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Drying of electrically conductive hybrid polymer-gold nanorods studied with *in situ* microbeam GISAXS

Peng Zhang^{*a}, Beate Reiser^a, Lola González-García^a, Sebastian Beck^a, Juraj Drzic^a and Tobias Kraus^{*a,b}

^a INM–Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany

^b Colloid and Interface Chemistry, Saarland University, Campus D2 2, 66123 Saarbrücken, Germany

ABSTRACT: Gold nanorods (AuNRs) with conductive polymer shells are interesting colloidal building blocks for electronics. Hybrid particles with AuNR cores and poly(3,4-ethylenedioxythiophene) or polystyrene sulfonate (PEDOT:PSS) shells were prepared as stable aqueous dispersions. Film formation during the drying of such dispersions is known to affect the electric conductivity of the material. We observed the mechanisms of drying in thin, spray-coated films with grazing incidence small-angle X-ray scattering (GISAXS). A sparse, uniform monolayer formed because the anisotropic shape of the AuNR inhibited “coffee-ring” effects. We used generalized two-dimensional correlation (2DC) spectroscopy to analyze the GISAXS data and to decipher the microscopic structure formation of the film during drying. Four major scattering peaks were attributed to porous PEDOT, PSS, Au, and the substrate layer. Their time-dependent intensity indicated the sequence of film formation: AuNR with mobile shells arranged on the substrate first, PEDOT and then PSS dried sequentially around the gold core. We discuss the final phase-separation of PEDOT:PSS on the hybrid rods.

Nanoparticle-based “electronic inks” are suitable to print touchscreen panels,¹ biosensors,² and organic solar cells³. “Wet” printing and coating processes can be applied to substrates of complex geometries, are scalable on existing equipment, and provide short time-to-market for new materials. They all have in common a drying step in which the solvent evaporates and leaves a solid fraction on the substrate. While the process engineering of drying is well-established, little is known about the microscopic structure formation in drying nanoparticle films and its effect on the properties (conductivity, mechanical flexibility, etc.) of the final coating. Previous studies have focused on the kinetics of gold nanoparticle (AuNP) assembly during liquid film drying. Alivisatos et al.⁴ and Park et al.⁵ studied the drying-mediated structure formation of nanoparticle superlattices with liquid phase transmission electron microscopy (TEM), and found

that the nanoparticles first condensed into amorphous agglomerates and then grew into regular superlattices via local fluctuations. Al-Hussein et al.⁶ and Roth et al.⁷ studied the drying of wet-deposited AuNPs with X-ray scattering and reported that the formation of AuNP film involved a multistage nanoscale ordering of the AuNPs.

Polymer shells that are now increasingly used on “hybrid” nanoparticles increase the colloidal stability of the dispersions considerably and change the interactions between particles during assembly^{8–11}. Such shells dominate important material properties of the dry film, for example its mechanical strength¹² or electrical conductivity^{13, 14}. Conductive polymers have recently been used as ligands in sintering-free electronic inks^{13, 15–17} that become electrically conductive immediately upon drying. The role of polymer shells during particle film formation therefore is of considerable interest, but the electron density of the shell only provides weak signals in standard electron or X-ray characterizations.^{13, 18–20}

Here, we study gold nanorods (AuNRs) that carry a shell of the water-soluble conductive polymer poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), a p-type material commonly used in organic electronics.^{21, 22} Hybrid particles with AuNR cores and PEDOT:PSS shells reach a conductivity of 1.01×10^4 S/cm¹³ after drying and are suitable to rapidly print circuitry. The polymer bridges the metal cores and provides electrical conductivity and mechanical flexibility.

AuNR suspensions were prepared using a published protocol²³. The original ligand, cetyltrimethylammonium bromide, was exchanged by PEDOT:PSS (cf. Supporting Information for experimental details). The resulting AuNR@PEDOT:PSS hybrid particle were readily dispersible in water without agglomeration, with a radius of 17.2 ± 2 nm and a length of 69.1 ± 10 nm obtained from transmission small-angle X-ray scattering data (analysis methods are explained in the Supporting Information).

