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Supercrystal Formation of Gold Nanorods by High Pressure Stimulation

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Abstract

We demonstrate the pressure-induced formation of supercrystals made from PEGylated gold nanorods in aqueous suspension. Utilizing the combined effect of hydrostatic pressure and salt on the solubility of the organic PEG shell that passivates the nanorods, the reversible formation of two-dimensional hexagonal supercrystals has been observed by means of small angle X-ray scattering. The pressure dependence of the crystal lattice's structural parameters is determined. By time-resolved measurements performed after a pressure-jump, the growth process of the crystals is found to be finished already after a few seconds. The presented results demonstrate that by PEGylating nanoparticles pressure-induced homogeneous supercrystals can be formed for different particle shapes, in particular anisotropic nanorods, which determine the resulting lattice type.

Introduction

The formation of nanoparticle supercrystals has been studied in great detail throughout the last decades motivated by the fact that these can exhibit exciting properties.¹⁻⁵ Ongoing research efforts aim at improving reproducibility, scalability, control and precision in supercrystal syntheses, understanding their emergent properties and their potential applications.^{3,6-15}

In the case of gold nanoparticles (AuNP), the according supercrystals are especially interesting because of their ensemble plasmonic properties and therefore termed plasmonic supercrystals.¹⁶ The localized surface plasmon resonances - collective, coherent oscillations of the conduction band electrons in metals - of the individual constituent nanoparticles can couple in such supercrystals resulting in new modes and strongly enhanced local electric fields, so-called hot spots, that can be utilized, *e.g.*, in enhanced spectroscopies and for the design of new optical metamaterials.¹⁷ Plasmonic properties strongly depend on the shape

of the NP, and accordingly, supercrystals of anisotropic NP are not only interesting because of their structural diversity,¹⁸ but also help to optimize properties for desired applications. Gold nanorods (AuNR) for instance absorb strongly in the biological window,¹⁹ where little background absorption of biological material occurs.

We recently observed well-defined crystallization directly from aqueous particle suspensions induced by pressure for PEGylated spherical AuNP.^{20,21} This crystallization is fast and largely reversible. Unlike previous high pressure studies on NP assemblies starting with preordered crystals,^{22–27} in our approach we observe pressure-induced crystallization directly from the liquid state. The basis of this transition is the combined effect of pressure^{28,29} and salt ions^{30–32} on the PEG solvency, which leads to a deswelling transition of the PEG-coating. This collapse of the ligand shell is accompanied by an increase of the attractive interparticle interactions,^{33,34} resulting in the supercrystal formation. Having investigated in detail the role of different salt types and concentrations and ligand lengths, ideal conditions for the supercrystal formation of spherical nanoparticles have been determined.²⁰

PEGylation of nanomaterials is well established,^{35,36} and thus the described fast pressure-induced crystallization of NP in solution could be an accessible general method, not only to form supercrystals in solution but also to tune the interparticle distances within the crystals with high precision reversibly by further increasing the pressure. Since plasmonic coupling sensitively depends on the interparticle distance, this tuning ability is valuable for fundamental studies of plasmonic properties.

In the present study we demonstrate that the previously discussed concepts are indeed also applicable for anisotropic particles, namely PEGylated AuNR with low dispersity. Applying high pressure on AuNR suspended in concentrated rubidium chloride (RbCl) solutions leads to the reversible formation of two-dimensional supercrystals with hexagonal lattice structure. Performing small angle X-ray scattering (SAXS) allows us to determine the structural parameters at different pressures (Fig. 1 a)). In addition, the formation kinetics following a pressure-jump are determined. Supercrystal formation is found taking place within a few

Figure 1: a) Structural assembly of PEGylated AuNR together with the corresponding 2D SAXS patterns at 1 bar (0.1 MPa; top) and 4000 bar (400 MPa; bottom). Without pressure, the AuNR@PEG are in an amorphous liquid state. Upon reaching the crystallization pressure, hexagonal supercrystals are formed. b) TEM image of dried AuNR@PEG assemblies on a TEM grid.

seconds.

