Ionic depletion at the crystalline Gibbs layer of PEG-capped gold nanoparticle brushes at aqueous surfaces

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Abstract
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Ionic depletion at the crystalline Gibbs layer of PEG-capped gold nanoparticle brushes at aqueous surfaces

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In situ surface-sensitive x-ray diffraction and grazing incidence x-ray fluorescence spectroscopy (GIXFS) methods are combined to determine the ionic distributions across the liquid/vapor interfaces of thiolated-polyethylene-glycol–capped gold nanoparticles (PEG-AuNP) solutions. Induced by the addition of salts (i.e., Cs2SO4) to PEG-AuNPs solutions, two-dimensional hexagonal lattices of PEG-AuNPs form spontaneously at the aqueous surfaces, as is demonstrated by x-ray reflectivity and grazing incidence small-angle x-ray scattering. By taking advantage of element specificity with the GIXFS method, we find that the cation Cs+ concentration at the crystalline film is significantly reduced in parts of the PEG-AuNP film compared with that in the bulk.

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I. INTRODUCTION

Natural self-assembly into ordered functional structures has long served as inspiration for developing artificially self-assembled novel structures for various applications. Many of the self-assembly processes, natural or artificial, take place in fluids that facilitate diverse interactions and that, in particular, can mimic biological ones [1]. In the past two decades, the programmable self-assembly of nano-objects in aqueous media have been exemplified by taking advantage of DNA functionalization and hybridization to crystallize colloidal nanoparticles (NPs) [2,3]. By varying parameters such as particle size, linker length, solution conditions, and other parameters, general rules for programmable three-dimensional (3D) superlattice formations have been gradually established [4]. At the same time, assembling NPs into two-dimensional (2D) crystalline and noncrystalline structures have also been developed. In one approach, charged Langmuir monolayers have been used as templates that attract and crystallize capped nanoparticles from solutions [5–7]. In a different approach, it has been found that by manipulating salt concentrations in NPs suspensions, a Gibbs-like monolayer can be spontaneously formed and crystallized [8–10]. It should be emphasized that for all these assemblies, 2D or 3D, salts play a decisive role in tweaking the charge of the DNA strands and facilitate specific 3D assembly of NPs or migration of NPs to the liquid interface [5–10]. In fact, a recent study suggests that the underlying mechanism that drives DNA-capped AuNPs to the surface and to crystallization has to do with the role of salt in tweaking the hydrophobic-hydrophilic character of the DNA-capped AuNPs [10]. This in turn led to the manipulation of salt (e.g., K2CO3) concentrations in assembling 2D and 3D ordered structures of polyethylene-glycol–capped (PEG-capped) AuNPs [11–13], taking advantage of the aqueous biphasic system (ABS) of PEG in salt solutions [14–16].

Herein, we report on x-ray reflectivity (XR), grazing incidence small angle x-ray scattering (GISAXS), and grazing incidence x-ray fluorescence spectroscopy (GIXFS) measurements (on the same samples) to determine the structure of the crystalline film that is formed when salt is added to PEG-AuNP suspensions. In particular, we use the GIXFS method, which is both element-specific and surface-sensitive, to determine interfacial ion distributions [17]. Recently, the GIXFS method has been extensively employed to determine the specific ion enrichment at air-liquid interfaces [18–20]. The GIXFS can probe the surface-specific ion enrichment with high sensitivity and accuracy under the condition that the ion bulk concentration is dilute (so that the bulk fluorescent signals are relatively weak compared with those from the surface). In this study, we encounter the opposite case, where the bulk fluorescent elemental concentration is quite high and the surface fluorescent elemental concentration may be reduced.

II. EXPERIMENTAL DETAILS

The PEG-capped AuNPs (PEG-AuNPs) are prepared by using a simple aqueous-phase ligand exchange method, as documented previously [11,21]. Briefly, in the aqueous solution the surface-bound citrate ligands on the unfunctionalized AuNPs (nominal size of 10 nm; Ted Pella, Inc.) are replaced with poly(ethylene glycol) methyl ethyl thiol (PEG-SH, average molecular weight 6000 Da; Sigma-Aldrich) through thiol-gold chemistry. The as-prepared PEG-AuNPs are then washed with ≥3 rounds of centrifugation (at 20 000g × 1 h) and redispersion in Millipore water. UV-visible absorption measurements are used to determine the final concentration of PEG-AuNPs. For the x-ray measurements, PEG-AuNP suspensions (24 nM in water) are mixed with an equal volume of PEG-AuNP suspensions (500 mM Cs2SO4;2m L ) and then washed with water-saturated helium gas for all x-ray measurements. Recently, we examined ionic specificity in interfacial crystallization of PEG-AuNPs [13] including, for instance, Na+, K+, and Cs+, and found Cs+ to be
GIXFS
GISAXS
XR

FIG. 1. Schematic setup for XR, GISAXS, and GIXFS measurements of the liquid/vapor interface. A point detector (Bicron) is used for both XR and GISAXS. In XR measurements, the detector rotates in the scattering plane and maintains \( \alpha_i = \alpha_f \). In GISAXS measurements, the detector rotates horizontally. An energy-dispersive detector (EDD, Vortex) is placed above the sample surface for GIXFS measurements. See details in the text.

appropriate for our fluorescence study using an in-house x-ray spectrometer (operating at \( \sim 8 \text{ keV} \)) and an energy-dispersive detector (EDD). Here, we seek to determine the distribution profiles of the Cs and Au based on GIXFS data. Thus, we choose Cs2SO4 salt to induce surface crystallization, taking advantage of the high fluorescence yield of Cs+ [22,23] and absorption cross section [24] (compared with K+). In addition, Cs fluorescent signals (in the energy range 3.5–6 keV) are at higher energies than those of K and thus less attenuated along the pathway from the fluorescent sources to the detector (through windows).

