Determination of the Surface Facets of Gold Nanorods in Wet-Coated Thin Films with Grazing-Incidence Wide Angle X-Ray Scattering

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This work studies the surface facets of gold nanorods (AuNRs) in wet-coated nanoparticle thin film with synchrotron-light based grazing-incidence wide angle X-ray scattering (GIWAXS) that provides statistically relevant results on many nanoparticles. Air-brush spraying deposits the monodisperse AuNRs into sparse monolayers where the long axis of rods is parallel to the substrate surface. It is found that the crystalline facets of individual AuNRs in the sparse monolayer are all in the same orientation, as indicated by narrow azimuthal widths of (200) reflections, over a macroscopic scale comparable to the substrate. This alignment is probably due to the rods' sitting on high-index surface facets such as (520) and (250). A quantitative analysis of the angles between bulk facets and the surface facets leads to a "nested-octagon" model for the cross sections of AuNRs: shell octagon with high-index crystalline facets (520), (5-20), (2-50), (-2-50), (-5-20), (-520), (-250), and (250), and core octagon consisting of low-index crystalline facets (100), (1-10), (0-10), (-1-10), (-100), (-110), (010), and (110).

Anisotropic gold nanoparticles are available in a range of shapes and sizes from wet-chemical synthetic protocols. They have been used to lend composite materials anisotropic optical and electrical properties, and they exhibit plasmon absorption

in the near-infrared region,^[1–3] which is of interest for biomedical applications, for example.^[4,5]

Many applications of gold nanorods involve chemical reaction of their surface facets. The chemical reactivity depends on the types and geometry of the surface facets, but it is difficult to provide statistically reliable information on the surface facet structure of a large number of rods today. Transmission electron microscopy (TEM) studies are inherently limited to individual rods; conventional X-ray scattering does not allow us to distinguish surface facets from the bulk ones, and atomic force microscopy (AFM) usually cannot provide atomic resolution on nanoparticles.^[6]

Reports on the crystalline structure of gold nanorod (AuNR) according to TEM data differ in their results.^[2,7–14]

Wang et al. reported an octagonal cross section with alternating (100)/(110) facets and tips covered with (110) and (111) facets.^[12] Carbo-Argibay et al.^[10] suggested high-index surface facets such as (250) and (520). The existence of high-index crystalline facets was also reported by Katz-Boon et al.^[7,9] and predicted in molecular dynamic simulations^[15] and density functional theory calculations.^[16] Recently, Goris et al.^[8] pointed out that the high-index (520) surface facets might coexist with low-index (100)/(110) surface facets. Data from alternative characterization techniques may resolve this debate.

Previous studies indicated that the crystalline structure information from TEM strongly depends on the sample preparation, and only facets that lie parallel to the electron beam provide good electron contrast and thus clear atomic-scale morphology.^[9,10] X-ray scattering^[6,17–20] is a well-established technique for the analysis of crystalline materials that can complement TEM measurements by penetrating many nanoparticles and providing statistical structure information.^[21–23] Traditional XRD integrates over statistically scattered signals from many of irregularly aligned nanodomains and provides bulk information.

In this work, we correlate synchrotron-light based grazing-incidence wide angle X-ray scattering (GIWAXS) with electron microscopy and atomic force microscopy to characterize the structure of AuNRs in sparse monolayers. We prepared the monodisperse AuNRs by adapting the protocol reported by Ye et al.^[24] and created a water-dispersible and colloidal stable

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Figure 1. a) Bright-field TEM image of rod-shaped AuNR. b) Selected-area electron diffraction pattern of single AuNR. c) TEM image of the AuNR lying in the selected-area diffraction aperture. In panel (b), the (111) and (222) reflections are indexed.