Materials & Methods

Materials

AuNR and the ligand α -methoxypoly(ethylene glycol)- ω -(11-mercaptoundecanoate) (PEG-MUA2k) with a molecular weight of 2000 g/mol were synthesized as described previ-

ously.^{37,38} For the AuNR synthesis the seeded-growth method using binary surfactant mixtures was used (for more details, see Ref. 37). For the ligand exchange, 160 ml of AuNR were concentrated by centrifugation (7000 g, 20 min) and 150 ml supernatant replaced with PEGMUA2k solution (27 μ M). After 2 d reaction under shaking on a lab shaker, the mixture was concentrated to 12 ml by centrifugation, the volume adjusted to 20 ml followed by fivefold extraction with chloroform (10 ml for each extraction). Then, 160 mg PEGMUA2k were added, and after 2 h reaction under shaking the AuNR@PEGMUA2k were purified and concentrated by repeated centrifugations ($5 \times 7000 \text{ g} \times 30 \text{ min}$). A detailed description and discussion of the ligand exchange and characterization of the AuNR@PEGMUA2k (herein referred to as AuNR@PEG) can be found in Ref. 37.

According to the analysis of transmission electron microscopy (TEM) images, the length and width of the AuNR were $(75.4 \pm 7.4) \text{ nm} \times (21.4 \pm 1.6) \text{ nm}$ corresponding to an aspect ratio of 3.6 ± 0.6 (Fig. 1 b)). The concentration of AuNR@PEG used for the pressure experiments was 8 nM in 25 mM TRIS buffer, corresponding to a volume fraction of 0.1 %, as determined by UV/vis spectroscopy.

AuNR@PEG solutions with 2 M RbCl were prepared by dissolving the according amount of RbCl in a defined volume of AuNR@PEG. Based on our previous study,²⁰ this salt condition was chosen as for this, homogeneous formation of supercrystals made by PEGylated spherical AuNPs was observed.

Small Angle X-ray Scattering

High pressure small angle X-ray scattering (SAXS) measurements were performed at beamline I22, Diamond Light Source, Didcot, U.K.,³⁹ employing the beamline's high pressure setup.⁴⁰ The setup consists of a high pressure sample cell, which is sealed by two diamond windows to allow the X-ray beam to pass. Hydrostatic pressure is generated using water as the pressurizing medium. The pressure increase is performed fully automatically. A $230 \mu\text{m} \times 140 \mu\text{m}$ (FWHM; $h \times v$) X-ray beam was used at an energy of $E = 18 \text{ keV}$ (wave length

$\lambda = 0.68 \text{ \AA}$). Two-dimensional SAXS patterns were recorded by a Pilatus 3-2M detector at a sample-detector-distance of 6.7 m. Freshly prepared AuNR@PEG suspensions were filled into polycarbonate capillaries (sample volume $\approx 25 \text{ }\mu\text{l}$), sealed and placed into the sample cell.

For static measurements 2D SAXS patterns were recorded at different pressures from $p = 1 \text{ bar}$ (0.1 MPa) to 4000 bar (400 MPa) in $\Delta p = 500 \text{ bar}$ (50 MPa) steps. The exposure time per image was 500 ms. In addition, time-resolved SAXS measurements after pressure jumps were performed. The pressure-jump method allows us to follow the kinetics of a temporal evolving system after a rapid change of pressure and has found recent applications for soft matter systems.^{41–44} In our experiment, a set of 7500 images was collected with a exposure time per single frame of 4 ms, yielding a total collection time of 30 s. The pressure jumps were performed 1 s after the data collection had been started to ensure covering the full kinetics. Pressure-jumps are performed within 5 ms.⁴⁰ We carefully checked for radiation damage of the sample by using different absorbers to attenuate the X-ray photon flux on the sample.

Two-dimensional SAXS patterns were azimuthally averaged (masking out the shadow of the beamstop and inter-module section) using the beamline data processing pipeline,⁴⁵ resulting in 1D SAXS profiles. From these, the scattering signals from the pure solvent (without AuNR@PEG) at the respective pressures were subtracted.

Results

Fig. 2 shows the 1D SAXS curves from AuNR@PEG suspended in 2 M RbCl solution. At ambient pressure, the data reveal scattering from concentrated nanoparticles in the liquid state without any crystalline order. Pronounced minima stemming from the particle shape are visible at $q \approx 0.35 \text{ nm}^{-1}$ and $q \approx 0.63 \text{ nm}^{-1}$ that reflect a low dispersity. A weak structure factor peak is present at $q_{\text{max}} \approx 0.155 \text{ nm}^{-1}$ which indicates short range order

Figure 2: SAXS curves of PEGMUA-coated AuNR suspended in 2 M RbCl solution at different pressures (0.1 MPa to 400 MPa). For the curve at $p = 1$ bar, the form factor fit $P(q)$ is shown (dash-dotted line). The position of the expected Bragg reflections for a hexagonal lattice are marked by dots and the respective indices h, k . All curves are shifted for clarity.

between the AuNR@PEG, characteristic for the liquid state.

