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Local orientational order in self-assembled nanoparticle films: the role of ligand composition and salt

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An X-ray cross-correlation study of the local orientational order in self-assembled films made from PEGylated gold nanoparticles is presented. The local structure of this model system is dominated by four- and sixfold order. Coadsorption of shorter ligands in the particle's ligand layer and variation of salt concentration in the suspension prior to self-assembly result in a change of local orientational order. The degree of sixfold order is reduced after salt addition. This decrease of order is less pronounced for the fourfold symmetry. The results presented here suggest complex symmetry-selective order formation upon ligand exchange and salt addition and demonstrate the versatility of X-ray cross-correlation methods for nanoparticle superlattices.

1. Introduction

Nanoparticle (NP) superlattices are periodic arrays of NPs. Such assemblies can exhibit exciting new collective properties, different from those of the superposition of the individual NPs or the corresponding bulk materials, *e.g.* exceptional mechanical properties (Dreyer *et al.*, 2016). Understanding and controlling NP assembly thus allow for the design of new materials and their integration into devices by various coating, casting or printing techniques (Vogel *et al.*, 2015; Yang *et al.*, 2016; Wu, 2017). However, the assembly of NPs is nontrivial because of the complex interplay of interparticle forces during the self-organization (Xu *et al.*, 2013; Batista *et al.*, 2015). In particular, the collective behavior of the stabilizing ligands on the NPs involves many interdependent processes, such as grafting layer transitions, stabilizer entropy, faceting and solvent structuring (Zeng *et al.*, 2016).

For a general understanding of the self-organization, defined model systems are required that can be characterized in detail. An established platform to study the self-assembly is gold NPs (AuNPs) stabilized with a shell of poly(ethylene glycol) (PEG) (Bishop *et al.*, 2009; Zhang *et al.*, 2017; Schroer *et al.*, 2018). The high level of flexibility and control regarding size, size dispersity, and colloidal and chemical stability in combination with the high contrast in transmission electron microscopy (TEM) and X-ray scattering makes them versatile for fundamental studies (Schulz *et al.*, 2013, 2016). Their suitability for inkjet printing was demonstrated recently (Su *et al.*, 2019).

Regarding the investigation of three-dimensional self-organization, a specific challenge for the analytical methods is

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the requirement for obtaining structural information on bulk materials. There, electron microscopy and spectroscopy are limited because of low penetration depths. X-ray and light diffraction studies typically average ensembles and lack spatial information. X-ray cross-correlation analysis (XCCA), also known as fluctuation X-ray scattering, has been shown to overcome this limitation. Recently, the potential of XCCA has been demonstrated by various theoretical and simulation studies on 2D systems (Altarelli *et al.*, 2010; Kurta *et al.*, 2012; Lehmkuhler *et al.*, 2014; Malmerberg *et al.*, 2015; Latychevskaia *et al.*, 2015; Martin, 2017; Lhermitte *et al.*, 2017) and shown experimentally for thin polymer systems and NPs (Gutt *et al.*, 2014; Schroer *et al.*, 2015; Liu *et al.*, 2017; Lehmkuhler *et al.*, 2018), liquid crystals (Zaluzhnyy, Kurta, Sulyanova *et al.*, 2017), and colloids and nanocrystals (Mendez *et al.*, 2014; Mancini *et al.*, 2016; Lehmkuhler *et al.*, 2016; Schroer, Westermeier *et al.*, 2016; Mendez *et al.*, 2016; Zaluzhnyy, Kurta, André *et al.*, 2017; Mancini *et al.*, 2018). We previously measured the local orientational order of self-assembled NP films of thicknesses of up to a few micrometres by means of XCCA (Schroer *et al.*, 2015; Lehmkuhler *et al.*, 2018).

In the present work, we apply XCCA to self-assembled AuNP films to demonstrate the strong sensitivity of the local orientational order on the NP's surface chemistry, and also on the salinity of the solvent present during the self-organization. XCCA proves to be a powerful tool to characterize NP superlattices and can contribute to the optimization of large-scale structures.