AuNRs' dispersion by exchanging the original ligand cetyltrimethylammonium bromide (CTAB) with a poly(3,4-ethylene dioxithiophene):polystyrene sulfonate (PEDOT:PSS) (see the Supporting Information).^[25]

We first studied the morphology and crystalline structure of individual AuNRs using TEM (JEM-2100, JEOL, Akishima, Japan) and electron diffraction (ED). **Figure 1a** shows a TEM image of monodisperse AuNRs with regular rod shape. Typical ED results with corresponding morphology are given in **Figure 1b** and **Figure 1c**, respectively. The diffraction spots in **Figure 1b** are attributed to the (111) and (222) reflections. The ED data analysis was carried out assuming a gold single crystal with face-centered cubic (FCC) cell and distances between the adjacent (111) and (222) lattice planes of 2.35 and 1.175 Å, respectively. Sharp diffraction spots in **Figure 1b** and regular atomic arrangement observed along the rod in high-resolution TEM (cf. **Figure S1**, Supporting Information) indicate that single crystal AuNRs formed.

It is difficult to detect surface facets in standard TEM, electron diffraction, or powder X-ray diffraction. High-index facets generally provide weaker scattering than the low-index ones. The high-index crystalline facets recently reported for AuNR^[7,8,10] and palladium^[26] show very low peak intensities (I_{hkl}) due to the synergistic interactions of structural factor (F_{hkl}), scale factor (K), multiplicity factor (p_{hkl}), Lorentz factor (L_{θ}), polarization factor (P_{θ}), absorption multiplier (A_{θ}), orientation factor (T_{hkl}), and extinction multiplier (E_{hkl}): $I_{hkl} = |F_{hkl}|^2 \times K \times p_{hkl} \times L_{\theta} \times P_{\theta} \times A_{\theta} \times T_{hkl} \times E_{hkl}$.^[27] The same problem limits electron diffraction detection of facets.^[8,10,12]

Here, we use an alternative strategy to study the surface morphology and crystal structure of AuNR films through atomic force microscopy and GIWAXS^[28] that allows for the determination of surface and hidden (the intensity of the scattered wave is zero) facets. Monodisperse, single-crystalline AuNRs were deposited on silicon substrates (<100> orientation, Si-mat Germany) by air brush spray-coating (cf. Supporting Information) to obtain sparse monolayers where the long axes of the rods were parallel to the substrate surface. We verified that all rods were sitting on the silicon substrate with one facet parallel to the substrate surface and used this information to extract the facets' geometry from synchrotron GIWAXS measurements.

The morphology of spray-deposited AuNR films was analyzed with AFM (cf. Supporting Information), and a typical height image is shown in **Figure 2a**. A sparse AuNR layer with AuNRs' diameters (**Figure 2b**) of (37 ± 2) nm was found consistent with SAXS data resulting (34.4 ± 4) nm.^[29] In addition, we ensured that there is no vertical packing of AuNRs by comparing the height fluctuations of the two adjacent particles in **Figure 2a**, as indicated by the line profiles of **Figure 2b**, and reconstructing the 3D topography (**Figure 2c**). We conclude that the vast majority of the rods have their long axes parallel to the substrate surface, with one facet in planar contact with the flat surface.

This geometry considerably simplifies GIWAXS data interpretation^[8,10,30] and enhances the facets' weak scattering signals.^[20,21] GIWAXS experiments were undertaken at beamline P03³¹ of the synchrotron facility Deutsches Elektronen Synchrotron (DESY) at an X-ray wavelength of 0.953 Å and a beam size of $22 \times 15 \mu\text{m}^2$ (horizontal $\times$ vertical); the scattering data were collected with a LAMBDA detector (type 750k, silicon sensor, X-spectrum GmbH) at an incident angle $\alpha_i = 0.4^\circ$ and a sample-to-detector distance of 135 ± 1 mm (cf. Supporting Information). **Figure 3a** illustrates a typical 2D GIWAXS pattern of the AuNR layer. Sharp diffraction spots caused by single crystal AuNRs are clearly visible. We attribute them to reflections from the (111) and (200) planes of the AuNR as expected for gold that forms FCC crystals with a cell parameter of 4.07 Å (**Figure 3b**). The reflexes are consistent with the lattice spacing found using high-resolution TEM (HRTEM; see the Supporting Information), too, as expected for single-crystal gold nanorods. The reflexes caused by (222) planes expected from the ED data in **Figure 3a** are probably out of the detector area. Note that facets such as (100), (110), (120), and (250) are not observed since they are forbidden reflections, i.e., the intensity of the scattered wave is zero due to the symmetry of the unit cell.^[27]