X-ray measurements (XR, GISAXS, and GIXFS) are carried out on a liquid-surface spectrometer (LSS) at Ames Laboratory with the setup illustrated in Fig. 1. The incident x-rays are generated by a Rigaku Ultraflx 18 operated at 50 kV and 250 mA using a copper rotating anode (Cu \( K\alpha \)) and pass through a monochromator (x-ray energy \( E = 8.048 \text{ keV} \), x-ray wavelength \( \lambda = 1.5404 \text{ Å} \)) and are further collimated by slits along the beam path. As is common, scattering and spectroscopic intensities (i.e., photon counts/s) are normalized by the incident beam intensities recorded with a monitor placed upstream (not shown in Fig. 1). Therefore, arbitrary units are used for intensities.

A specular XR method is employed to determine the electron-density (ED) profiles along the aqueous surface normal (designated as the \( z \) axis). The monochromatic and collimated incident x-ray beam with the wave vector \( \mathbf{k}_i \) impinges on the aqueous surface at an incident angle \( \alpha_i \), with respect to the surface. A Bicron detector is adjusted in the scattering plane to intercept the specularly reflected x-rays with the exit angle \( \alpha_f \) and the wave-vector \( \mathbf{k}_f \) (see more detail in Ref. [17]). The measured reflectivity, \( R \), is expressed as a function of \( Q_z \) (\( = 2k_0 \sin \alpha_i \), with \( k_0 \) being the wave number \( 2\pi/\lambda \)), which is the \( z \)-axis component of the scattering vector \( \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i \).

The GISAXS method is used to probe the lateral packing of the surface-bound PEG-AuNPs by fixing \( \alpha_i \approx 0.9 \alpha_c \) (\( \alpha_c = 0.154^\circ \) is the critical angle for total reflection from pure water) and collecting the scattered beam by adjusting the detector arm at a series of angle \( \Psi \) corresponding to the in-plane components of the scattering vector; namely, \( Q_{x,y} \approx 2k_0 \sin (\Psi/2) \) (see Fig. 1). The vertical slits after the sample and in front of the Bicron detector are kept wide open to allow integration over a range of \( Q_z \) values (in our case from 0 to \( Q_z \approx 0.085 \text{ Å}^{-1} \)). The horizontal slits are adjusted to allow for partial resolution between the \( K\alpha_1 \) and \( K\alpha_2 \) lines in the direct beam (both lines are superimposed such that \( K\alpha_2 \) peak shows as a distinct shoulder on the main \( K\alpha_1 \) peak).

For the GIXFS, we use a Vortex energy-dispersive detector (EDD) that is mounted above the sample surface collecting characteristic photons emitted from the illuminated volume including the elastic (Thomson) and inelastic (Compton) scattering [17,25]. The fluorescence spectra are collected as a function of incident beam angle \( \alpha_i \) such that below the critical angle for total reflection \( \alpha_c \), the penetration depth of the evanescent x-rays is finite, and thus surface sensitive (only fluorescent species within the \( \sim 100 \text{ Å} \) are excited and fluoresce for \( \alpha_i < \alpha_c \)). For \( \alpha_i > \alpha_c \), the x-rays penetrate into the bulk, probing multiple micrometers deep, and excite fluorescent species on the beam path.

In general, the goodness of the model-based profile fitting is represented by \( \chi^2 \), i.e., \( \sum (Y_{\text{model},i} - Y_{\text{exp},i})^2/Y_{i}^{2} \), where \( Y_{\text{model},i} \) and \( Y_{\text{exp},i} \) are the calculated, experimental \( i \)th data point and its associated error, respectively. \( \chi^2_{\text{min}} \) is the lowest \( \chi^2 \) value that corresponds to the most optimal profile fitting.

The characterization of our PEG-AuNPs including small-angle x-ray scattering (SAXS), dynamic light scattering (DLS), and UV-vis spectroscopic methods have been described in detail elsewhere [11,12]. The average diameter of the AuNPs used in this study is determined as \( 88 \pm 8 \text{ Å} \). It is worth noting that the XR and GISAXS results in this study have been reproduced by employing synchrotron radiation under otherwise similar conditions [13]. Here, for consistency and completeness, we present the x-ray data collected from the same sample with all three methods.

III. RESULTS AND DISCUSSION

Specular x-ray reflectivity, \( R(Q_z) \), from 0.5 M Cs2SO4 solution (without the PEG-AuNPs), normalized to the Fresnel reflectivity \( R_F \) (calculated for an ideally smooth and flat vapor-solution interface), is shown in Fig. 2(a). The \( R/R_F \) profile from the salt solution surface resembles that of an air-water interface where \( R/R_F \sim \exp(-\xi^2Q^2) \), and \( \xi \) is a measure of the instrumental resolution-dependent interfacial roughness [17,26,27]. In the presence of PEG-AuNPs in solutions, the \( R/R_F \) profile dramatically changes, showing a clear interference pattern that is characteristic of a highly uniform film at the interface. The alternating maxima, separated by \( \Delta Q_z \approx 0.052 \text{ Å}^{-1} \) up to \( Q_z \approx 0.15 \text{ Å}^{-1} \) in the \( R/R_F \) curves, resemble the Kiessig fringes that are typical of a reflectivity curve from a homogeneous slab of thickness \( 2\pi/\Delta Q_z \approx 120 \text{ Å} \) [26]. We note that the reflectivity from PEG-AuNPs solution in the absence of salt (in this case Cs2SO4; data not shown) does not show an obvious interference pattern and resembles that of a water surface, although GISAXS of such solutions indicates a partially populated surface with dispersed PEG-AuNPs [11]. Quantitatively, we determine the electron-density profile across the interfaces, \( \rho(z) \), with finer structural details, that yields the best fit to the measured...
shows the optimal ED profiles that best fit the Parratt recursion formalism \[17,26,27\]. Figure 2(b) are the calculated ED-uniform AuNPs (are the calculated PEG-AuNP film can also be envisioned as a stack of ED-uniform ED segment with respect to the subphase ED. The ED profile for the air-solution interfaces based on the best-fit structural parameters. The ED profiles are generated by refinement of the effective-density model \[28\] by calculating the reflectivity. The ED profiles are proportional to \((D/2)^2 - (z - z_0)^2\), with a maximum ED at \(z = z_0\) and a FWHM = \(D/\sqrt{2}\). In our case the calculated FWHM = 62 ± 5 Å. This is remarkably close to the FWHM extracted from the XR reflectivity (≈60 Å), indicating the PEG-AuNPs form a very flat layer at the interface. This is also consistent with the surface ED profiles determined for aqueous surface superlattices of PEG-AuNPs induced by K_2CO_3 \[11\]. The topmost layer is associated with a PEG-rich phase, as depicted in Fig. 2(c).