2. Experimental

2.1. Sample preparation

Quasi-spherical gold nanoparticles (diameter $d = 27.7 \pm 2.1$ nm) were synthesized with a seeded growth protocol (Bastús *et al.*, 2011). The ligand α -methoxypoly(ethylene glycol)- ω -(11-mercaptoundecanoate) (PEGMUA) with $M \simeq 2000$ g mol⁻¹ was synthesized as described previously (Schulz *et al.*, 2013). The syntheses of AuNP coated with PEGMUA (AuNP@PEGMUA) or 1:1 mixed ligand layers of PEGMUA and 11-mercaptoundecanoic acid (MUA) were conducted as described earlier for smaller AuNPs (Schulz *et al.*, 2016). An as-synthesized aqueous solution of citrate-stabilized AuNP [$c(\text{AuNP}) = 1$ nM, 100 ml] was added under rapid stirring to PEGMUA or a 1:1 ligand mixture of PEGMUA and MUA in ethanol to yield 80 μM of ligands in total in the final mixture at room temperature. After several hours of stirring, the AuNP conjugates were purified and concentrated by repeated centrifugations (6000 g for 30 min) to 200 nM. The AuNP concentrations were determined by UV/vis spectroscopy (Haiss *et al.*, 2007); the diameter was obtained by TEM analysis. Absorbance measurements were carried out using a Varian Cary 50 spectrometer. UV microcuvettes sealed with lids (Plastibrand, Carl Roth GmbH, Karlsruhe, Germany) were used for all experiments. The concentrated AuNP-conjugate solutions are colloidally stable and can be dried and redispersed on various substrates without aggregation.

We prepared thin films assembled from different AuNP dispersions: (1) AuNP@PEGMUA, (2) mixed ligands of 1:1 PEGMUA and MUA (denoted as 50% MUA), (3) AuNP@PEGMUA with 5 mM NaCl, and (4) 50% MUA dispersions with 5 mM NaCl. The nanoparticle films were prepared on square silicon nitride membranes in square silicon supporting frames (Silson Ltd, UK). The membrane area was 3.0×3.0 mm with a thickness of 1 μm . The frame size was 7.5×7.5 mm and the frame thickness was 535 μm . Under these conditions the solutions dry in a well defined volume and the film thickness can be controlled by the AuNP concentration. This way, film thicknesses between approximately 100 and 600 nm are obtained (Lehmkuhler *et al.*, 2018). For each film, 7.5 μl solutions of AuNP with the different ligands and salt content described above were pipetted onto the framed membrane and dried at 338 K.

2.2. X-ray scattering experiments

The X-ray scattering experiments were performed on the coherence applications beamline P10 at PETRA III (DESY, Hamburg). We used the GINIX setup in small-angle scattering geometry (Kalbfleisch *et al.*, 2011) in order to achieve beam sizes of 400×400 nm by a Kirkpatrick–Baez mirror system. The X-ray photon energy was set to $E = 13.8$ keV. As detector, a Dectris Eiger X 4M was placed 5 m downstream of the sample.

After the samples had been put into the sample holder, representative regions of interest (ROIs) were defined by optical microscopy. Scattering patterns were taken from these ROIs in grids of typically 30×30 μm ($x \times y$) in steps of 500 nm and with 1 s exposure time per pattern. At least four ROIs were measured for each sample, which results in ensembles of more than 15 000 individual scattering patterns per sample. The patterns were corrected for scattering background from the empty chamber and SiN membranes. Afterwards, XCCA was applied following the procedures discussed elsewhere (Lehmkuhler *et al.*, 2014).