A qualitative analysis of the 2D GIWAXS pattern suggests that the two clearly visible (200) diffraction spots that are nearly equally separated along polar direction of the detector plane indicate orientational ordering of the (200) facets in AuNR. GIWAXS probes very many (on the order of hundred thousand; cf. Supporting Information) AuNRs in the scanned area (about $0.02 \times 2 \text{ mm}^2$). For a quantitative analysis of the distribution of AuNR orientation, we integrated the GIWAXS data by fixing

Figure 2. a) Typical AFM height image showing the surface morphology of the spray-deposited AuNR sparse monolayer. b) Height profiles along the marked lines in panel (a). c) 3D AFM tomography image, corresponding to the height image in panel (a), showing the packing of many AuNRs.

the scattering angle (2θ) at the (200) reflection and extracted the azimuthal distribution as shown in Figure 3c. Two Gaussians fit the azimuthal profile at $(72.7 \pm 8.9)^\circ$ and $(107.9 \pm 9)^\circ$, where the “ $\pm$ ” indicates the full-width at half maximum (FWHM), a measure of the misalignment among AuNRs.

The narrow FWHM value in the azimuthal curve confirms the orientation ordering of (200) facets in individual AuNRs. An even larger number of AuNRs (on the order of ten millions) were analyzed in a lateral GIWAXS scan covering an area of $\approx 2.2 \times 2 \text{ mm}^2$ and with the same results (cf. Supporting Information).

The (200) reflections of an FCC crystalline lattice whose (010) facet is parallel to the substrate surface are expected in the polar direction (i.e., 90°) of the detector plane. This does not agree with the experimental result of a tilt angle of $\alpha \approx 18^\circ$ away from the polar direction of the detector plane. The (200) facets must be tilted as illustrated in Figure 4. In the following sections, we will discuss the origin of this tilting and reconstruct the arrangement of surface facets on the AuNR core.

The AFM data exclude vertical packing in the sparse monolayers. To verify this result and check whether vertical packing could cause the tilted (200) reflection, we prepared

Figure 3. a) Typical 2D GIWAXS pattern of the spray-deposited AuNR sparse monolayer taken at an incident angle of $\alpha_i = 0.4^\circ$. b) Diffractogram of data in panel (a). Two typical diffraction peaks attributed to (111) and (200) reflections are marked in panel (b). c) Azimuthal distribution of the radially integrated data by fixing 2θ at the (200) reflection. The peaks were fitted with Gaussian curves.

Figure 4. Schematic illustrations of the crystalline structure of individual AuNR with a height of 37 nm. a) “nested-octagon” models showing the cross section of the AuNR body. The typical angle between the crystalline facets (520) and (100) as well as (-250) and (010) of $\alpha \approx 18^\circ$ is indicated in the pattern. b) Tilting of the (100) crystalline facet for AuNR with (520) crystalline facets parallel to the substrate surface. c) Tilting of the (010) crystalline facet for AuNR with (-250) crystalline facets parallel to the substrate surface. d) Predicted crystalline structure of an AuNR body with a “nested-octagon” cross section. Structural parameters, including low-index crystalline facets (010), (110), and (100); high-index crystalline facets (-250), (250), (520), and (-5-20); and supplementary angles between adjacent directions (i.e., 135° for core octagon and alternating $133.6^\circ/136.4^\circ$ for shell octagon), are marked with arrows. The sketch in panels (b) and (c) showing the surface facets of Au core are adapted from the works of Zhang et al.^[1] and Katz-boon et al.^[9]

films by repeating the spray-coating process five times with 60 s drying time in between subsequent spray pulses to provoke some stacking. GIWAXS data taken in parallel did not indicate any change in the α value of (200) reflection. We conclude that the tilt must be due to the surface facet structure of individual AuNR.