The experimental data can be well described by the form factor of a long cylinder with log-normal distributed radius R for $q > 0.1 \text{ nm}^{-1}$ using the software *SASFIT*.⁴⁶ The refinement yields a mean radius $R_{\text{mean}} = (11.0 \pm 0.5) \text{ nm}$ and size polydispersity of $\Delta R/R_{\text{mean}} = 9\%$. Due to the presence of interparticle correlations at small angles, the cylinder length L can only be approximately estimated to $L = 80 \text{ nm}$. These parameters are consistent with the TEM data (Fig. 1 b)).³⁷ In particular, they reflect the size of AuNR core without the PEGMUA coating. As shown previously, SAXS measurements are dominantly sensitive to the Au core, as the ligand shell has a much weaker scattering contrast.^{20,33,34}

With increasing hydrostatic pressure up to $p = 2000 \text{ bar}$ (200 MPa), only slight changes of the SAXS profile are present. In particular, the form factor does not change, while the intensity of the structure factor peak drops and the peak position shifts slightly to larger scattering angles ($q_{\text{max}} \approx 0.17 \text{ nm}^{-1}$).

In contrast, when reaching a pressure of $p = 2500$ bar (250 MPa), strong Bragg reflections are present indicating the formation of supercrystals by the AuNR@PEG within the suspension. The underlying crystal structure can be identified with a 2D hexagonal lattice with four observable Bragg reflections (1,0), (2,0), (2,1), and (3,1) (Fig. 2). Such triangular and hexagonal lattice structures have been reported for high-aspect-ratio NR previously.^{47,48}

When reaching the crystallization pressure, supercrystals form within the whole suspension. Isotropic, continuous Debye-Scherrer rings indicate that these supercrystals are fully randomly orientated (Fig. 1 a)). With further pressure increase, the Bragg reflections shift to larger q while the width and number of peaks stay constant. This indicates a continuous compression of the supercrystal lattice without further pressure-induced crystal growth.

After releasing the pressure, no Bragg reflections are present anymore (curve ‘1 bar (b)’ in Fig. 2). This shows that the pressure-induced supercrystal formation for AuNR@PEG is reversible, as also reported previously for spherical nanoparticles.²⁰

The position of the Bragg reflections for a 2D hexagonal lattice are connected to the lattice constant a via

$$q_{(h,k)} = \frac{2\pi}{a} \sqrt{\frac{4}{3}} \sqrt{h^2 + hk + k^2}, \quad (1)$$

where h and k denote the Miller indices.

At the crystallization pressure, the lattice constant a is found to be $a = (35.9 \pm 0.3)$ nm. Here, a reflects the interparticle spacing between the AuNR@PEG along the short axis of the nanorods. The resulting supercrystals are therefore formed by a lateral ordering of the nanorods along their short axis. Notably, there is no ordering along the long axis observed, which would result in a peak around $q = 2\pi/L = 0.07 \text{ nm}^{-1}$, that could be resolved with the given experimental settings. Therefore, the supercrystals exhibit long-range order in lateral direction while having no order along the long cylinder axis.

The interparticle spacing for the liquid and crystalline state at different pressures is shown

in Fig. 3. For the crystals, the distance is directly given by the lattice constant a . In case of the liquid state, the position of the structure factor maximum can be connected to an interparticle correlation distance $d_{\text{corr}} = \frac{2\pi}{q_{\text{max}}} \sqrt{\frac{4}{3}}$ as it reflects a local pre-ordering similar to the (1,0) reflection. For $p = 1$ bar we find $d_{\text{corr}} \approx 47$ nm, revealing that the AuNR@PEG are already weakly correlated along the short axis in radial direction at the beginning.

