Supporting information for

Exploiting GISAXS for the study of a 3D ordered superlattice of self-assembled colloidal iron oxide nanocrystals

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GISAXS Experiment

Figure S1  Angular scan: sequence of GISAXS data for several values of the angle of incidence $\alpha_i$ (from 0.05° to 0.55°).
SR-XRPD analysis
Synchrotron radiation X-ray powder diffraction (SR-XRPD) characterization was performed at the Synchrotron Light Source (SLS) in Villigen, in transmission geometry, on the SLS Materials Science beamline Powder Diffraction station. The beamline optics was optimized for high angular resolution (FWHM) and aberration free operation of the MYTHEN II detector [1], which has a 50 µm strip pitch. The instrumental resolution function (IRF) was evaluated by fitting the XRPD pattern recorded on a LaB$_6$ NIST standard, measured under the same experimental beamline optics and detector conditions adopted for the samples of interest. The IRF file was provided separately to the program for XRPD data analysis. The XPRD measurements were performed on dry nanocrystal powders (i.e., made of randomly oriented NCs) obtained upon solvent evaporation from the corresponding colloidal solution.

The XRPD patterns were analyzed by the program FullProf [2], based on Rietveld whole profile fitting. The crystal structure models, used to fit experimental data, were maghemite (Fe$_2$O$_3$, space group P 43 3 2) and magnetite (Fe$_3$O$_4$, space group F d -3 m), having the same lattice parameter $a = 8.342566$ Å. Peak broadening and the unit cell parameter were refined. A modified Scherrer formula [3] was adopted to model the full width at half maximum of anisotropic peaks.

The fit reported in Figure S3 shows the results obtained if only the maghemite structure is included in the model. Indeed, the presence of the (211) and (220) peaks with comparable intensities (in the red circle in Figure S3) is characteristic of the only maghemite, so that this phase is certainly present in the sample. The presence of magnetite however can not be ruled out, as most of the relevant reflections are overimposed to the maghemite ones (red marks in Figure S3). Moreover, the fit returned a mean diameter of 9 nm and a basically spherical shape for the NCs.
Fig. S3 Experimental (symbols) and calculated (solid line) XRPD profiles. The expected peak positions for magnetite and maghemite are reported as well (red and black bars, respectively).

Theoretical model (GISAXS)

Description of the scattering process. Numerical simulation of GISAXS intensity maps is based on the solution of the wave equation

\[(\nabla + \mathbf{k}^2)\mathbf{E}(\mathbf{r}) = \mathbf{\tilde{E}}(\mathbf{r})\] (s1)

using distorted-wave Born approximation (DWBA) [4-6], where \(k = \frac{2\pi}{\lambda}, \quad \mathbf{\tilde{E}} = \mathbf{g}_{\text{add}} + 2\mathbf{k}^2\mathbf{\delta}(\mathbf{r})\) is the scattering operator, with \(\mathbf{\delta}(\mathbf{r}) = 1 - \mathbf{n}(\mathbf{r})\), where \(\mathbf{n}(\mathbf{r})\) is the position-dependent refraction index of the sample (here \(\mathbf{r}\) is the generic position vector). In the DWBA approximation, we divide the investigated sample into two parts – a non-disturbed system with the scattering operator \(\mathbf{\mathcal{V}}\), and the disturbance \(\mathbf{\mathcal{V}}\); we choose a semi-infinite Au substrate as a non-disturbed system and the system of nanocrystals deposited on it as a disturbance. The differential scattering cross-section calculated within the DWBA is a coherent superposition of two terms [4]:

\[
\left(\frac{d\sigma}{d\Omega}\right)_{\text{DWBA}} = \frac{1}{16\pi^2} \left| \left\langle \mathbf{E}_2^{(-)}|\mathbf{\tilde{\psi}}(1)|\mathbf{E}_1^{(\omega)} \right\rangle + \left\langle \mathbf{E}_2^{(-)}|\mathbf{\tilde{\psi}}(\mathbf{\mathcal{V}})|\mathbf{E}_1^{(\omega)} \right\rangle \right|^2
\] (s2)
where $E_{1,2}^{(\pm)}$ are two independent solutions of the non-disturbed wave equation, the latter time inverted, and $E_{1}^{(\text{in})}$ is the incident (vacuum) wave belonging to the solution of eq. s1. In Eq. (s2), the first matrix element describes the scattering from the non-disturbed system calculated dynamically, i.e., including multiple scattering effects, while the second matrix element accounts for the scattering from the disturbance (nanocrystals). Since the non-disturbed system contains only one ideally flat surface, the corresponding wavefield consists of ideally plane waves (the incident wave, the specularly reflected wave above the surface, and the transmitted wave under the surface), so that the reciprocal-space distribution of the scattered intensity corresponds to an infinitely narrow crystal truncation rod (CTR) perpendicular to the sample surface. In our experiments the CTR is completely screened out by a beam-stop and therefore we completely neglect the first matrix element in Eq. (s2) in the calculation of the diffuse part of the scattering cross-section.