The high-resolution TEM and ED data discussed above prove the single-crystalline structure of our AuNRs. Literature reports^[7,8,12] on AuNR from wet-chemical synthesis indicate a series of characteristic crystallographic structures; Park et al. report an octagonal prismatic structure for AuNRs prepared in a CTAB-based growth solution as used here.^[14] We believe that our AuNRs’ body has the same overall structure. There are diverging reports on the surface facets of the octagons; alternating (110)/(100) facets are reported by Wang et al.,^[12] and (250) facets were found by both Carbo-Argibay et al.^[10] and Katz-Boon et al.^[7,9] In the following, we consider both models and assume that one surface facet from (110), (100), and (250) or their families was parallel to the substrate surface. The resulting tilt angles were then calculated for the (200) facet families. A similar protocol was also used by Choi et al.^[30] to deduce the ordering of crystalline facets in individual PbS nanoparticle from the particles’ superlattices based on GISAXS/GIWAXS data.

A thorough quantitative comparison of the theoretical and the experimental angle values is provided in the Supporting Information. We find that only rods with (250) surface facets parallel to the substrate surface fit our GIWAXS data. This

model predicts angles of 68.2° and 111.8° , close to the experimental reflections at $(72.7 \pm 8.9)^\circ$ and $(107.9 \pm 9)^\circ$, respectively. The slight difference between the experimental and predicted values might come from the deviation of the atomic assembly in surface facets from the ideal model in Figure 4.

Considering all data from electron microscopy, electron diffraction, and GIWAXS, we consistently find that the AuNRs have crystalline FCC structure with (250) surface facets. The combined data suggest a “nested-octagon” model of the AuNRs’ cross section (Figure 4); two sets of octagonal crystalline facets delineate the rods, one forming an octagon with alternating (110)/(100) facets close to the FCC lattice core, and another forming an octagon with (250) facets at the surface.

The nested-octagon model agrees with theoretically predicted atomic structure for individual AuNR^[15,16] and rationalizes the orientation ordering of crystalline facets observed in GIWAXS. The angle between the crystalline facets (520) and (100), (-250) and (010) of $\alpha \approx 18^\circ$ is indicated in Figure 4a. In Figure 4b,c, we illustrate the atomic assembly of surface and the neighboring bulk facets, by taking (520) and (100), (-250) and (010) as two examples. Note that (200) and (020) facets are parallel to (100) and (010) facets, respectively. Figure 4d shows the body of the AuNRs with the “nested-octagon” cross sections. This model gives angles between adjacent facets (-250) and (250), (250) and (520), and (110) and (010)/(100) of 136.4° , 133.6° , and 135° , respectively. These values agree well with reports by Zhang et al.^[1] and Carbo-Argibay et al.^[10]

The coexistence of high-index and low-index crystalline facets is also reported by Goris et al.^[8] and Almora-Barrios et al.^[16] who found high-index (520) facets as common lateral surface coexisting with small terraces of low-index (110) facets. Recent studies on the structure-formation mechanism of AuNRs help us to understand the coexisting of low-index and high-index crystalline facets. Park et al.^[14] reported a surface reconstruction process that minimizes the thermodynamically unfavorable (110) facets; Almora-Barrios et al.^[16] demonstrated that the surface of (520) facets could accommodate the surfactants more effectively during particle growth. This is consistent with our model; the (520) surface facets may have formed during particle synthesis to stabilize the beneath FCC crystalline cells by replacing the original thermodynamically unfavorable (110) surface facets.

In conclusion, we used sparse AuNR monolayers where the long axes of AuNRs were aligned parallel to the substrate surface. Synchrotron-light-based GIWAXS yielded sharp reflexes that indicated that the bulk crystalline structure of the AuNR was homogeneous over most or all AuNRs in the layer, which is consistent with the structure of representative individual AuNRs that we analyzed via ED. The facets of all AuNRs over a macroscopic area had the same preferential orientation because they all sit on the (250) family of surface facets. Further analysis of the influence of surface facets on the orientation of bulk facets led us to suggest a “nested-octagon” model for the cross section of AuNR’s body that comprises surface (250) facets, inner alternating (100)/(110) facets, and a bulk FCC crystalline lattice. This model is consistent with predictions that the high-index (250) surface facets offer AuNRs improved thermodynamic stability by minimizing the thermodynamically unfavorable (110) surface facets.