We developed a technique to observe the structure formation of the polymer shell while the hybrid particle dispersion was drying. Grazing incidence small-angle X-ray scattering

(GISAXS) with the high-flux microbeam of a synchrotron light source gives *in situ* data on the drying-mediated structure formation process at high spatial and time resolutions.^{6, 7, 24, 25}

Four strong scattering peaks (cf. arrows in Figure 1b) dominated the GISAXS image of dried film. In the following, we discuss whether these scattering peaks are Yoneda peaks of components in the drying film, and of the substrates. There are several indications pointing in this direction: a) several of the peaks are transient and only occur during the drying process, probably when the scattering objects have become immobile, as expected for Yoneda peaks but not the form factor, b) the sequences of the peaks' occurrence is consistent with the expected sequence of immobilization: the substrate peak is initial present, followed by the peak of the Au core and finally, of the ligand shell, and c) the peaks appear at the critical angle (α_c) of the respective materials²⁶.

Some of the transient peaks are weak (Figure 1b). We performed reference experiments to examine the effect of packing density on the strength of the Yoneda signal and we used the generalized two-dimensional correlation (2DC) analysis²⁷ of the scattering peaks' evolutions to detect small changes that are not visually obvious.

Figure 1. (a) A typical 2D GISAXS pattern of dried AuNR thin film. SBS indicates the specular beam stop; the black strips labeled with IDG are due to the intermodular detector gaps. (b) Vertical integration of the region between the vertical dotted lines in panel (a). Four major peaks are marked with arrows. Grey rectangles indicate SBS and IDG. α_i and α_f indicate the incident and exit angle, respectively. (c) Horizontal integration of the region between the horizontal dotted lines in panel (a), at the silicon Yoneda peak ($\alpha_{f, \text{Si}} + \alpha_i = 0.54^\circ$). (d) Scanning electron micrograph of a typical central region of the spray-coated film.

A volume of 50 μL of the aqueous AuNR suspension (with a AuNR content of 1 mg/mL) was deposited on a clean silicon wafer ($\langle 100 \rangle$ orientation, Si-mat Germany) using an air-brush spray setup at the beamline Po3²⁹ at DESY (Hamburg, Germany). The diameter of the central region of the spray cone was 30 mm. The surface/interface structure was observed with X-rays at a wavelength of 0.0953 nm at an incident angle (α_i) of 0.4° using a Pilatus 1M detector (Dectris, Switzerland). Further details of the spray coating with *in situ* GISAXS are provided in the Supporting Information.

Typical GISAXS patterns of the dried hybrid rod thin film (Figure 1a) had Yoneda bands that extended from the critical angle of the organic ligands to that of Au, following the increase of electron density. Four major peaks with $\alpha_i + \alpha_f$ of 0.45° , 0.51° , 0.54° , and 0.73° are visible in the vertically integrated curve in Figure 1b. The signals at 0.51° and 0.54° appear at the angles expected for the polymer (calculated from bulk sample) and silicon Yoneda peaks, respectively.

Figure 1c shows the horizontally integrated signal around the silicon Yoneda peak. We attribute the pair of peaks that occurs at $q_y = \pm 0.355 \text{ nm}^{-1}$ to the form factor of AuNR, as explained in the following. The Vineyard effect is known to enhance particles' scattering at the substrate's critical angle. This explains why the strong scattering of the nanorods is only visible under this angle. The peaks have the positions and shapes expected for a cylinder with the AuNRs' dimensions. An additional pair of peaks occur at lower absolute q values. It can be fitted with a paracrystalline structure of AuNRs, see Supporting Information. Electron microscopy (Quanta 400F, FEI Europe, Eindhoven, Netherlands, operating voltage 10 kV) of the dried film (Figure 1d) indicates a sparse layer of particle clusters that probably cause this pair of peaks in addition to well-separated particles.

Note that spherical particles deposited using similar parameters in previous work did form such rings¹⁸. The absence of the common "coffee stain rings" that is probably due to the anisotropic shape of AuNRs that affected the deposition of particles, as discussed by Yunker et al. (i.e., the anisotropic shape of the particles significantly deforms interfaces, producing strong interparticle capillary interactions)³⁰.

In situ GISAXS allowed us to follow the formation of the hybrid particle film at a time resolution of 100 ms (Figure 2). We identified 3 stages of coating that were indicated by changes of the Si Yoneda peak^{24, 25} (marked with horizontal arrow in Figure 2 and always be visible after shutter opening): spraying, drying, and fully dry particle layer (Figure 2a). The Si Yoneda peak was narrow when the film-substrate interface was flat (e.g., Figure 2b) and broad when it was rough (e.g., Figure 2 c-e) because the reflected beam was scattered by the rough film that had formed.