Figure 3 shows the GISAXS intensity integrated over the \(Q_z\) range from 0 to 0.085 \(\text{Å}^{-1}\) as a function of \(Q_{xy}\). The main peak at \(Q_{xy} = 0\) is due to the specularly reflected beam and the contribution from diffuse scattering. The symmetric diffraction pattern indicates the formation of a 2D hexagonal structure of the PEG-AuNPs induced by the addition of salt to the suspension, in this case 0.5 M Cs_2SO_4. The solid line is the profile constituted by superposing a number of Lorentzian functions. The dashed lines (in red, blue, green, and magenta), indicated by 1, \(\sqrt{3}\), \(\sqrt{4}\), and \(\sqrt{7}\) (i.e., the ratio of the \(Q_{xy}\) position of each peak with respect to the primary peak), correspond to the primary up to the fourth-order diffraction peaks (each is modeled as a Lorentzian function), characteristic of a 2D hexagonal lattice.

reflectivity. The ED profiles are generated by refinement of the effective-density model \[28\] by calculating the reflectivity with the Parratt recursion formalism \[17,26,27\]. Figure 2(b) shows the optimal ED profiles that best fit the \(R/R_F\) data presented in Fig. 2(a). The ED profile for an air-solution (i.e., 0.5 M Cs_2SO_4) interface in the absence of the PEG-AuNPs presented in Fig. 2(a). The ED profile for an air-solution (i.e., 0.5 M Cs_2SO_4) interface in the absence of the PEG-AuNPs resembles a smooth step-like function with a gradual transition and a plateau regime \((\text{FWHM = 0.39 } e/\text{Å}^3)\), characterized with \(\xi \sim 6 \text{ Å}\) from zero to the bulk ED. In the presence of PEG-AuNPs with salt, the ED profile exhibits a prominent bell-shaped ED segment with a FWHM ≈ 60 Å (measured with respect to the subphase ED). The total film depth is extended over about 100 Å contiguous to the subphase and a plateau regime \((\leq 50 \text{ Å})\) adjacent to the vapor phase. It is obvious that the bell-shaped ED segment can be associated with a monoparticle layer of AuNPs such that their centers form a well-defined plane parallel to the liquid surface. This is supported by the FWHM which is comparable to the diameter of the AuNPs used in this study, \(D = 88 ± 8 \text{ Å}\) (the uncertainty arises mainly from the particle-size distribution). The ED of spheres (centers forming a plane at \(z = z_0\)) in a uniform medium varies along the surface normal, \(z\) axis.

\[\text{FIG. 2. (a) } R/R_F \text{ for Cs}_2\text{SO}_4 \text{ solutions in the absence of PEG-AuNPs (○) and in the presence of PEG-AuNPs (□). The solid lines are the calculated } R/R_F \text{ based on the refined structural parameters. (b) The corresponding electron-density profiles (solid line for the PEG-AuNP-laden surface and dashed line for the bare surface) across the air-solution interfaces based on the best-fit structural parameters. The FWHM marks the full width at half maximum for the bell-shaped ED segment with respect to the subphase ED. The ED profile for the PEG-AuNP film can also be envisioned as a stack of ED-uniform slabs with smeared interfaces (≈10 Å) for the Au-rich slab. The Au-rich slab has an ED of 0.76 \(e/\text{Å}^3\) and the top slab has an ED of 0.39 \(e/\text{Å}^3\). (c) A side-view depiction of the air-solution interface that is crystalline Gibbs film of PEG-AuNPs induced by the addition of 0.5 M Cs_2SO_4 to the aqueous suspension of PEG-AuNPs.}\]
to $\sqrt{3}\sigma^2 D/2$ (i.e., the volume of a unit cell) is only $\sim 5.7\%$. Moreover, the ratio of a AuNP compared with the total volume of capped PEG-AuNP is even smaller, which is important to our estimate below regarding cationic concentration at the interface; i.e., ignoring solution volume displacement by AuNPs does not significantly affect ion counting in the crystalline film.

Figure 4(a) shows the fluorescent spectra integrated over the $\alpha_i < \alpha_{c,\text{water}}$ (high sensitivity for interfacial ions; note the $\alpha_{c,\text{water}}$ is slightly smaller than the $\alpha_c$ of 0.5M Cs$_2$SO$_4$ solution). The spectra in the 3.5 to 6 keV energy range are all identifiable as Cs characteristic emission lines [29], (for instance, L$_\alpha_{1,2}$, L$_\beta_1$, L$_\gamma_1$, and L$_\gamma_2$). The Cs spectra exhibit a significant reduction in intensity in the presence of PEG-AuNPs. The solid lines are calculated profiles based on Eqs. (A3) and (A4) for scattering from a bare surface of water or salt solution. The shaded area in panels (a) and (b) represent acceptable optimal profiles for the multiple-layer model shown in Fig. 6 and the matrix method.