Experimental Section

Nanoparticle Synthesis: The AuNRs capped by cetyltrimethylammoniumbromide (AuNR@CTAB) were synthesized using a protocol adapted from Ye et al.^[24] Briefly, 7 g of CTAB ($\geq 99\%$, Sigma-Aldrich, Germany), 1.234 g of sodium oleate ($\geq 99\%$, Sigma-Aldrich, Germany), 12.47 mg of silver nitrate (99.9%, ABCR, Germany), 100 mg tetrachloroauric acid trihydrate, 1.734 mL of hydrochloric acid solution (32 wt% in water, Sigma-Aldrich, Germany), and 14.1 mg of ascorbic acid (99%, Sigma-Aldrich, Germany) were sequentially dissolved in 500 mL of water at 30 °C to yield a growth solution. Then 400 μ L of a seed solution, prepared by reducing a 0.2 M CTAB, 0.5 $\times 10^{-3}$ M tetrachloroauric acid solution with 1 mL of a 0.006 M sodium borohydride ($\geq 99\%$, Sigma-Aldrich, Germany) solution, were added to the growth solution. The resulting mixture was left undisturbed at 30 °C for 16 h for reaction. The resulting dispersion was concentrated and purified by centrifugation and redispersion in 5 $\times 10^{-3}$ M CTAB solution.

Ligand Exchange: Polymer ligands, PEDOT:PSS, were capped to the AuNRs by a protocol developed by this research group.^[25] The excess CTAB from the AuNR@CTAB dispersion was then reduced to obtain a complete ligand exchange. The AuNR@CTAB dispersion was set to $\approx 250 \times 10^{-6}$ M CTAB at a gold concentration of 10 mg mL⁻¹ by centrifugation. 5 mL of this dispersion was immediately injected into 45 mL of a 0.9 mg mL⁻¹ aqueous solution of PEDOT:PSS (dry, re-dispersible pellets; resistance: 200–450 Ω sq⁻¹, Sigma-Aldrich, Germany) under vigorous stirring. After gentle stirring for 16 h at room temperature, the excess of free ligands was removed, and the AuNR@PEDOT:PSS solution was concentrated to a stock solution of 3.3 mg mL⁻¹ ((3.3 $\pm$ 0.1) mg mL⁻¹, measured with inductively coupled plasma optical emission spectrometry), by centrifugation. The stock

solution was diluted with water to 1 mg mL⁻¹ AuNR@PEDOT:PSS dispersion used for the spray-coating experiments.

Air-Brush Spray Coating: The spray deposition was achieved through atomization of the Au nanorod dispersion with compressed N₂ gas at a pressure of 1 bar. A commercial spraying device (Grafo T3, Harder & Steenbeck GmbH & Co. KG, Germany) was modified to adapt to the beamline environment and the in situ X-ray measurements, as reported in previous work.^[32] The spray time was set to 0.1 s, corresponding to a deposition of ≈ 50 pL solution. The central part of the spray cone is expected to have a diameter around 30 mm and a nearly homogeneous material dispersion.^[32] The nozzle-to-substrate distance was 10 cm. Clean silicon wafers ((100) orientation, Si-mat Germany) were used as substrates. The environmental temperature during the spray deposition was 25 $\pm$ 0.5 °C.