Figure 2. (a) 2D contour plot of the *in situ* GISAXS data: in-plane cut at the Yoneda peak of silicon (Y_{si}) at $\alpha_f = \alpha_{c,si}$, see horizontal dotted lines in Figure 1a. The time at which spray coating started and the time at which the intensity of Y_{si} became stable are marked with solid and dotted arrows, respectively. (b) 2D GISAXS pattern of the bare silicon wafer before spray-coating. (c,d) 2D GISAXS patterns of the drying particle film at (c) 1.5 s and (d) 5.0 s after spraying had ended. (e) 2D GISAXS pattern of the fully dried particle layer. The Yoneda peak of silicon is marked with horizontal arrows. In panels c and d, the corresponding tilted reflexes with a tilting angle ϕ are marked with R. In panel c-e, insets illustrate the correlations between solvent-AuNR interfaces at a base angle that is identical with tilting angle of the rod-shaped reflection. The time scale was set relating to the opening of the beam shutter.

Tilted, rod-shaped reflexes in the GISAXS patterns (marked with “R” in Figure 2 c-d) indicate ordered packing with long-range order already in the sprayed dispersion. Similar reflexes have been reported previously for the drying of spherical AuNP dispersion⁶; they have been attributed to solvent-AuNP interfaces, where the tilt angle of a reflex (ϕ) is identical with the base angle of the correlated interfaces of the AuNPs. We believe that drying hybrid rods cause similar scattering and illustrate the implied arrangements of our hybrid rods in the insets of Figure 2 c-e. The value of ϕ changed as the particles rearranged in the drying liquid film. A semi-quantitative analysis of this change, indicated by inclined scattering rods marked with “R” in Figure 2c,d, can be found in the supporting information. The appearance of high-order reflexes in Figure 2d indicates long-range order of the particles. These reflections disappeared in the dry film, probably because all rods eventually arranged with their long axis parallel to the substrate (illustrated in inset of Figure 2e) but did not stack normal to the substrate as shown in the SEM data (Figure 1d).

Note that films of fully dried particles did not cause such reflexes (c.f. Figure S9 in the Supporting Information). The particles in such films formed agglomerates without the long-range order required to cause tilted, rod-shaped reflexes. A video of the *in situ* real-time GISAXS data (c.f. Supporting Information) illustrates the transition from the original dispersion to the ordered state and the final dried film.

The interpretation of the other two major peaks (0.45° and 0.73° in Figure 1b) is more challenging, as there are strong effects of the form factor. The time-dependent evolution of these peaks gives an important insight into their origin, because Yoneda peaks only emerge for a stable particle film while the form factor causes peaks already in liquid particle dispersion. We therefore analyzed the time-dependent peak intensities in detail using a generalized two-dimensional correlation (2DC) spectroscopy analysis. The principles of 2DC spectroscopy and its application in GISAXS data analysis are provided in the Supporting Information. Briefly, 2DC spectroscopy analysis can enhance the signals’ effective resolution and resolves the sequence of the complex events during solvent evaporation. The 2D contour plot indicates the correlation of two peaks over time, and the synchronous (Figure 3a) and asynchronous (Figure 3b) spectra indicate

correlations between two separate peaks during drying and quantify simultaneous and sequential changes of the peaks’ intensities. Red and blue colors indicate positive and negative correlations between α_x (peak on x-axis, e.g., $\alpha_i + \alpha_f = 0.45^\circ$) and α_y (peak on y-axis, e.g., $\alpha_i + \alpha_f = 0.45^\circ$), respectively; stronger colors indicate greater correlation (I).

Figure 3. Contour plots of (a) synchronous and (b) asynchronous correlation spectra of the GISAXS signal during liquid thin film drying. Four major peaks with $\alpha_i + \alpha_f = 0.45^\circ$, 0.51° , 0.54° , and 0.73° are marked with double-headed arrows. (c) Synchronous and (d) asynchronous slice spectra for $\alpha_i + \alpha_f = 0.51^\circ$ and 0.73° . Reference lines at 0 in panels (c) and (d) are for clarity only. Missing data due to intermodular detector gaps are marked with single-headed arrows in panel (a) and (b) and are covered with grey rectangles in panels (c) and (d).