Taking into account the structure of the wavefields $E_{1,2}^{(\pm)}$, the second matrix element in Eq. (s2) can be written as a coherent sum of four scattering processes, sketched in Figure S4,

![Figure S4](image)

**Figure S4** Sketch of the four scattering processes entering in Eqs. s2, s3, and described in Tab. s1.

...and takes the form

$$v_s = \langle E_{1}^{(\pm)} | \hat{\psi}_s | E_{1}^{(\pm)} \rangle = 2k^2 \delta \sum_{\alpha=1}^{4} A_{\alpha} F(Q_{\alpha})$$

(s3)

being $\delta = 1 - n$, $n$ the refractive index of the nanocrystal material, $A_{\alpha}$ and $Q_{\alpha}$ the amplitude and scattering vector of the process $\alpha$, respectively.

The amplitudes $A_{\alpha}$ of the scattering processes are expressed by the Fresnel reflection coefficients $r_{1,2}$ of the substrate surface belonging to the non-disturbed states 1 and 2. The scattering vectors $Q_{\alpha}$ equal the difference of the wave vectors of the incident and specularly reflected waves.

The four processes are summarized in Tab. s1. In the first order Born approximation (kinematic approximation – BA) the scattering processes 2-4 in Tab. s1 are neglected and only the first (direct) scattering process is considered. Therefore, in this approximation we completely neglect the influence of the substrate; the BA approximation is normally applicable for large incidence and exit angles $\alpha_{i,f}$. 


Tab. s1 Scattering processes in the DWBA description.

<table>
<thead>
<tr>
<th>Process</th>
<th>$A_\alpha$</th>
<th>$Q_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$k_2^{(nc)} - k_1^{(nc)}$</td>
</tr>
<tr>
<td>2</td>
<td>$r_1$</td>
<td>$k_2^{(nc)} - k_1^{(ncf)}$</td>
</tr>
<tr>
<td>3</td>
<td>$r_2$</td>
<td>$k_2^{(ncf)} - k_1^{(nc)}$</td>
</tr>
<tr>
<td>4</td>
<td>$r_1 r_2$</td>
<td>$k_2^{(ncf)} - k_1^{(ncf)}$</td>
</tr>
</tbody>
</table>

**Calculation of the GISAXS intensity**

The function $F$ in Eq. (s3) contains the positions $R_n$ and form factors $\Omega_n$ of individual nanocrystals:

$$F(\mathbf{Q}) = \sum_{n=1}^{N} \Omega_n(\mathbf{Q}) e^{-i \mathbf{Q} \cdot \mathbf{R}_n}$$

(s4)

where we have denoted $N$ the total number of nanocrystals in a coherently irradiated domain, and

$$\Omega_n(\mathbf{Q}) = \int \Omega_n(\mathbf{r}) e^{-i \mathbf{Q} \cdot \mathbf{r}} d\mathbf{r}$$

(s5)

is the Fourier transform of the shape function of the $n$-th nanocrystal.

In the structure model described in the next section we assume that both the positions and sizes of the nanocrystals are random and the irradiated sample surface consists of many coherently irradiated domains. Then, the measured intensity distribution is averaged over a statistical ensemble of all positions and sizes of the nanocrystals. The ensemble-averaged scattering cross-section is then

$$\left\langle \frac{d\sigma}{d\Omega} \right\rangle = \frac{1}{16\pi} \left\langle \left| r_{\alpha} \right|^2 \right\rangle \frac{k^2}{4\pi^2} \delta^{(2)} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} (\Omega_n(\mathbf{Q}) \Omega_n(\mathbf{Q}) e^{-i(\mathbf{Q} \cdot \mathbf{R}_n + \mathbf{Q} \cdot \mathbf{R}_\beta)}) = \text{const.} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} A_\alpha A_\beta G(\mathbf{Q}_\alpha, \mathbf{Q}_\beta)$$

(s6)

The correlation function $G$ is calculated assuming a suitable structure model of a self-organized nanocrystal array, as explained in the following.

The averaging procedure in the calculation of the correlation function $G$ depends on the statistical correlation of the nanocrystal sizes with their positions.