Figure 4(b) shows the spectra collected above the critical angle for total reflection (at $\alpha_i = 1.6\alpha_{c,\text{water}}$) that are dominated by signals from the bulk water and ions. Above the critical angle, the penetration depth of the primary beam significantly decreases due to the attenuation by Cs ions. (see the appendix for more details).

Figure 5(a) shows the fluorescent intensity integrated over the emission lines of Cs$^+$ in the 4.0 to 5.4 keV range.
versus the normalized incident beam angle ($\alpha_i/\alpha_{water}$) for a 0.5 M Cs$_2$SO$_4$ solution in the absence and presence of PEG-AuNPs. It is evident that, over the entire $\alpha_i$ range, the intensity of the Cs signal is lower in the presence of PEG-AuNPs at the interface, providing qualitative evidence of reduced [Cs$^+$] at the PEG-AuNP film compared with the same Cs$_2$SO$_4$ solution without the NPs. We emphasize that such ion reduction in the film is not due to the well-known ion surface depletion of salt solutions, which can be hardly detected by x-ray methods and only for much higher salt concentrations (few molar) [30] compared with the concentrations used in this study. Figure 5(b) shows the direct-beam scattering intensity (Thomson and Compton) as a function of $\alpha_i$ for pure water, salt solution, and salt solution with PEG-AuNPs. In the absence of the PEG-AuNPs, the common trend in the scattering intensity profiles for water and Cs$_2$SO$_4$ solutions in Fig. 5(b) is a balance between the high concentration of the [Cs$^+$] with large scattering cross sections (increasing scattering intensity) and the resulting shortened x-ray penetration depth (decreasing the effective volume of scattering), as described in the appendix. In the presence of PEG-AuNPs in solution, the intensity below the critical angle is higher compared with that from Cs$_2$SO$_4$ solution and the other way around above the critical angle. This is an indication that the accumulation of interfacial PEG-AuNPs as strong scatterers significantly attenuates the beam that penetrates the subphase. To model the $\alpha_i$ dependence of the fluorescence-intensity profiles, we use standard procedures [17,31] and extend them to simultaneously fit the spectra of Cs and the scattering from the direct beam. For that, we simplify the crystalline film structure as a stack of two strata (based on and consistent with the XR and GISAXS), each of which has a distinct chemical composition, as is shown in Fig. 6. The topmost stratum consists of densely packed PEG of thickness $\Delta_I \lesssim 50$ Å, and a AuNP-rich stratum of thickness $\Delta_{II}$ adjacent to it (Au core occupying only 5.7% of the volume in this stratum when $\Delta_{II} = 88$ Å, as shown above). A third stratum of the PEG attached to the AuNPs and in contact with the subphase is assumed to be a continuum of the subphase because it has practically the same ED as the solution [11], and it is considered as indistinguishable from the bulk subphase. Combining the direct beam scattering (Thomson and Compton) and the fluorescence allows for self-consistent evaluation of the electric field (of x-rays) in the film, taking into account x-ray absorption and scattering processes assuming the stratified model shown in Fig. 6. We also note that the in-plane density of AuNPs is kept constant consistent with GISAXS. The x-ray intensity at a depth $z$, is a function of incident beam intensity, incident angle $\alpha_i$, depth $z$, and the optical properties of the medium with respect to x-rays; namely, linear attenuation coefficient $\mu$ and atomic number density $\rho_a$, represented by the refractive index $n = 1 - \delta + i\beta$ [26] using the optical matrix method summarized in the appendix. For each stratum, $\delta = (r_e\lambda^2/2\pi)\sum\rho_a Z_i$ and $\beta = (\lambda/4\pi)\sum\sigma_a\alpha_i$, where $\alpha_i$ in the subscript represents the $i$th elemental species, $Z$ is the atomic number, and $\sigma_a$ is the x-ray absorption cross section listed in Table I. The solid lines in Figs. 5(a) and 5(b) for water and the 0.5 M Cs$_2$SO$_4$ solution without PEG-AuNPs are obtained without any fitting parameters, as described in the appendix. The solid lines to the spectra of the PEG-AuNPs/Cs$_2$SO$_4$ in solution are obtained from the best, nonlinear least squares parallel fitting to the combined spectra of Cs and direct beam. To fit the data we use four parameters: $\Delta_I$ (in a limited range 10–50 Å), $\Delta_{II}$ (in a limited range of 60–120 Å), and [Cs$^+$] concentration with an upper limit of 1 M (i.e., the bulk concentration) and the PEG volume ratio (denoted $V_{PEG/\%}$) in the mixture of PEG and water. To a first approximation, media I and II possess the same [Cs$^+$] and $V_{PEG/\%}$. Our analysis shows that, within these limits, and to be consistent with the spatial limit posed by XR results (i.e., $\Delta_I + \Delta_{II} \lesssim 100$ Å), the optimal fitting is obtained for $\Delta_I = 15 \pm 10$ Å, $\Delta_{II} = 90 \pm 20$ Å, $V_{PEG/\%} = 0.2 \pm 0.2$ and [Cs$^+$] = 0.4 ± 0.1 M with a significant decrease compared with 1 M in the bulk (uncertainties correspond to at most 20% change in $\chi^2$ with respect to $\chi^2_{min}$). The generated profiles in terms of these parameters including uncertainties are shaded as shown in Fig. 5. Again, we emphasize that such a dramatic reduction has nothing to do with the classical ionic surface.
TABLE I. Reference data for x-ray (elastic and inelastic) scattering intensity per atom and absorption cross section per atom. $f$ represents the mean atomic scattering factor (in units of $r$, the classical radius of the electron) at $2\theta = 90^\circ$ [i.e., $(\sin \theta)/\lambda = 0.46 \text{Å}^{-1}$] for a free atom. $I_{\text{ac}}$ represents the incoherent intensity of Compton scattering per atom at $(\sin \theta)/\lambda = 0.46 \text{Å}^{-1}$. The value is obtained through linear interpolation by using two neighboring, consecutive tabulated values. Data source for $f$ and $I_{\text{ac}}$ is the International Tables for Crystallography [36]. $\sigma_x$ represents the absorption cross section per atom (in units of barns, 1 barn = $10^{-28}$ cm$^2$) for x-rays at $E = 8.0$ keV. Data source for $\sigma_x$ is XCOM: Photon Cross Sections Database, a web database provided by the National Institute of Standards and Technology (NIST) [24].