The four major peaks with $\alpha_i + \alpha_f$ of 0.45° , 0.51° , 0.54° , and 0.73° marked with double-head arrows in Figure 3 a have strong positive correlations with time (i.e., scattering increasing with time). Figure 3c and d show synchronous and asynchronous correlations for slices with $\alpha_i + \alpha_f = 0.51^\circ$ and 0.73° . The correlations of the four major peaks are summarized in Table 1. Noda’s rules²⁷ indicate a sequence of major peaks during liquid film drying with $\alpha_i + \alpha_f = 0.73^\circ$ first, then 0.45° , 0.51° , and

finally 0.54° (see Table 1). This strongly suggests that all four are Yoneda peaks, for the following reasons.

Table 1. Summarized correlations of selected Yoneda peaks ($\alpha_i + \alpha_f$) based on 2D GISAXS correlations in Figure 3 c,d.

Yoneda peaks	Sync. correlations	Async. correlations	Sequential order of peaks
(0.45° , 0.51°)	+	+	0.45° bef. 0.51°
(0.51° , 0.51°)	+	o	0.51° simul 0.51°
(0.54° , 0.51°)	+	-	0.51° bef. 0.54°
(0.73° , 0.51°)	+	+	0.73° bef. 0.51°
(0.45° , 0.73°)	+	-	0.73° bef. 0.45°
(0.51° , 0.73°)	+	-	0.73° bef. 0.51°
(0.54° , 0.73°)	+	-	0.73° bef. 0.54°
(0.73° , 0.73°)	+	o	0.73° simul 0.73°

For the sake of argument, assume that the peaks at 0.45° and 0.73° would be 1st and 3rd order peaks of the form factor (cf. Supporting Information). The 3rd order peak (at 0.73°) cannot appear before the 1st order signal (at 0.45°) because it is weaker. We find, however, that the 0.73° peak appears before the 0.45° peak. We therefore reject the hypothesis that these are form factor peaks.

Instead, we attribute the 0.73° peak to the Yoneda signal of AuNR. The peak appears at the theoretically predicated position of the Yoneda peak of bulk gold ($\alpha_i + \alpha_f = 0.737^\circ$, see Supporting Information). Recent reports confirm that sparse layers of metal clusters have Yoneda peaks³²⁻³³ at the same position. It is also instructive to compare the change of the AuNR form factor peaks found by horizontal integration (Figure 1c) with the evolution of the AuNR Yoneda peak at $\alpha_i + \alpha_f = 0.73^\circ$. After the Yoneda peak appears, indicating a stable AuNR film on the substrate, the (previously stable) form factor peak changes its intensity (cf. Supporting Information).

The peak at $\alpha_i + \alpha_f = 0.45^\circ$ was unexpected, and we believe that it belongs to a porous polymer film on the hybrid rod that we discuss in the following. Pure PEDOT is too hydrophobic to be dispersed in water. PEDOT:PSS in water consists of colloidal particles in which the two polymers are mixed³⁴ and would not phase-separate during drying unless forced by a strong interaction (a selective interaction between PEDOT and particle, for example). In a dried thin film, Zhou et al.³⁵ and Ouyang et al.³⁶ found micelles with PEDOT-rich cores and PSS-rich shells. He et al.³⁷ reported that selective interactions between graphene oxide (GO) sheets and PEDOT enhanced the demixing of PEDOT:PSS during film formation and improved the conductivity of the hybrid network.

The hybrid rods used here were synthesized using PEDOT:PSS dispersions in water. We believe that the PEDOT:PSS layer on the AuNR undergoes a phase separation during drying: PEDOT remains attached to the AuNR core, while PSS segregates to the outside that forms a continuous layer, corresponding to the Yoneda signal of $\alpha_i + \alpha_f = 0.51^\circ$. This creates a porous PEDOT layer on the AuNRs with an additional Yoneda peak with $\alpha_i + \alpha_f = 0.45^\circ$. We undertook reference experiments to test our hypothesis and to show that the porosity of the polymer layer can cause a Yoneda peak at an exit angle below that of the bulk.

