000         | 0.001        |
| 3      | 0.022          | 0.000        | 0.001         | 0.021         | 0.000         | 0.001        |
| 4      | 0.024          | 0.000        | 0.002         | 0.020         | 0.001         | 0.001        |
| 5      | 0.020          | 0.000        | 0.002         | 0.020         | 0.001         | 0.001        |
| 6      | 0.021          | 0.000        | 0.002         | 0.019         | 0.001         | 0.001        |
| 7      | 0.022          | 0.000        | 0.001         | 0.019         | 0.000         | 0.001        |
| 8      | 0.023          | 0.000        | 0.002         | 0.020         | 0.002         | 0.001        |
| 9      | 0.020          | 0.000        | 0.002         | 0.019         | 0.001         | 0.001        |
| 10     | 0.028          | 0.000        | 0.002         | 0.020         | 0.001         | 0.001        |
3. Results for Clamped vs. Free SLBT with Stretching Only.

**Figure S6.** Model results for dimensional ratios, comparing results from the (a-c) free and (d-f) clamped SLBT models.

4. Effect of Varying L on Bending Strain.

**Figure S7.** Dimensional ratios of encapsulated Fe islands vs. \( h \). Dashed lines show the result of the CE model, with \( U_c \) given by the SLBT model with bending strain only (B), for different values of \( L_c \).
We considered the possibility that different-sized islands might be associated with different values of \( L_C \). If small islands had larger \( L_C \), bending strain would have a relatively larger effect. However, as these plots show, increasing \( L_C \) does not significantly improve the agreement with any of the experimental data at small \( h \).

5. Comparison of \( \gamma \) and \( \beta \) for Cu and Fe.

Table S3. Comparison of \( \gamma_M \), \( \beta_{MGt} \), and \( \beta_{MGn} \) for \( M = \) Cu and Fe. DFT values for Cu are taken from Ref. \(^8\). DFT values for Fe are taken from the present work.

| System       | Method | \( \gamma_M \), J/m\(^2\) | \( \beta_{MGt} \), J/m\(^2\) | \( \beta_{MGn} \), J/m\(^2\) |
|--------------|--------|----------------------------|-------------------------------|-------------------------------|
| fcc-Cu(111)  | DFT    | 1.609                      | 0.405                         | 0.394                         |
| hcp-Fe(0001) | DFT    | 2.664                      | 0.464                         | 0.424                         |
| Cu           | Experiment\(^9\) | 1.790                      |                               |                               |
| Fe           | Experiment\(^6\) | 2.417                      |                               |                               |

6. Derivation and Implementation of the Stretching + Bending (S+B) Model.

6.1. Derivation

To account for the influence of both bending and stretching in the deformation of graphene, a term, \( U_e \), representing the strain energy in the graphene—hereafter referred to as the “stretching and bending” (S+B) model—was derived. The model was derived based on the derivation presented in Chapter 13, Article 97 of \(^10\) for the strain energy of circular plates under large deflection. In this analysis, an approximation of the vertical deflections of the plate is made by using the vertical profile of a uniformly loaded circular plate undergoing bending deflection, only.

\[
w(r) = w_0 \left(1 - \frac{r^2}{c^2}\right)^2
\]

where \( w_0 \) and \( c \) are depicted in Fig. S8.
While this profile is neither wholly representative of the profile of a plate subjected to a ring load due to the presence of a cylindrical island, nor wholly representative of such a plate after stretching has become dominant, it is selected because: (i) the bending profile of a plate subjected to a ring load is analytically intractable; and (ii) a bending-type profile is needed to satisfy the boundary conditions of a plate undergoing both bending and stretching, namely, $w(c) = 0$, $dw/dr|_{r=c} = 0$, and $dw/dr|_{r=0} = 0$.

In addition to vertical displacements, for a circulate plate undergoing large deflections, radial points along the plate also undergo radial displacements. A form for the radial displacements that satisfies the boundary conditions of $w(c) = w(0) = 0$ is given by

$$u(r) = r(c - r)(c_1 + c_2r + c_3r^2 + \cdots)$$  

(2)

The bending strain energy of a circular plate can be represented as

$$U_{e,b} = \pi D \int_0^c \left[ \left(\frac{d^2w}{dr^2}\right)^2 + \frac{1}{r^2} \left(\frac{dw}{dr}\right)^2 + \frac{2\nu}{r} \left(\frac{d^2w}{dr^2}\right) \left(\frac{dw}{dr}\right) \right] r \, dr$$  

(3)
where $D$ is the flexural rigidity of the plate, given by $D = Y t^3 / 12 (1 - \nu^2)$ with $Y$ the Young’s modulus, $t$ the thickness, and $\nu$ the Poisson’s ratio of the plate. Substitution of (1) into (3) yields

\[ U_{e,b} = \frac{16}{9} \frac{\pi Y t^5}{c^2 (1 - \nu^2)} \left[ \frac{1}{2} \left( \frac{w_0}{t} \right)^2 \right] \]  