3. Results

An example of a scattering pattern is shown in Fig. 1(a). The beamstop, beamstop holder and inactive detector areas have been masked. The pattern suggests a sixfold local orientational order as expressed by the six strong reflections at the maximum of $I(q)$. This agrees with our previous study, where we reported a well developed four- and sixfold local orientational order in such thin films (Lehmkuhler *et al.*, 2018).

The azimuthally integrated intensity $I(q)$ of all samples is shown in Fig. 1(b). As the sample preparation procedure results in heterogeneous films of different thicknesses on a local scale (Lehmkuhler *et al.*, 2018), $I(q)$ has been averaged for regions of similar thickness of all samples, as expressed by the average intensity from each pattern. All $I(q)$ show a well developed structure factor peak around $q = 0.21\text{--}0.24$ nm⁻¹; however, its amplitude differs for all samples. A strong peak can be observed for the AuNPs with PEGMUA ligands, which

Figure 1

(a) Example of a diffraction pattern taken from the PEG sample. The modulus q and the azimuthal difference Δ are indicated. (b) Integrated intensity $I(q)$ for all samples studied. The data are offset vertically for clarity.

is less pronounced upon addition of salt to the solvent prior to self-assembly. The same trend can be observed for the 50% MUA ligands, which show less prominent peaks compared with the corresponding PEGMUA samples. This suggests that (i) the addition of salt and (ii) the presence of MUA in the particles' shell lead to less ordered films. The latter has been observed in assembled monolayers (Schulz *et al.*, 2016); however, the effect of MUA on the assembly of thin 3D films has not been studied so far. In addition, for 50% MUA + salt the forward scattering is increased, suggesting the formation of disordered clusters of different shape, e.g. rod-like assemblies. A fit of $I(q)$ for $q \leq 0.18 \text{ nm}^{-1}$ yields a power-law dependence of $I(q) \propto q^{-1.6}$, which resembles the exponents expected for differently shaped quasi-2D aggregates of between -1 and -2 , shown as dashed lines in Fig. 1(b) (de Jeu, 2016). Such aggregates may originate from the

formation of cracks during drying and are in addition visible by scanning electron microscopy as shown previously (Lehmkuhler *et al.*, 2018).

In order to obtain quantitative information on the degree of order upon self-assembly, the data were analyzed in the framework of XCCA. XCCA experiments probe the orientational order of the sample via angular correlation functions. In our case we calculate correlations of intensity $I(q, \phi)$ at fixed wavevector transfer $q = (4\pi/\lambda) \sin(\theta/2)$, with the X-ray wavelength λ , the scattering angle θ and azimuthal angle ϕ . The correlation function of intensity at angular differences Δ is thus given by (Wochner *et al.*, 2009)

$$C(q, \Delta) = \frac{\langle I(q, \phi)I(q, \phi + \Delta) \rangle_\phi - \langle I(q, \phi) \rangle_\phi^2}{\langle I(q, \phi) \rangle_\phi^2}. \quad (1)$$

The type and degree of local orientational order are expressed by the Fourier coefficients of ℓ th order $\hat{C}_\ell(q)$ of $C(q)$ with respect to Δ (Altarelli *et al.*, 2010; Kurta *et al.*, 2012; Lehmkuhler *et al.*, 2014; Kurta *et al.*, 2016). Applying the Wiener–Khinchin theorem, these are given by the Fourier coefficients $\hat{I}_\ell(q)$ of normalized intensity via

$$\hat{C}_\ell(q) = |\hat{I}_\ell(q)|^2. \quad (2)$$

To obtain access to the ensemble-average orientational order of the sample, the variance

$$\Psi_\ell(q) = \langle \hat{I}_\ell(q)^2 \rangle_c - \langle \hat{I}_\ell(q) \rangle_c^2 \quad (3)$$

has been introduced (Lehmkuhler *et al.*, 2014), where $\langle \rangle_c$ denotes the average over the studied ensemble.