In the literature [6,7] two limiting approximations can be found: the decoupling approximation (DA), and the local monodisperse approximation (LMA). The former assumes that the sizes of the nanocrystals are statistically not correlated with their positions; the last assumes the sample consisting of many domains, each containing nanocrystals having well defined size and statistical properties of their positions. In our implementation of the LMA model we assume that the nanocrystals in a given coherently irradiated domain have a given uniform size, while the sizes in different domains are different. On the other hand, the parameters related to the nanocrystal positions do not differ in different domains. Then, the DA and LMA correlation functions have the following forms

$$G_{DA}(\mathbf{Q}_\alpha, \mathbf{Q}_\beta) = \left\langle \Omega_n(\mathbf{Q}) \Omega_n(\mathbf{Q}) \right\rangle_{\text{size}} \left\langle \Omega_n(\mathbf{Q}) \right\rangle_{\text{position}} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \left\langle \Omega_n(\mathbf{Q}) \right\rangle_{\text{size}} \left\langle \Omega_n(\mathbf{Q}) \right\rangle_{\text{position}}^* G(\mathbf{Q}_\alpha, \mathbf{Q}_\beta)_{\text{position}}$$

$$G_{LMA}(\mathbf{Q}_\alpha, \mathbf{Q}_\beta) = \left\langle \Omega_n(\mathbf{Q}) \Omega_n(\mathbf{Q}) \right\rangle_{\text{size}} G(\mathbf{Q}_\alpha, \mathbf{Q}_\beta)_{\text{position}}$$

(s7)

where the explicit formula for the correlation function
has been derived and reported in ref. [27] of the main text. The model of nanocrystal positions described above assumes the existence of averaged basis vectors \((a', b', c')\) with defined directions. This assumption however does not necessarily describe well the reality, since in an actual set of nanocrystals usually no pre-defined directions exist, as in the present case.

In order to take into account the many different azimuthal orientations of different ordered domains, in the calculation of the intensity distribution, the correlation function \(G(\mathbf{Q}, \mathbf{Q}')\) has been integrated numerically over all azimuthal directions of the basis vectors, keeping their mutual angles constant.

**GISAXS fitting procedure**

For each simulated 2D GISAXS map, the correlation (C) with the experimental one is calculated, as

\[
C = \text{FFT}^{-1} \left[ \frac{F_{\text{exp}} \cdot F_{\text{cal}}^*}{\text{abs}(F_{\text{exp}} \cdot F_{\text{cal}}^*)} \right]
\]

(s8)

where \(F_{\text{exp}}\) and \(F_{\text{cal}}\) are the Fast Fourier Transform of the 2D experimental (\(I_{\text{exp}}\)) and simulated (\(I_{\text{cal}}\)) map respectively, and \(\text{FFT}^{-1}\) is the inverse Fast Fourier Transform. The symbol * indicates the complex conjugate.

A correlation coefficient (CC) is then calculated, as

\[
CC = \max[\text{abs}(C)]
\]

(s9)

which represents the maximum value of the modulus of eq. s8 (the largest the CC value, the better the goodness of fit).

For each of the linear cuts along \(Y\) or \(Z\) (see Figures 4 and S5), the function \(\chi\) is evaluated, defined as

\[
\chi_n = \text{norm}(I_{\text{exp}}^n - I_{\text{cal}}^n) = \sum_i |I_{\text{exp}}^i - I_{\text{cal}}^i|
\]

(s10)

where \(I_{\text{exp}}^n\) and \(I_{\text{cal}}^n\) are the experimental and calculated intensities in the linear cut number \(n\), along the \(y\) or \(z\) direction, and the summation is taken over all the \(i\) points in the linear cut (the smaller the \(\chi\) value, the better the goodness of fit).

Finally an overall figure of merit (FOM) is evaluated, as the average of the CC and \(\chi\) coefficients:

\[
FOM = \frac{CC + \sum_{n=1}^N \chi_n}{N + 1}
\]

(s11)

where \(N\) is the number of selected cuts for the fit.

The best fit reported in Figure 4 (as well as the one in Figure S5) was obtained by minimizing the FOM, eq. s11.
Additional GISAXS simulations

Figure S5: fit in the DWBA description (parameters as in Tab. 1 of the main text).

Figure S6a shows the larger diffuse scattering produced in the BA/DA description (simulation parameters as in Tab. 1 of the main text). In Figures S6b and S6c are respectively reported the GISAXS simulation (BA/LMA description) for a perfect (111)-oriented \textit{fcc} structure, and the one for a (111)-oriented \textit{fcc} structure distorted along the diagonal parallel to the orientation direction, to show how this distortion is not sufficient to reproduce the “bending” of the first correlation peaks (around $2\theta_f = 0.9^\circ$), while keeping $\gamma = 120^\circ$.

Figure S5 (a) GISAXS experiment, and (b-e) fit in the DWBA description, with the same parameters as in Tab. 1 (main text).
**Figure S6** (a) GISAXS simulation with best fit parameters (as in Tab.1 of the main text), in the BA/DA approach; (b) BA/LMA simulations for a perfect *fcc* structure and (c) for a *fcc* distorted along the diagonal.

**References**