<table>
<thead>
<tr>
<th>Elements</th>
<th>H</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Cs</th>
<th>Au</th>
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</thead>
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<td>$f$ [$r_e$]</td>
<td>0.09</td>
<td>1.77</td>
<td>2.56</td>
<td>7.34</td>
<td>30.85</td>
<td>49.06</td>
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<tr>
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<td>4.36</td>
<td>5.60</td>
<td>8.58</td>
<td>19.45</td>
<td>n/a</td>
</tr>
<tr>
<td>$\sigma_x$ [barn]</td>
<td>9.816 $\times 10^{-3}$</td>
<td>8.459 $\times 10^3$</td>
<td>2.967 $\times 10^2$</td>
<td>4.986 $\times 10^3$</td>
<td>7.015 $\times 10^4$</td>
<td>6.584 $\times 10^4$</td>
</tr>
</tbody>
</table>

depletion due to high salt concentrations in solutions. First, for pure salt solutions, the length scale over which the depletion falls off is merely a few Å [30] and, second, the overall depletion (total ions in the illuminated volume) is not as dramatic as we observe over the depth of the crystalline film. It is in fact expected that ion concentration in the corona of the capped AuNPs is at the so-called $\theta$ point; however, it has not been demonstrated yet. Below, we examine the Cs concentration in relation to the PEG and water content in the region of the crystalline film.

IV. THEORETICAL CONSIDERATION

We consider a general salt consisting of ions $A^{z_A}$ and $B^{z_B}$ and chemical formula $A_p^{z_A}B_n^{z_B}$, where the condition $p z_A + q z_B = 0$ enforces charge neutrality. In the presence of two media of dielectric constants $\varepsilon_1$ (the index 1 refers to the content in $\Delta_1 + \Delta_H$) and $\varepsilon_2$ (the bulk), the salt concentrations are $n_1 = [C\text{s}\text{[}_{\text{film}}$ and $n_2 = [C\text{s}\text{]}_{\text{bulk}}$ for the surface PEG-AuNP film and the bulk, respectively. The equilibrium condition between the PEG-AuNP film, salt and water, and the bulk is

$$(p + q)k_B T \ln n_1 = \Delta G + (p + q)k_B T \ln n_2,$$  

(1)

where we assume that the free-energy cost of transferring ions between the two media (film and bulk) is given by the Born approximation

$$\Delta G = -e^2/8\pi \varepsilon_0 \left(1 - 1/\varepsilon_2 \right) \left(p z_A^2/r_A + q z_B^2/r_B \right).$$  

(2)

Combining Eqs. (1) and (2) and assuming $\varepsilon_2 = \varepsilon_w$ (i.e., the dielectric constant of water) leads to the relation

$$\ln \left( n_1/n_2 \right) = 1/p + q \left(1 - \varepsilon_2/\varepsilon_1 \right) \left(p z_A^2/r_A + q z_B^2/r_B \right) l_B,$$  

(3)

where $r_A$ and $r_B$ are the ionic radii of ions $A^{z_A}$ and $B^{z_B}$, respectively, and $l_B = e^2/(8\pi \varepsilon_0 e k_B T)$ is the Bjerrum length in water.

We assume that the film consists of water with a dilute species whose intrinsic dielectric constant is $\varepsilon_p$, which is PEG in our case. We define a quantity $x$ as the fraction of PEG within the film as follows:

$$x = \frac{N_{\text{PEG}}}{N_{\text{PEG}} + N_w},$$  

(4)

where $N_{\text{PEG}}$ and $N_w$ are the number of PEG monomers and the number water molecules in the crystalline film, respectively. The dielectric constant in the film is then given by

$$\varepsilon_1 = (1 - x) \varepsilon_w + x \varepsilon_p = \varepsilon_w [1 - (1 - \gamma) x],$$  

(5)

where $\gamma = \varepsilon_p/\varepsilon_w$ is the ratio of the dielectric constant of the dilute species and water. Therefore, the equation relating the two densities is

$$\ln \left( n_1/n_2 \right) = - \frac{l_B}{p + q} \left(p z_A^2/r_A + q z_B^2/r_B \right) \frac{1 - (1 - \gamma) x}{1 - (1 - \gamma) x}.$$  

(6)