GIWAXS: The GIWAXS measurements were carried out at the microfocus endstation of P03 beamline at PETRA III at the DESY, Germany.^[31] The X-ray wavelength and the beam size were 0.953 Å and 22 $\times$ 15 μ m² (horizontal $\times$ vertical), respectively. A LAMBDA detector (type 750k, Silicon sensor, X-Spectrum GmbH) was employed to collect 2D GIWAXS patterns. The sample-to-detector distance was 135 $\pm$ 1 mm, and the incident angle was set to 0.4°, which is above the critical angles for total reflection of ligands, silicon substrate, and Au. The corresponding X-ray footprint along beam direction was ≈ 2.2 mm. The influence of spatial location on the tilted (200) diffraction reflexes was checked by ex situ lateral scanning of the dried film. Acquisition time was 500 ms. Calibration was done using a lanthanum hexaboride standard. The analysis of the data was performed with the software DPDAK.^[33]

TEM Measurements: The TEM measurements were undertaken with a JEM-2100, (JEOL, Akishima, Japan) operating at 200 kV. A drop of AuNR aqueous dispersion was placed on a holey carbon TEM grid (S147-4, Plano, Wetzlar, Germany) and dried in air before investigation.

AFM Measurements: The AFM measurements were carried out with a Nanowizard 3 setup (JPK Instruments, Berlin, Germany) at room temperature. The scanner size was 25 $\times$ 25 μ m². Classical silicon tips (PPP-NCHR-50, Nanosensors) with a nominal force constant of 42 N m⁻¹ were used for the tapping-mode AFM measurements. The data analysis was made with software Gwyddion^[34] (version 2.42).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] Q. Zhang, L. Han, H. Jing, D. A. Blom, Y. Lin, H. L. Xin, H. Wang, *ACS Nano* **2016**, *10*, 2960.
- [2] C. J. Murphy, L. B. Thompson, A. M. Alkilany, P. N. Sisco, S. P. Boulos, S. T. Sivapalan, J. A. Yang, D. J. Chernak, J. Y. Huang, *J. Phys. Chem. Lett.* **2010**, *1*, 2867.
- [3] L. Zhang, K. Xia, Z. Lu, G. Li, J. Chen, Y. Deng, S. Li, F. Zhou, N. He, *Chem. Mater.* **2014**, *26*, 1794.
- [4] I. Chakraborty, W. J. Parak, *Adv. Mater. Interfaces* **2019**, *6*, 1801407.
- [5] A. Ambrosone, P. del Pino, V. Marchesano, W. J. Parak, J. M. de la Fuente, C. Tortiglione, *Nanomedicine* **2014**, *9*, 1913.
- [6] P. Mulvaney, W. J. Parak, F. Caruso, P. S. Weiss, *ACS Nano* **2016**, *10*, 9763.
- [7] H. Katz-Boon, M. Walsh, C. Dwyer, P. Mulvaney, A. M. Funston, J. Etheridge, *Nano Lett.* **2015**, *15*, 1635.
- [8] B. Goris, S. Bals, W. Van den Broek, E. Carbo-Argibay, S. Gomez-Grana, L. M. Liz-Marzan, G. Van Tendeloo, *Nat. Mater.* **2012**, *11*, 930.
- [9] H. Katz-Boon, C. J. Rossouw, M. Weyland, A. M. Funston, P. Mulvaney, J. Etheridge, *Nano Lett.* **2011**, *11*, 273.
- [10] E. Carbo-Argibay, B. Rodriguez-Gonzalez, S. Gomez-Grana, A. Guerrero-Martinez, I. Pastoriza-Santos, J. Perez-Juste, L. M. Liz-Marzan, *Angew. Chem., Int. Ed.* **2010**, *49*, 9397.