Following our previous work, a dispersion of polystyrene particles (spheres with a diameter of 100 nm, *Kisker Biotech GmbH & Co. KG, Germany*) was used as a model system for our hybrid rods and deposited on silicon substrates through spray-coating²⁵ (cf. Supporting Information). Three samples were heated to 54°C , 100°C , and 120°C , respectively, to obtain films with different porosities. GISAXS measurements were undertaken at DESY's Po3 beamline using an X-ray wavelength of 0.1088 nm at $\alpha_i = 0.45^\circ$.²⁵ Films annealed at 54°C exhibited a Yoneda peak at $\alpha_i + \alpha_f = 0.5^\circ$, below the peak of bulk PS (0.57°). Films annealed at 100°C (close to the glass transition temperature T_g of bulk PS) had an angle $\alpha_i + \alpha_f = 0.52^\circ$. Films annealed at 120°C had the Yoneda peak of bulk PS because the particles had merged into a continuous layer²⁵. We conclude that the shifted GISAXS peak indicates porosity in the PEDOT layer, too.

There are indications that the demixing of PEDOT:PSS that ultimately leads to porous PEDOT already occurs in the dispersed hybrid nanorods. The zeta potential of the rods in dispersion (cf. Supporting Information) was $-24.9 \pm 1.0\text{ mV}$, far below the $0.2 \pm 0.7\text{ mV}$ of the original PEDOT:PSS dispersion. A negatively charged PSS shell that phase-separates from PEDOT might explain this deviation. We are organizing neutron scattering experiment that is sensitive to the light elements to get more structural information about phase segregation of PEDOT and PSS, as reported by Murphy et al.³⁸.

Now that all major GISAXS peaks have been identified, we can use their evolution during solvent evaporation to understand the drying of the coated hybrid particle film. Thus, the first stable layer that formed consisted of AuNR ($\alpha_i + \alpha_f = 0.73^\circ$), followed by the porous PEDOT layer ($\alpha_i + \alpha_f = 0.45^\circ$), the PSS layer ($\alpha_i + \alpha_f = 0.51^\circ$), and the silicon substrate ($\alpha_i + \alpha_f = 0.54^\circ$). Therefore, the microscopic structural evolution in a spray-coated AuNR@PEDOT:PSS hybrid rod film occurred in the following steps:

1. Hybrid rods form long-range correlated structure in the liquid dispersion film (Figure 4a),
2. Hybrid rods with mobile shells arrange in a film on the substrate (Figure 4b),
3. PEDOT and then PSS dry sequentially on the gold cores of the hybrid rods (Figure 4b,c).

Figure 4. Microscopic structure evolution in a sprayed-coated AuNR@PEDOT:PSS hybrid rod film. (a) Hybrid particles attain long-range order in the liquid dispersion layer. (b) AuNR with mobile shells arrange on the substrate first, then PEDOT and then PSS dry sequentially around the gold core. (c) Fully dry AuNR@PEDOT:PSS thin film. Note: the sizes of AuNR cores and, PSS and PEDOT layers are not to scale.

In summary, we sprayed a dispersion of AuNR@PEDOT:PSS hybrid rods onto a horizontal substrate and obtained sparse layers of the hybrid rods upon drying. *In situ* GISAXS with 2D correlation spectroscopy analysis was used to reconstruct structure formation. In the drying liquid film, the hybrid rods first formed assemblies with long-range order and then arranged on the silicon substrate. The polymer shell with its PEDOT and PSS components phase-separated; a conductive PEDOT layer and then a non-conductive PSS layer formed around the gold core as the swollen polymer layers dried. We believe that this sequence contributes to the formation of a network in the particle film¹³ that leads to high conductivity immediately after drying.

ASSOCIATED CONTENT

Supporting Information

Nanoparticle synthesis and solution preparation, air-brush spray deposition, SAXS, GISAXS, zeta potential measurements, Φ vs. time, generalized 2DC spectroscopy analysis, porous structure of PS colloidal monolayer, Yoneda peak calculation and movie S1.

AUTHOR INFORMATION

Corresponding Authors

P. Zhang, zhangpeng3@mail.sysu.edu.cn

T. Kraus, tobias.kraus@leibniz-inm.de

Present address

P.Zhang: School of materials science and engineering, Sun Yat-sen University, 510275, Guangzhou, China

Conflicts of interest

The authors declare no competing financial interests.

Contributions

P.Z. and T.K. conceived the idea and designed the experiments. B.R. and J.D. conducted the synthesis of nanoparticles. L.G.G. conducted the SEM measurement and P.Z. conducted the Zeta-potential measurements. All the authors participated in the *in situ* GISAXS measurements. P.Z. analyzed the GISAXS data and wrote the manuscript. All authors discussed the results.

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