To apply this formula to (Cs$^{1+}$)$_2$(SO$_4^{2-}$)$_2$ ($p = 2, q = 1, z_A = 1, z_B = -2$), we use $r_A = 0.169$ and $r_B = 0.23$ [32] (in nm) and $\varepsilon_p \approx 10$ [33]. We note that $n_2$ varies close to the interface; however, this variation is negligible compared with the depletion due to the presence of a crystalline film of PEG-AuNPs at the interface. The relation between $x$ (PEG fraction) and the amount of ion depletion $n_1/n_2$ is shown in Fig. 7. As implied in the discussion above, our experimental results (XR, GISAXS, and GIFXS) are not sensitive to the ratio $x$. So, by evaluating the experimental (GIFXS) upper limit $\frac{d\sigma}{dx} \approx 0.4$, we obtain a lower limit for $x \approx 0.12$, namely, that the crystalline film contains about 12% of PEG monomers and 88% water molecules in which the salt is

![FIG. 7. Ratio of the Cs ion concentration at interface ($n_1$) compared with bulk ($n_2$) vs $x = N_{\text{PEG}}/(N_{\text{PEG}} + N_w)$, where $N_{\text{PEG}}$ and $N_w$ are the number of PEG monomers and number water molecules in the film (within $\Delta_1 + \Delta_H$). Note that the quantity $n_1/n_2 \equiv [C\text{s}\text{]}_{\text{film}}/[C\text{s}\text{]}_{\text{bulk}}$.](image-url)
dissolved. Such a ratio corresponds to over approximately 6 M PEG monomers in the film compared with the average 2.6 × 10^{-4} M in the bulk. [Note that PEG monomer bulk concentration is estimated based on the number of monomers per PEG_{6k} (≈136), the grafting density of PEG_{6k} per AuNP (≈160) [11, and the bulk concentration of PEG-AuNPs in the solution, i.e., 12 nM.] Given the measured hydrodynamic diameter (measured with DLS) of PEG-AuNPs in the bulk, \( D_h = 38 \) nm, one can assume PEGs are contained in the shell surrounding the Au core with thickness \((D_h - D)/2 \approx 14\) nm and estimate that the PEG monomer concentration in the shell of a PEG-AuNP that is suspended in the bulk is approximately 1.3 M. Therefore, it can be concluded that a significant amount of water is squeezed out of the shell of PEG-AuNPs as they populate and crystallize at the surface.

V. CONCLUSION

In this study, we combine surface-sensitive x-ray scattering and spectroscopy methods to characterize the structure, coverage, and ionic depletion at an interface that consists of crystalline AuNPs capped with PEG induced by the presence of salt in solution. The angular dependence of the fluorescence spectra allows us to determine a significant reduction in the cation (i.e., Cs\(^{+}\)) concentration at the interface, from 1 M in bulk to 0.4 M in the crystalline film. We also show that such a reduction results from the difference in dielectric constant between the bulk and the interface due to the accumulation of polymers at the interface, where the polymer concentration at the crystalline film is approximately 10^4 times that of the bulk.

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APPENDIX A: FLUORESCENCE AND SCATTERING CONSIDERATIONS

In the grazing incidence fluorescence spectroscopic measurements, the x-ray beam is incident on the aqueous surface at a series of incident angle \( \alpha_i \) near the critical angle for total reflection, \( \alpha_c \). The energy-dispersive detector (EDD) is pointed at the surface along the surface normal. The resulting x-ray fluorescence signals are omnidirectional and only a small portion at the surface along the surface normal. The resulting x-ray fluence and spectroscopic measurement configuration for a simple air-liquid interface. X-rays impinge on the air-liquid interface at a grazing incident angle \( \alpha_i \). Within the x-ray penetration depth, the liquid molecules (e.g., water) and other present ions, if any, interact with x-rays and give off elastic and inelastic scattering, and fluorescence if excited. The EDD above the surface collects x-rays emanating from the surface along the surface normal.

\[ I_{sc}(\alpha_i) = \eta_{sc} A_0 \int \left| E(\alpha_i, z) \right|^2 \sum C_i(z) (I^2 + I_{inc,i}) dz, \]  

(A1)

where \( C \) represents concentration of certain constituent species in the solution. The subscript \( i \) represents a particular element, as listed in Table I. \( \eta_{sc} \) is a scaling factor accounting for detector efficiency for the x-ray signals at the relevant photon energy. \( A_0 \) is the overlap between the area of the incident x-ray-beam footprint and the EDD effective detecting area. Likewise, the angular fluorescence intensity of a specific element (i.e., Cs in this case), \( I_{flu}(\alpha_i) \), can be expressed similarly as

\[ I_{flu}(\alpha_i) = \eta_{flu} A_0 \int \left| E(\alpha_i, z) \right|^2 C_{Cs}(z) dz, \]  

(A2)

where \( \eta_{flu} \) is the intensity scaling constant and \( C_{Cs}(z) \) is the Cs\(^{+}\) ion concentration at depth \( z \).

1. Single vapor-liquid interface

The single interface between the vapor phase and solution, i.e., the air-liquid interface, is by far the simplest case. The concentrations of the scattering and fluorescent entities (i.e., ions, atoms, or molecules) are considered constant throughout the aqueous solutions thus the integrals in Eqs. (A1) and (A2) are reduced to the closed form, i.e., the product of the functions \( T(\alpha_i) \) and \( D(\alpha_i) \), where \( T(\alpha_i) \) is the Fresnel intensity transmission function at the vapor-bulk interface and \( D(\alpha_i) \) is...
the x-ray penetration depth function [17,26–28,34]. Given the x-ray wavelength, \( T(\alpha_i) \) and \( D(\alpha_i) \) can be calculated based on the index of refraction (a complex number) \( n = 1 - \delta + i\beta \) of the media onto which the x-rays are incident from vacuum [17,26–28,34]. The \( \delta \) and \( \beta \) for a given medium can be explicitly expressed as a function of x-ray wavelength \( \lambda \), electron number density \( \rho_e \), and linear absorption coefficient \( \mu \) [26]. Figures 9(a) and 9(b) show the calculated \( T(\alpha_i) \) and \( D(\alpha_i) \) for pure water and a Cs\(_2\)SO\(_4\) solution (0.5 M), respectively. The presence of Cs\(_2\)SO\(_4\) (0.5 M) changes the optical properties of the media (i.e., water) and significantly reduce the x-ray penetration depth at incident angles above the critical angle. Given the same parameters (i.e., \( \eta_{sc} \) and \( A_0 \)) and intensity normalization by incident beam flux \( \Phi_0 \), the obtained scattering intensity by the EDD is simply the product of function \( T(\alpha_i) \) and \( D(\alpha_i) \), and the total scattering from the constituent atoms or ions.