For the whole pressure range the interparticle distance decreases, while there is a sharp drop reaching the crystallization pressure. Interestingly, the strength of compression is higher for the liquid state than for the crystalline state. This pressure dependence of the particle separation allows us to determine the effective compressibilities κ_{eff} for both phases. We find $\kappa_{\text{eff,liquid}} = (10.6 \pm 0.7) \times 10^{-10} \text{ Pa}^{-1}$ and $\kappa_{\text{eff,cryst}} = (6.8 \pm 0.7) \times 10^{-10} \text{ Pa}^{-1}$. The slightly larger value for $\kappa_{\text{eff,liquid}}$ might reflect more swelling of the ligand shell than for the crystalline state.

Although the ligand shell cannot be directly determined by SAXS, the difference between d_{corr} and the NR core diameter can yield indirectly information on the shell thickness.^{33,34} We determine an effective correlation length $s = d_{\text{corr}}/2 - R_{\text{mean}} = (12.5 \pm 0.5)$ nm for $p = 1$ bar. This value is slightly larger than (10 ± 1) nm, the shell thickness of PEGMUA2k on spherical NPs, and than theoretical expectations considering a ligand grafting density of $3.0 - 3.3 \text{ nm}^{-2}$ that was determined for these AuNR@PEG.^{34,37} This implies that despite some weak and presumably transient correlations, the AuNR@PEG are not firmly attached to each other. We note that PEG high grafting densities are critical to achieve concentrations of AuNR@PEG as used in this study and that the specific PEG-ligand used, PEGMUA2k, allows for such high grafting densities.^{34,37}

For the crystal state, the ligand shell thickness can be determined as $t = a/2 - R_{\text{mean}}$, which yields $t = 7.0 - 7.5$ nm, pointing to a still hydrated PEG-shell. It is thus likely that not only attractive van der Waals interactions between the AuNR cores, but also the interactions between PEG-shells determine the crystallization.⁴⁹ At high pressure and high salt conditions, the polymer–polymer interactions of the ligand chains seem to be favored

Figure 3: Interparticle spacing between the AuNR@PEG at different pressures (0.1 MPa to 400 MPa). For p up to 2000 bar (200 MPa), the AuNR@PEG are in the liquid state (red squares), while for higher pressures, the AuNR@PEG form supercrystals in solution (blue circles). Also shown are the data after the pressure-jump (black diamonds, lattice constants for start and end).

over the polymer–solvent interactions given rise to additional preferred interactions between the AuNR@PEG.

Inline with the previous findings on PEGylated nanoparticles under high pressures, the polymeric ligand gets compressed with increasing pressure.^{20,33,34} Upon reaching a critical pressure, the combined effect of the high salt concentration and pressure, both decreasing the solubility of the PEG-coating, leads to a collapse of the shell. This collapse is accompanied by an increase of the interparticle attraction of the coated nanorods which then results in supercrystal formation. Within the crystal state, the polymer shells are not fully dehydrated as these can be still compressed furthermore up to 4000 bar (400 MPa), the limit studied here.

Based on our previous findings for PEGylated AuNPs,²⁰ we speculate that also for other alkali chloride salts pressure-induced supercrystal formation of AuNR@PEG will take place, likely at higher crystallization pressures. Notably, divalent ions have been shown to induce

Figure 4: a) SAXS profiles collected at different time points t after a p -jump from 1700 bar (170 MPa) to 2040 bar (240 MPa). The curves have been shifted for clarity. Temporal evolution of first Bragg reflection's parameters: b) Peak position q_{max} . c) Intensity at the peak maximum, $I(q_{\text{max}})$. d) Peak width w . Solid lines mark exponential fits and dashed ones linear fits.

crystal formation of PEGylated NPs under ambient conditions.^{20,50} However, in comparison to those assembled under high pressures, they exhibit a lower degree of crystallinity. We attribute this to the homogenous assembly conditions at high pressures, in which all parts of the suspension are affected simultaneously, whereas the pure addition will result in a concentration gradient of the ions and therefore more heterogeneous conditions.

In order to study the time-dependence of the supercrystal formation process, a pressure-jump from the liquid into the crystalline state has been performed. Starting from a pressure $p = 1700$ bar (170 MPa), at which no crystals are formed, a rapid increase to $p = 2050$ bar (250 MPa) within 5 ms induces the formation of supercrystals as reflected by the (1,0)-reflection (Fig. 4 a)).