- [11] Z. L. Wang, R. P. Gao, B. Nikoobakht, M. A. El-Sayed, *J. Phys. Chem. B* **2000**, *104*, 5417.
- [12] Z. L. Wang, M. B. Mohamed, S. Link, M. A. El-Sayed, *Surf. Sci.* **1999**, *440*, L809.
- [13] J. L. Elechiguerra, J. Reyes-Gasga, M. J. Yacaman, *J. Mater. Chem.* **2006**, *16*, 3906.
- [14] K. Park, L. F. Drummy, R. C. Wadams, H. Koerner, D. Nepal, L. Fabris, R. A. Vaia, *Chem. Mater.* **2013**, *25*, 555.
- [15] S. K. Meena, M. Sulpizi, *Angew. Chem., Int. Ed.* **2016**, *55*, 11960.
- [16] N. Almora-Barrios, G. Novell-Leruth, P. Whiting, L. M. Liz-Marzan, N. López, *Nano Lett.* **2014**, *14*, 871.
- [17] P. Zhang, H. Huang, Y. Chen, S. Yu, C. Krywka, S. K. Vayalil, S. V. Roth, T. He, *Chin. J. Polym. Sci.* **2014**, *32*, 1188.
- [18] P. Zhang, H. Huang, T. He, Z. Hu, *ACS Macro Lett.* **2012**, *1*, 1007.
- [19] M. C. Weidman, D.-M. Smilgies, W. A. Tisdale, *Nat. Mater.* **2016**, *15*, 775.
- [20] X. L. Chen, J. Schroder, S. Hauschild, S. Rosenfeldt, M. Dulle, S. Forster, *Langmuir* **2015**, *31*, 11678.
- [21] Y. Ren, X. Zuo, *Small Methods* **2018**, *2*, 1800064.
- [22] H. Zhu, Y. Huang, H. Zhu, L. Wang, S. Lan, X. Xia, Q. Liu, *Small Methods* **2019**, *3*, 1900223.
- [23] S. Merckens, M. Vakili, A. Sánchez-Iglesias, L. Litti, Y. Gao, P. V. Gwozdz, L. Sharpnack, R. H. Blick, L. M. Liz-Marzan, M. Grzelczak, M. Trebbin, *ACS Nano* **2019**, *13*, 6596.
- [24] X. Ye, C. Zheng, J. Chen, Y. Gao, C. B. Murray, *Nano Lett.* **2013**, *13*, 765.
- [25] B. Reiser, L. Gonzalez-Garcia, I. Kanelidis, J. H. M. Maurer, T. Kraus, *Chem. Sci.* **2016**, *7*, 4190.
- [26] Z. Y. Zhou, N. Tian, Z. Z. Huang, D. J. Chen, S. G. Sun, *Faraday Discuss.* **2008**, *140*, 81.
- [27] V. K. Pecharsky, P. Y. Zavalij, *Fundamentals of Power Diffraction and Structural Characterization of Materials*, Springer, New York, NY **2005**.
- [28] W. Ohm, A. Rothkirch, P. Pandit, V. Körstgens, P. Müller-Buschbaum, R. Rojas, S. Yu, C. J. Brett, D. L. Söderberg, S. V. Roth, *J. Coat. Technol. Res.* **2018**, *15*, 759.
- [29] P. Zhang, B. Reiser, L. González-García, S. Beck, J. Drzic, T. Kraus, *Nanoscale* **2019**, *11*, 6538.
- [30] J. J. Choi, C. R. Bealing, K. F. Bian, K. J. Hughes, W. Y. Zhang, D. M. Smilgies, R. G. Hennig, J. R. Engstrom, T. Hanrath, *J. Am. Chem. Soc.* **2011**, *133*, 3131.
- [31] A. Buffet, A. Rothkirch, R. Döhrmann, V. Körstgens, M. M. A. Kashem, J. Perlich, G. Herzog, M. Schwartzkopf, R. Gehrke, P. Müller-Buschbaum, S. V. Roth, *J. Synchrotron Radiat.* **2012**, *19*, 647.
- [32] P. Zhang, G. Santoro, S. Yu, S. K. Vayalil, S. Bommel, S. V. Roth, *Langmuir* **2016**, *32*, 4251.
- [33] G. Benecke, W. Wagermaier, C. H. Li, M. Schwartzkopf, G. Flucke, R. Hoerth, I. Zizak, M. Burghammer, E. Metwalli, P. Müller-Buschbaum, M. Trebbin, S. Forster, O. Paris, S. V. Roth, P. Fratzl, *J. Appl. Crystallogr.* **2014**, *47*, 1797.
- [34] D. Nečas, P. Klapetek, *Cent. Eur. J. Phys.* **2012**, *10*, 181.