

# A Nondestructive Method to Quantify Polymer Graft Density on Nanoparticles Using Optical Extinction Spectra

Masoud Abdi, Irene Andreu,\* and Ryan Poling-Skutvik\*



Cite This: <https://doi.org/10.1021/acsnano.6c11390>



Read Online

ACCESS |



Metrics & More



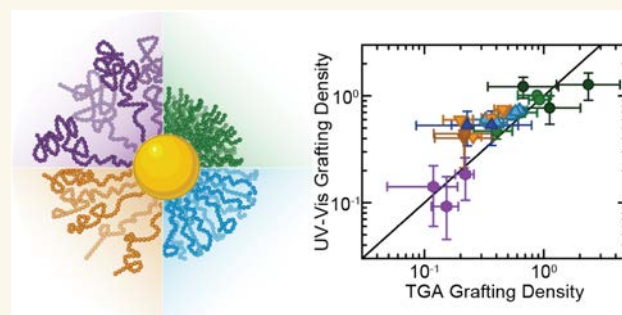
Article Recommendations



Supporting Information

**ABSTRACT:** Grafting density is the key parameter governing colloidal stability and structure for polymer-grafted nanoparticles (PGNPs). Existing methods to quantify grafting density either destroy the sample, require prior knowledge of polymer molecular weight  $M_n$ , or rely on complex instrumentation. Here, we present a nondestructive optical approach that determines grafting density directly from shifts in the localized surface plasmon resonance peak caused by the grafted polymer changing the local effective refractive index. To interpret this shift, the grafted polymer chains are approximated as cylindrical segments passing through differential spherical shells to obtain radial profiles for the polymer volume fraction and refractive index across the polymer corona. The local refractive-index profile is weighted by the plasmonic near-field decay to calculate the effective refractive index sensed by the nanoparticle. The grafting density is finally determined by iteratively adjusting the effective refractive index until the calculated refractive-index sensitivity of the polymer-grafted nanoparticle matches that of the gold core. The grafting densities obtained from this optical method quantitatively agree with established experimental benchmarks across different polymer  $M_n$ , grafting densities, nanoparticle sizes, and solvents. Our approach uses common laboratory equipment, eliminates the need for prior knowledge of polymer  $M_n$ , and preserves the sample for further experiments, bypassing challenges provided by existing characterization approaches. Together, these advantages provide a framework for predicting and understanding the physical and chemical properties of PGNPs for specific applications.

**KEYWORDS:** localized surface plasmon resonance, polymer-grafted nanoparticles, grafting density, polymer brushes, refractive index sensitivity, plasmonic nanoparticles



## 1. INTRODUCTION

Metallic nanoparticles exhibit localized surface plasmon resonance (LSPR), which is a phenomenon that arises when an incident electromagnetic field couples to the free conduction electrons in the nanoparticle.<sup>1</sup> The LSPR sensitivity to the local dielectric environment has enabled the use of plasmonic nanoparticles in various applications including biosensing,<sup>2</sup> drug delivery,<sup>3</sup> photothermal therapy,<sup>4</sup> solar cells,<sup>5</sup> catalysis,<sup>6</sup> photoacoustic imaging,<sup>7</sup> and surface-enhanced Raman spectroscopy.<sup>8,9</sup> This sensitivity has enabled impressive success in the quantitative monitoring of molecular adsorption and binding on AuNP surfaces through LSPR peak shifts.<sup>10–13</sup> In many applications, however, nanoparticles aggregate under attractive interactions introduced by van der Waals forces or electrostatics, for example, quenching the LSPR response and reducing their performance.<sup>14,15</sup> To promote stability, nanoparticles are commonly functionalized with polymer chains to form a tunable stabilizing interfacial

layer.<sup>16–18</sup> The result is a polymer-grafted nanoparticle (PGNP) whose stability is largely governed by the properties of the tethered chains, especially the grafting density  $\sigma$ .<sup>19,20</sup> Consequently, measuring  $\sigma$  is crucial for characterizing PGNPs for both fundamental investigations and practical applications.