The growth and shift of the first Bragg reflection was characterized by fitting Gaussian

profiles to the data. From these, the temporal evolution of the peak position $q_{\max}$, intensity of the peak maximum, $I(q_{\max})$, and the peak FWHM w were determined (Fig. 4 b) – d)). Immediately after the p -jump ($t = 0$ s), the intensity increases, while the peak position and width start changing after $t \approx 1$ s.

In order to characterize the temporal evolution of the crystal formation, a limited kinetic growth model

$$X(t) = X_0 + \Delta X \left(1 - \exp\left(-\frac{t - t_0}{\tau}\right) \right) \quad (2)$$

was used for $q_{\max}$ and $I(q_{\max})$, which both increase after the p -jump. Herein, X_0 refers to the baseline value at the beginning, ΔX the growth amplitude, and t_0 a (possible) time shift. The characteristic time of the process is given by τ .

For the crystal width w , which decays as the crystals are forming, the data were refined using an exponential decay model

$$w(t) = w_{\infty} + \Delta w \left(\exp\left(-\frac{t - t_0}{\tau}\right) \right), \quad (3)$$

where w_{∞} is the width at $t \rightarrow \infty$.

The data reveal characteristic times of $\tau = 2 - 8.5$ s, as given in the legends of Fig. 4, using the exponential models for $q_{\max}$, $I(q_{\max})$ and w . This model hints to a crystallization and growth process. First, the peak position $q_{\max}$ is established, reflecting that the AuNR@PEG are assembling with an effective interparticle separation within a timescale of $\tau = 2$ s. Thereafter, these assemblies are growing to form crystals within $\tau = 4$ s, as can be deduced by the reducing peak width, which continues to grow further as can be seen from the peak intensity. The hexagonal crystals are therefore already formed within a few seconds time. At longer times, an additional temporal evolution is present which exhibits a linear dependence. This might be due to additional growth and relaxation processes within the formed supercrystals.

The peak position can be directly related to the lattice constant, which decreases from

$a(t = 0 \text{ s}) = (43 \pm 1) \text{ nm}$ to $a(t = 29 \text{ s}) = (36.3 \pm 0.1) \text{ nm}$, and fits with the observed values for the static measurements (Fig. 3). While the peak intensity and width reflect an increase of the degree of crystallinity, the lattice constant depends also on the swelling state of the ligand. The first step of the underlying mechanism for the crystal formation is suggested to be the pressure-induced deswelling of the PEG-ligand upon reaching the critical pressure, which has been determined to be a function of salt type and concentration.²⁰ For the present solution, the data point to a crystallization pressure between 2000 bar (200 MPa) and 2050 bar (205 MPa), indicating a narrow transition range. Previous studies report a relaxation rate of such a deswelling process on the millisecond time scale,^{43,51} suggesting that the PEG-ligands would be already collapsed immediately after the p -jump. After this deswelling transition, crystallization and growth is suggested to take place on a second time scale. This is followed by an additional relaxation and growth process which further leads to an increase in crystal order.

Conclusions

We have shown that the PEGylation of monodisperse nanorods allows the pressure-induced formation of supercrystals in concentrated salt solutions. The resulting supercrystals have 2D hexagonal structure which is based on the nanoparticle shape. The formation process is homogeneous and reversible, and takes place within several seconds as revealed by time-resolved SAXS measurements. The lattice size depends on the swelling state of the PEG-ligand.

This study thus demonstrates, that with the presented approach also anisotropic NP can be assembled into supercrystals. By varying the design parameters of the nanoparticles indeed different supercrystal structures can be formed whose actual lattice type depends on the NP shape as is shown in this study for NR forming a 2D hexagonal lattice and previously for spherical NP forming face-centered cubic lattices.

As hypothesized earlier, this strongly indicates that the crystallization is dictated predominantly by the PEG-ligand shells and should therefore be quite general and versatile. Using PEG-ligands with different molecular weights, *i.e.* ligand lengths, allows for tailoring the interparticle spacing within the supercrystals, that can be further tuned with subnanometer resolution by using pressure to compress the formed crystals reversibly. In the context of plasmonics this behaviour is very interesting for fundamental studies. Future work should address the experimental realization of according experiments, which could also pave the way to reversible enhanced spectroscopies in situ. We expect that pressure studies will also help to develop new synthetic approaches for the reproducible, scalable production of high quality NP supercrystals.

Conflicts of interest

There are no conflicts to declare.

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