(4)

The stretching strain energy in the plate can be represented as

\[ U_{e,s} = \frac{\pi Y t}{1 - \nu^2} \int_0^c (\epsilon_r^2 + \epsilon_t^2 + 2\nu \epsilon_r \epsilon_t) \ r \ dr \]  

(5)

where $\epsilon_r$ and $\epsilon_t$ are the radial and tangential strains in the plate, given by

\[ \epsilon_r = \frac{du}{dr} + \frac{1}{2} \left( \frac{dw}{dr} \right)^2 \]

and

\[ \epsilon_t = \frac{u}{r} \]

For simplicity, we only take the first two terms of (2), such that

\[ u(r) = r (c - r) (c_1 + c_2 r) \]  

(6)

Substituting (1) and (6) into (5) yields an expression for $U_{e,s}$ in terms of $c_1$ and $c_2$, which can be solved for $c_1$ and $c_2$ by finding the minimum of $U_{e,s}$ in terms of them, namely $\partial U_{e,s} / \partial c_1 = 0$ and $\partial U_{e,s} / \partial c_2 = 0$, giving

\[ U_{e,s} = \frac{16}{9} \frac{\pi Y t^5}{c^2 (1 - \nu^2)} \left[ \frac{\delta}{4} \left( \frac{w_0}{t} \right)^4 \right] \]  

(7)

where

\[ \delta = 0.1582 (2.689 + 1.523 \nu - \nu^2) \]

Finally, the total strain energy is given by

\[ U_{e,s+b} = U_{e,b} + U_{e,s} \]

whereby substitution of (4) and (7) gives

\[ U_{e,s+b} = \frac{16}{9} \frac{\pi Y t^5}{c^2 (1 - \nu^2)} \left[ \frac{1}{2} \left( \frac{w_0}{t} \right)^2 + \frac{\delta}{4} \left( \frac{w_0}{t} \right)^4 \right] \]  

(8)

The above is modified to account for the inclusion of a cylindrical island (Fig. S9), by noting that

\[ h = w(b) = w_0 \left( 1 - \frac{b^2}{c^2} \right)^2 \]

yielding
\[ w_0 = \alpha \, h \]  \hspace{1cm} (9)

where
\[ \alpha = \frac{1}{\left(1 - \frac{b^2}{c^2}\right)^2} \]

Substitution of (9) into (8) gives the strain energy in terms of the island height
\[ U_{e,s+b} = \frac{16}{9} \, \frac{\pi \, Y \, t^5}{c^2(1-\nu^2)} \left[ \frac{1}{2} \left( \frac{ah}{t} \right)^2 + \frac{\delta}{4} \left( \frac{ah}{t} \right)^4 \right] \]  \hspace{1cm} (10)

Finally, recasting the radii in terms of island dimensions, \( b = d/2 \) and \( c = d/2 + a \), gives the expression
\[ U_{e,s+b} = \frac{16}{9} \, \frac{\pi \, Y \, t^5}{c^2(1-\nu^2)} \frac{\pi^2}{4(c+d)^2} \left[ \frac{1}{2} \left( \frac{ah}{t} \right)^2 + \frac{\delta}{4} \left( \frac{ah}{t} \right)^4 \right] \]  \hspace{1cm} (11)

where
\[ \alpha = \frac{(d+2a)^4}{((d+2a)^2 - d^2)^2} \]

This is the same as Eq. (7) in Table 1 of the main text.

**6.2. Numerical Implementation**

The strain energy expression given in (11) can be substituted into the expression for total potential energy, \( \Pi \) (Eq. (1) in main text), in place of the bending or stretching strain energy. The entire expression can then be solved for the minimum total potential energy for parametric values of the island volume, \( V \), in the same manner as described in Sec. 2.3 of the main text.
7. Effect of $\gamma_{\text{Fe}}$.

We evaluated the effect of different $\gamma_{\text{Fe}}$, within reasonable limits based on Table 1 values. The lower limit of 2.432 J/m$^2$ is set by bcc-Fe(110) calculated from DFT with PBE, and the upper limit of 3.021 J/m$^2$ is set by hcp-Fe(0001) calculated from DFT with optB88. The results in Fig. S10 show that there is negligible effect.

![Graphs showing comparison of theoretical and experimental results for different values of Fe surface energy.](image)

**Figure S10.** Comparison of theoretical and experimental results for different values of Fe surface energy. The strain energy is taken from the free SLBT model with stretching only. Averages are shown by heavy tic marks on the y-axis. Vertical red line on the x-axis shows $h = 7$ nm, above which the islands are used to generate average values of $d/h$ and $d/a$. 
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