The scattering from pure water can be expressed as the \( T(\alpha_i)D(\alpha_i) \) scaled by the scattering factors of individual H\(_2\)O molecules. The concentration of water, denoted as [H\(_2\)O], is constant, i.e., 55.56 mol/L (corresponding to a mass density of 1 g/cm\(^3\)), throughout the bulk. Equation (A1) is expressed as

\[
I_{sc}(\alpha_i) = \eta_{sc} \Phi_0 A_0 \frac{f_{H_2O}}{\{[H_2O]f_{\text{inc,H}_2O} + f_{\text{inc,H}_2O}\}} T(\alpha_i) \cdot \frac{D(\alpha_i)}{\text{Cs}_2\text{SO}_4 \text{ solution}},
\]

where both \( T(\alpha_i) \) and \( D(\alpha_i) \) are calculated for the water subphase [17,25]. For a concentrated Cs\(_2\)SO\(_4\) solution, the scattering is as follows:

\[
I_{sc}(\alpha_i) = \eta_{sc} \Phi_0 A_0 \left[[\text{Cs}_2\text{SO}_4]\{f_{\text{inc,Cs}_2\text{SO}_4} + f_{\text{inc,Cs}_2\text{SO}_4}\}\right] \frac{T(\alpha_i)D(\alpha_i)}{\text{Cs}_2\text{SO}_4 \text{ solution}},
\]

where \( f_{\text{inc,H}_2O} \) and \( f_{\text{inc,Cs}_2\text{SO}_4} \) are the scattering form factors per molecule and can be approximated by using the tabulated, individual atom scattering factors (see Table I). For instance, \( f_{\text{H}_2\text{O}}^2 \approx 2f_{\text{H}}^2 + f_{\text{O}}^2 \) on the ground that the scattering angle \( 2\theta \) is considered large enough, hence the scattering from the H\(_2\)O molecule is the incoherent sum of the scattering from the individual atoms (\( f_{\text{H}}^2 \) for a hydrogen atom and \( f_{\text{O}}^2 \) for an oxygen atom).

Similarly, the fluorescent signals from the Cs bulk solution (i.e., Cs\(_2\)SO\(_4\) solution) can be handled in the same manner. The angular Cs fluorescent intensity, \( I_{\text{fluorescence}}(\alpha_i) \), is expressed as follows:

\[
I_{\text{fluorescence}}(\alpha_i) = \eta_{fluorescence} \Phi_0 A_0 \left[[\text{Cs}^+]\{f_{\text{inc,Cs}^+} + f_{\text{inc,Cs}^+}\}\right] \frac{T(\alpha_i)D(\alpha_i)}{\text{Cs}_2\text{SO}_4 \text{ solution}},
\]

where the constant \( \eta_{fluorescence} \) represents the EDD detecting efficiency of the x-ray photon energy at the Cs emission line energy (4.2–5.3 keV for \( \alpha_{\text{L}\alpha} \), \( \alpha_{\text{L}\beta} \), and \( \alpha_{\text{L}\gamma} \)). Both constants \( \eta_{sc} \) and \( \eta_{fluorescence} \) can be calibrated with the pure subphase solution of known concentrations [see Figs. 5(a) and 5(b) in the main text].

Figure 9 shows the two important functions, \( T(\alpha_i) \) and \( D(\alpha_i) \), with \( \alpha_i \) being normalized to the critical angle for total reflection of water (denoted as \( \alpha_{c,water} \)) against \( \alpha_i \). For dilute salt solution, these two functions are nearly identical to their counterparts of water. For Cs\(_2\)SO\(_4\) solution at high concentration, the two relevant x-ray optical properties for the media are significantly different from water, shown in Table II, which result in the conspicuous difference in the \( T(\alpha_i) \) and \( D(\alpha_i) \). With the known \( T(\alpha_i) \) and \( D(\alpha_i) \) for the known media (i.e., water and Cs\(_2\)SO\(_4\) solution), the only parameter to be determined experimentally is \( \eta_{sc} \). The scattering factors for all constituent atoms in the x-ray path are given in Table I. The \( \eta_{sc} \) is determined by simultaneously profile fitting Eqs. (A3) and (A4), as shown in Fig. 5(b). In the presence of the PEG-AuNPs in the solution, the total scattering can be viewed as the sum of the portion from the bulk and from the multilayers on the surface. To gain more quantitative insight of the surface Cs concentration variation in response to the presence of the surface AuNPs, we analyze the spectral intensity as a function of incident angle [17]. The quantitative analysis based on the

### Table II. Parameters to evaluate x-ray transmission coefficient and penetration depth. The attenuation lengths \( \Lambda \) for pure water and salt solution are calculated based on their mass density. The values for PEG are estimated based on its bulk properties [35].