Thermogravimetric analysis (TGA) is the most common technique to measure grafting density, where  $\sigma$  is estimated from polymer mass loss during thermal decomposition.<sup>21–25</sup> Despite its ubiquity, TGA suffers from significant drawbacks. It is a fully destructive technique that requires  $\sim 1$  mg of sample,

**Received:** June 16, 2026

**Revised:** September 19, 2026

**Accepted:** September 21, 2026

which can be prohibitive when PGNP synthesis yields are low or costly. Additionally, converting mass loss into  $\sigma$  requires prior knowledge of polymer molecular weight  $M_n$ , often necessitating additional polymer characterization using techniques such as gel permeation chromatography (GPC), which increases experimental cost and complexity.<sup>26–28</sup> Other destructive methods have similar limitations. Electrochemical reductive desorption estimates  $\sigma$  by cleaving thiol–surface bonds and measuring the desorption charge, but competing reactions can overestimate surface coverage and the required voltammetry instrumentation may not be routinely available in many nanomaterials laboratories.<sup>29</sup> The silver ion probe method quantifies bound ions by mass spectrometry, but incomplete or nonselective ion recovery during the multistep process can propagate substantial errors.<sup>30</sup> Likewise, total organic carbon (TOC) analysis is destructive because the entire sample is acidified and oxidized to quantify carbon content. In this approach, residual free polymer or contaminants left after purification can be misidentified as grafted polymer, leading to overestimation of grafting densities.<sup>31</sup>

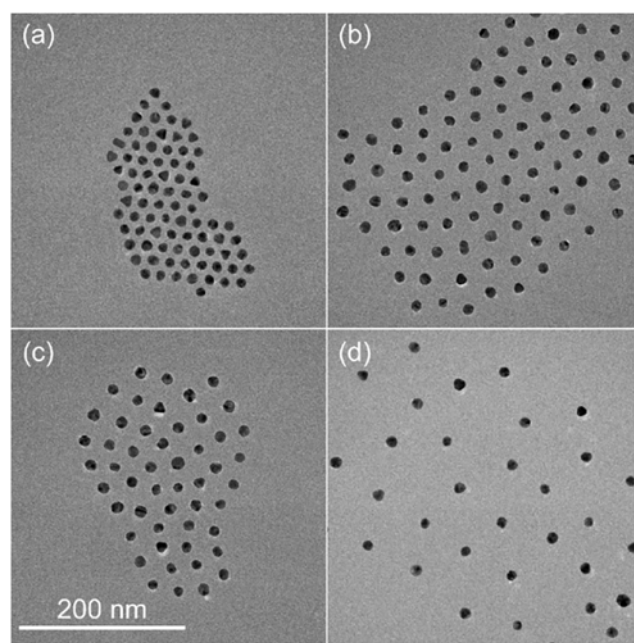
By contrast, nondestructive approaches aim to preserve the sample during characterization but they are often limited by relying on indirect measurements, model assumptions, and instrumental complexity. Nuclear magnetic resonance (NMR) spectroscopy estimates  $\sigma$  by integrating characteristic proton signals from the grafted polymer relative to a standard.<sup>32</sup> However, the NMR method is limited by the difficulty of accurately quantifying polymer-derived protons relative to other signals in the sample, particularly when peak overlap, signal broadening, or baseline uncertainty obscure the integrated peak areas.<sup>33,34</sup> When  $M_n$  is unknown, the NMR method can become destructive because grafted chains may need to be cleaved from the nanoparticle surface for independent  $M_n$  characterization.<sup>33</sup> Analytical ultracentrifugation estimates  $\sigma$  indirectly from sedimentation behavior, which reflects both particle mass and hydrodynamic diameter. Accurate analysis requires prior knowledge of  $M_n$ , a monodisperse core diameter, and reliable polymer-shell thickness, since uncertainty in these parameters can propagate into the calculated grafting density.<sup>31</sup> Spectroscopic ellipsometry can estimate  $\sigma$  from the dry polymer-layer thickness, polymer density, and  $M_n$  only when particles form a uniform layer on a flat substrate. The accuracy of this approach is limited by the optical model used to extract thickness.<sup>35</sup> Infrared spectroscopy estimates  $\sigma$  indirectly by correlating characteristic polymer vibrational bands with calibrated polymer loading curves, but peak overlap, baseline correction, and background signals from the metallic nanoparticles can affect accuracy.<sup>36</sup> Atomic force microscopy (AFM) measures  $\sigma$  by fitting force–distance curves, but strong tip–polymer interactions can deform polymer brushes. Its measurements are also sensitive to tip shape and surface heterogeneity, and it requires expertise in both instrument operation and data analysis.<sup>37</sup> Finally, X-ray photoelectron spectroscopy (XPS)<sup>38,39</sup> and small-angle neutron scattering (SANS)<sup>40</sup> offer indirect assessments of  $\sigma$ , but both require highly specialized instrumentation, advanced data processing, and simplifying analytical assumptions.