In our previous study (Lehmkuhler *et al.*, 2018) we reported an increase of orientational order with sample thickness. For thin films the scattered intensity is proportional to the sample thickness in small-angle X-ray scattering (SAXS) experiments. So that we can neglect the impact of sample thickness on the XCCA results, only patterns with a similar average intensity and thus similar film thickness were used for the analysis.

The ensemble averages $\Psi_\ell(q)$ are shown in Fig. 2 for $\ell \leq 20$ as a function of q and ℓ . The results have been averaged over

Figure 2

Orientalional order $\Psi_\ell(q)$ for all studied samples.

Figure 3
Degree of orientational order Ψ_ℓ for $q = 0.24 \text{ nm}^{-1}$.

all studied sample spots. Only even coefficients contribute significantly, which underlines the validity of Friedel's law for the thin samples (Lehmkühler *et al.*, 2014; Liu *et al.*, 2016). Comparing all samples, the PEGMUA sample shows the highest amplitudes, followed by PEGMUA with salt, 50% MUA and 50% MUA with salt. Similarly to our previous study (Lehmkühler *et al.*, 2018), the PEGMUA samples show dominant four- and sixfold symmetries. This is less pronounced for the 50% MUA samples, suggesting the formation of less ordered films. Furthermore, the highest degree of Ψ_ℓ can be found around $q = 0.25 \text{ nm}^{-1}$, *i.e.* in the vicinity of the maximum of $I(q)$.

The degree of orientational order Ψ_ℓ at $q = 0.24 \text{ nm}^{-1}$ is displayed in Fig. 3. As discussed above, dominant four- and sixfold symmetries are present for all samples. For $\ell \geq 8$, the orientational order Ψ_ℓ is similar for all samples, with slightly larger values for PEGMUA. Ψ_4 and Ψ_6 show the discussed trend, *i.e.* $\Psi(\text{PEGMUA}) > \Psi(\text{PEGMUA} + \text{salt}) \simeq \Psi(50\% \text{ MUA}) > \Psi(50\% \text{ MUA} + \text{salt})$. The amplitude changes by a factor of about 2–3 between PEGMUA and 50% MUA + salt. For the latter, the amplitude of Ψ_ℓ varies only slightly with ℓ , suggesting less preferred local orientational order as present in the other samples.

In order to study the orientational order in more detail, the q dependence of Ψ_6 is shown in Fig. 4(a). Note that the asymptotic behavior is similar for other even values of ℓ , as can be seen from Fig. 2. In general, Ψ_ℓ was found to show an asymptotic q^{-2} behavior, best developed for $\ell = 4$ and $\ell = 6$. In contrast, Malmerberg *et al.* (2015) reported a q^{-8} dependence of the coefficients. This should thus asymptotically approach a constant value by normalization to $I(q)^2$ as done in equation (1), because $I(q) \propto q^{-4}$ for spheres. We assign the remaining q dependence to a particular fingerprint of existing orientational order, because it is less defined for weak even and odd ℓ .

While the general q dependence is similar for all samples, the results differ in amplitude between approximately 10^{-2} for PEGMUA and 3×10^{-3} for 50% MUA with salt at $q = 0.25 \text{ nm}^{-1}$.

As discussed in earlier publications (Lehmkühler *et al.*, 2014, 2016, 2018) and shown in Fig. 2, the odd coefficients do

Figure 4
(a) q dependence of Ψ_6 for all studied samples. (b) Ψ_6 normalized to the average of odd coefficients between $\ell = 3$ and $\ell = 19$. (c) Same as (b) for Ψ_4 .