<table>
<thead>
<tr>
<th>Media</th>
<th>Pure water</th>
<th>Cs(_2)SO(_4) solution (0.5 M)</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Lambda \times 10^7 ) Å</td>
<td>1.0</td>
<td>0.19</td>
<td>1.4</td>
</tr>
<tr>
<td>( \rho_e ) [g/Å(^3)]</td>
<td>0.334</td>
<td>0.381</td>
<td>0.369</td>
</tr>
</tbody>
</table>
matrix method [34], which treats each layer as a chemically distinct slab where all constituent elements are homogeneously distributed, are carried out to calculate how x-ray waves propagate, reflect, and attenuate within each layer, depending on the electron density and absorption coefficient for particular chemical compositions.

2. Multi-interfaces representing surface structures

The matrix method [34] is employed to determine the x-ray propagation within the stratified media, as shown in Fig. 6. The incident x-ray plane wave of unit amplitude, traveling in medium 0 (i.e., vapor phase) down into the multilayer is expressed as \( \exp(i\omega t - k_0 \cdot \mathbf{r} - k_z z) \), where \( k_0 = \left( |k_{\parallel,0}|^2 + k_z^2 \right)^{1/2} = 2\pi/\lambda \), with \( k_0 \) being the wave number of x-rays in medium 0 (vapor phase). The amplitude of the reflected wave (\( r \); exiting the multilayer back into the vapor phase) and the transmitted wave (\( t \), into the subphase, medium III) shown in Fig. 6(c) can be expressed in a matrix operation:

\[
\begin{bmatrix}
1 \\
\mathbf{r}
\end{bmatrix} = \begin{bmatrix}
p_{0-1} & m_{0-1} & 0 \\
m_{0-1} & p_{0-1} & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
e^{-ik_z \Delta_1} & 0 & 0 \\
0 & e^{ik_z \Delta_1} & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
\mathbf{t} \\
\mathbf{r}
\end{bmatrix},
\]

where

\[
p_{i,j} = \frac{k_{z,i} + k_{z,j}}{2k_{z,i}}, \quad m_{i,j} = \frac{k_{z,i} - k_{z,j}}{2k_{z,i}},
\]

and

\[
k_{z,j} = \frac{1}{2} \sqrt{Q_i^2 - \frac{8k_0^2 \delta_j + i8k_0 \beta_j}{2k_0}},
\]

where \( \delta_j = 2\pi r_{\sigma,j} r_0 / k_0^2 \) and \( \beta_j = \mu_j / 2k_0 (i, j = 0, I, II, III) \). The reflectivity \( R \) equals \( |\mathbf{r}|^2 \) and the intensity transmission coefficient \( T \) equals \( |\mathbf{t}|^2 \). Within each layer, the electric field \( \mathbf{E}(z, \mathbf{r}, t) \) can be considered as the sum of the wave traveling down and up, as indicated in Fig. 6, and the amplitude of the field is the sum of the two items corresponding to wave down (\( z+ \)) and up (\( z- \)), i.e., \( |\mathbf{E}(z)| = |\mathbf{E}(+ \exp(-ik_{z,j} z) + \mathbf{E}(- \exp(ik_{z,j} z))| \), where \( \mathbf{E}(+) \) and \( \mathbf{E}(-) \) are the amplitude of each and can be determined based on the boundary conditions; a matrix approach similar to Eq. (A6) [34].

We first consider the hypothetical case where both Cs and water are absent in the top two media shown in Fig. 6. The top layer (medium I) is considered as exclusively PEG and is characterized with \( \mu_1 \) and \( \rho_{e,1} \) which are derived from the bulk properties of PEG and are listed in Table II. The thickness of the layer is denoted as \( \Delta_1 \) as depicted in Fig. 2(b). Here \( \Delta_1 \) is a variable parameter. The second layer (medium II) is considered as a mixture of PEG and Au. The AuNPs are regarded as an array of monodisperse pure gold spheres of diameter \( D \) (the mean value is used based on the SAXS measurement). Thus the total volume of gold is considered as distributed throughout layer II with PEG. The corresponding \( \mu_{II} \) and \( \rho_{e,II} \) are then dependent on the thickness \( \Delta_{II} \). The layer of PEG attached to the AuNPs in contact with the solution is considered as the same as the aqueous subphase regarding the x-ray optical properties.

Now, in the presence of the Cs, depending on the specific scheme, the concentration of Cs modifies the \( (\mu_1, \rho_{e,1}) \) and \( (\mu_{II}, \rho_{e,II}) \) by which the electric field in the respective media can be determined. Finally, the water can be incorporated into media I and II assuming both have certain PEG volume fraction (denoted \( V_{\text{PEG}} \% \)).

APPENDIX B: SUMMARY OF PREVIOUS RESULTS ON BRUSH POLYMERS

The main parameters of the model are \( N \), the number of Kuhn lengths; \( b \), the Kuhn length; \( \sigma \), the grafting density; and \( D = 2R \), the core nanoparticle diameter, where \( R \) is the radius. In our previous study [11], we established that the grafted NPs in solution have a hydrodynamic diameter \( D_h \):

\[
\left( \frac{D_h}{D} \right)^2 = 1 + 4 \frac{Nb}{D} (\sigma b^2)^{1/2}(2w_0)^{1/4}.
\]

Using the parameters \( b = 0.724 \) (nm), \( \sigma = 1.51 \) chains/nm², \( w_0 = \frac{1}{2} \) (a dimensionless three-body interaction), \( N = 68.5 \). For \( R = 5 \) nm, this gives \( D_h = 38 \) nm, which is in good agreement with the value of 40 nm obtained by light scattering in our previous study [11]. Thus, if we assume \( \Delta_{II} \approx D = 10 \) nm, then \( \Delta_{III} \approx (D_h - D)/2 \approx 15 \) nm. The fact that our experimental data are consistent with \( \Delta_{I} < \Delta_{III} \) clearly shows that the PEG chains are highly compressed in the air-water interface, as previously pointed out in Ref. [37].