Due to these technological limitations, a widely deployable, nondestructive method for directly quantifying  $\sigma$  still remains to be developed. Here, we introduce an approach for quantifying  $\sigma$  from LSPR shifts using widely available UV–visible extinction spectroscopy (UV–vis). The method first

calculates the effective local refractive index generated by the polymer corona using a plasmonic near-field model. An analytical assumption for the polymer brush conformation is then used to convert this optical response into a quantitative measurement of  $\sigma$ . Our analytical approach is tested across multiple polymer  $M_n$ , grafting densities, particle sizes, and solvent choices with excellent quantitative agreement with TGA benchmarks. Unlike current methods, this approach is straightforward, nondestructive, and widely accessible. Finally, we provide an open-source application that directly calculates  $\sigma$  from UV–vis measurements to facilitate broad implementation of this method within the plasmonic nanoparticle community.

## 2. RESULTS AND DISCUSSION

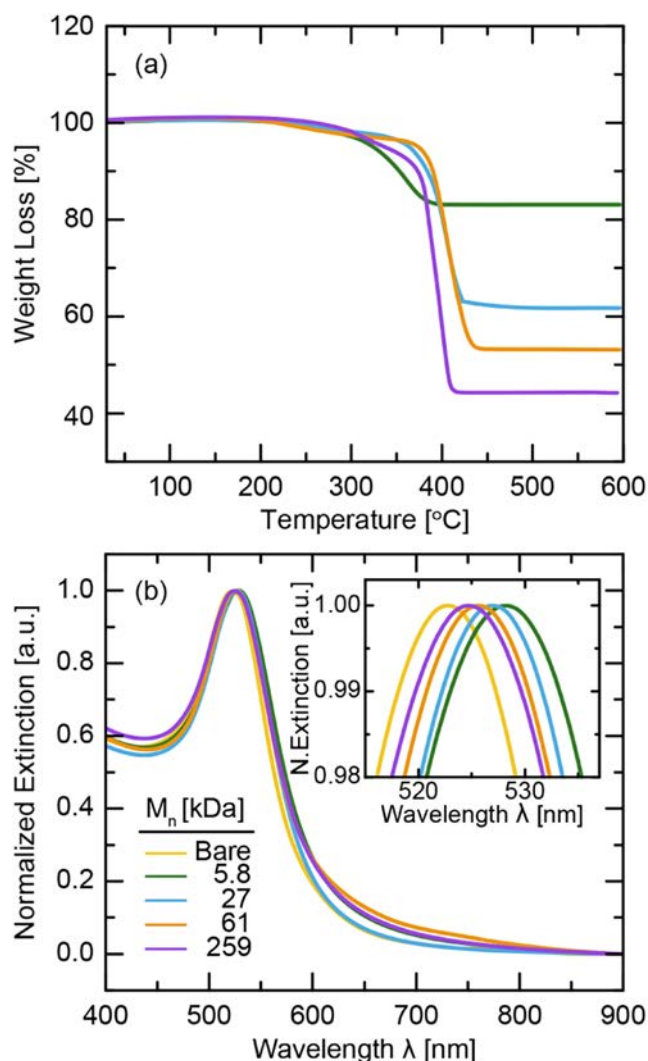
We prepare PGNPs with AuNP cores with sizes  $R_{NP} = 7 \pm 1$  and  $31 \pm 4$  nm, and characterize the PGNP structure with TEM, as shown in Figure 1. TEM images demonstrate that all



**Figure 1.** TEM images of polystyrene-functionalized AuNPs with  $R_{NP} = 7$  nm with increasing polymer molecular weights of (a) 5.8 kDa, (b) 27 kDa, (c) 61 kDa, and (d) 259 kDa.

PGNPs present the same core radius with no noticeable aggregation following functionalization. The increasing edge-to-edge distances between functionalized particles with higher  $M_n$  indicate that the polymer corona thickness  $h$  increases with  $M_n$ , consistent with theoretical predictions and our earlier work.<sup>41,42</sup>

After confirming successful grafting of PS-SH to the AuNPs through TEM images, we quantify the grafting density  $\sigma$  of polymer chains on the PGNP surface using TGA. The PGNPs show significant mass loss in the range 300–450 °C corresponding to the thermal decomposition of the grafted polystyrene (Figure 2a and Supporting Information).<sup>43–45</sup> TGA results show a significant increase in weight loss with increasing  $M_n$ , for example increasing from 18% for PSS.8 to 56% for PS259 on AuNPs with  $R_{NP} = 7$  nm, indicating more polymer mass on the AuNPs surface.