not differ significantly and represent basically a background measure, *e.g.* reflecting noise and setup-dependent contributions (Lehmkühler *et al.*, 2014). They may also originate from the curvature of the Ewald sphere (Liu *et al.*, 2016), which is otherwise negligible for the thin samples studied here. Moreover, they account for intensity variations between different sample systems (Lehmkühler *et al.*, 2018). Therefore, we normalize Ψ_6 and Ψ_4 to the average Ψ_{odd} of the odd coefficients between $\ell = 3$ and $\ell = 19$. The results are shown in Figs. 4(b) and 4(c). For Ψ_6 the results resemble the observation from Figs. 3 and 4(a). In addition, a splitting of the second peak around $q = 0.4 \text{ nm}^{-1}$ becomes obvious for the PEGMUA samples, which is absent for 50% MUA. This is accompanied by a peak shift to larger q for 50% MUA. We associate this with the thinner effective ligand layer upon addition of MUA (Schulz *et al.*, 2016), which affects the length scales of order formation. These observations are mirrored for Ψ_4 ; however, its amplitudes are slightly lower than those of Ψ_6 . Most interestingly, the results for PEGMUA and PEGMUA + salt match each other. This indicates that the addition of salt leads to a reduced degree of sixfold order, while the fourfold structure remains unaffected.

4. Summary and conclusions

We have studied the structure of self-assembled films of gold nanoparticles as a function of PEG-based ligand composition

and salt content in the colloidal dispersion. The SAXS data suggest a decrease of order upon addition of MUA to the ligand shell as well as upon the addition of salt. The orientational order studied by XCCA is governed by four- and sixfold order for both types of ligands. This agrees with our previous study, where heterogeneous films with cubic and hexagonal local orientational order were obtained (Lehmkuhler *et al.*, 2018). The comparison between PEGMUA and 50% MUA indicates that the presence of MUA in the ligand shell results in less ordered self-assembled films. This is in agreement with previous observations of monolayers, where particles with pure PEGMUA ligands form a hexatic 2D film whose order is disturbed when MUA is present (Schulz *et al.*, 2016). It is related to different surface charges of PEGMUA-coated AuNPs and those with mixed ligand shells affecting the assembly of monolayers. The addition of salt results in a similar effect for both samples, *i.e.* a significant decrease of the degree of orientational order. In addition, MUA addition leads to different ligand layer conformations that affect the stability of the particles (Schulz *et al.*, 2018). Obviously, this way the assembly of layers in the (sub-)micrometre range as studied in this work is affected as well.

Addition of salt decreases the solubility of PEG in water (Ren *et al.*, 2011). Recently, the formation of supercrystals of AuNP@PEG in solution at high salt concentrations was observed (Zhang *et al.*, 2017; Schroer *et al.*, 2018). This suggests the formation of well ordered self-assembled structures after addition of salt to the dispersion. In contrast to those observations, the degree of orientational order decreases for the salt samples, which is accompanied with a less defined averaged structure obtained by SAXS. In particular for the 50% MUA sample, the increased forward scattering suggesting the formation of disordered clusters is reflected by the low degree of orientational order obtained by XCCA.

For samples with PEGMUA ligands, the degree of sixfold symmetry expressed by $\Psi_6(q)$ is reduced by the addition of salt. In contrast, $\Psi_4(q)$ remains unchanged. Most importantly, samples with 50% MUA ligands show a reduced orientational order for all q upon salt addition. This suggests complex symmetry-selective effects of salt and ligand exchange on the formation of self-assembled superstructures during the drying process. Recently we observed changes of the compressibility of PEG-based ligands after salt addition as well as after ligand modification with MUA (Schroer, Schulz *et al.*, 2016; Schulz *et al.*, 2018; Schroer *et al.*, 2018). Therefore, the plasticity of ordered and ordering clusters may change during drying, as reported recently for shear band formation in directed drying processes (Yang *et al.*, 2018). This may further lead to modifications of local orientational order as reported in this study.

In summary, we have analyzed the role of ligand layer composition and salt addition for the local orientational order of self-assembled AuNP@PEG films with XCCA. PEG and other polymer coatings allow one to stabilize NPs effectively and to tune their properties but will also affect their self-assembly behavior. Detailed structural analyses of such materials will contribute to the understanding of NP assembly,

thus assisting the design of materials and devices based on NP films.

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