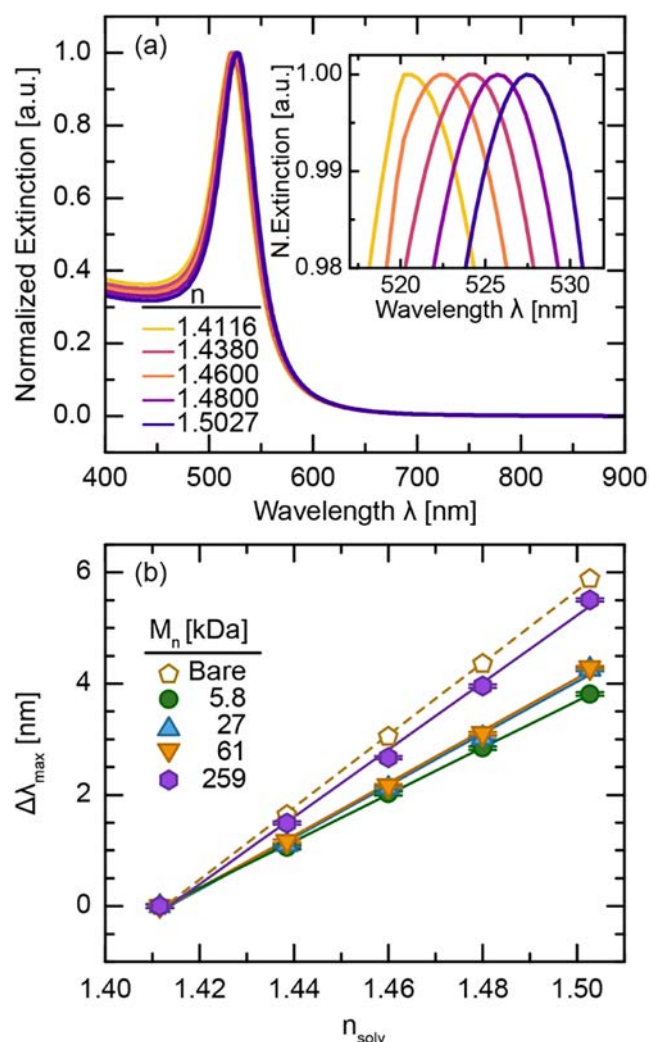
**Figure 2.** (a) Weight loss of PGNPs with  $R_{NP} = 7$  nm functionalized with various  $M_n$  at similar concentrations as a function of temperature under a heating rate of  $5^\circ\text{C min}^{-1}$ . (b) Normalized UV-vis extinction spectra for PGNPs with  $R_{NP} = 7$  nm as a function of wavelength  $\lambda$ , for bare AuNPs in a water-glycerol solution ( $n = 1.4116$ ) and PGNPs with different  $M_n$  in THF ( $n = 1.4116$ ).

Additionally, this PS functionalization promotes stability in organic solvents<sup>42,46</sup> which we characterize through the PGNP optical response. All PGNPs exhibit a narrow, symmetric LSPR peak (Figure 2b and Supporting Information), indicating that PGNPs are stable in THF. For all PGNPs, we observe red shifts in the LSPR peak position relative to that of bare AuNPs. This red shift is expected because PS has a higher refractive index than the surrounding solvent and therefore increases the local dielectric environment near the AuNP surface.

TGA and UV-vis results, however, show opposite trends with polymer  $M_n$ . As  $M_n$  increases, the total grafted polymer mass measured by TGA increases, whereas the LSPR red shift measured by UV-vis decreases. For example, we find that the low  $M_n$  sample (5.8 kDa) exhibits the largest red shift, from 523 to 529 nm, but has the lowest weight loss of 18%. This contrast in trends between TGA and UV indicates that the LSPR response is not governed by the total polymer mass; instead, we hypothesize that the peak shift must be controlled

by  $\sigma$ , which quantifies the density of polymer near the AuNP surface and thereby the local dielectric environment.

If the observed red shift results from the polymer corona increasing the local refractive index within the LSPR near field, the effect should be described by Mie theory,<sup>47</sup> which solves the differential equations underlying the electromagnetic response.<sup>48,49</sup> We calculate the extinction spectra for AuNPs using the MiePlot software<sup>50,51</sup> with the McPeak dielectric function for gold.<sup>52</sup> These calculations show excellent agreement with the measured LSPR peak of bare AuNPs of both sizes suspended in water-glycerol mixtures, quantitatively reproducing the peak position and qualitatively matching the experimental peak shape (Supporting Information). Following this success, we use Mie calculations to predict the LSPR peak position of bare AuNPs of both sizes across the refractive-index range of organic solutions of THF and toluene and compare those predictions to measurements for PGNPs suspended in the same solutions (Figure 3 and Supporting Information).



**Figure 3.** (a) Predicted UV-vis extinction spectra from Mie theory as a function of wavelength  $\lambda$  for bare AuNPs with  $R_{NP} = 7$  nm in solutions of varying refractive indices. (b) Peak shift  $\Delta\lambda_{max}$  of PGNPs with  $R_{NP} = 7$  nm (closed symbols) from pure THF and Mie theory predictions for bare AuNPs (open symbols) as a function of the refractive index of THF-toluene mixtures. Solid lines show linear fits to the experimental data, and dashed lines show linear fits to the calculated data.

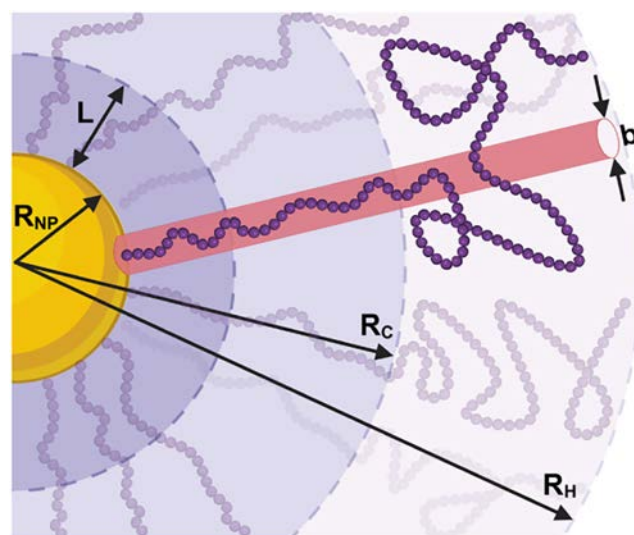
Indeed, Mie theory calculations for bare AuNPs show that peak shift  $\Delta\lambda_{\max}$  increases linearly with refractive-index. For AuNPs with  $R_{\text{NP}} = 7$  nm, the total peak shift is 5.9 nm as refractive-index increases from  $n = 1.4116$  (THF) to  $n = 1.5027$  (toluene), as shown in Figure 3b. The AuNPs with  $R_{\text{NP}} = 31$  nm exhibit a corresponding total peak shift of 11.5 nm over the same refractive-index range (Supporting Information). We find that all PGNP samples show similar linear increases in  $\Delta\lambda_{\max}$  over the same range in solvent refractive index  $n_{\text{solvr}}$ , but with different magnitudes for each  $M_n$ . For example, PGNPs with  $R_{\text{NP}} = 7$  nm with high and low  $M_n$  exhibit peak shift magnitudes of 5.5 and 3.8 nm, respectively, which is significantly smaller than the predicted shift of 5.9 nm for bare AuNPs. In Mie theory, the LSPR response depends only on the particle size, geometry, and the dielectric environment, and from TEM, we confirm that there is no change in particle size or shape during functionalization. Therefore, the observed differences in the magnitude of the peak shifts between bare AuNPs and PGNPs must result from differences in the local dielectric environment caused by the grafted polymer corona within the plasmonic near-field decay.<sup>1,53</sup>

Because the plasmonic field decays exponentially with distance from the AuNP surface, monomers near the particle surface contribute more strongly to the resulting LSPR shift than those farther from the surface. Earlier studies<sup>54–56</sup> identified an empirical relationship between LSPR peak position and the change in local index of refraction  $\Delta n$  according to

$$\Delta\lambda_{\max} = m\Delta n[1 - \exp(-2d/L)] \quad (1)$$

where  $m$  is the refractive index sensitivity (RIS),  $d$  is the thickness of a bound analyte layer, and  $L$  is the electromagnetic field decay length that depends on particle size and geometry.<sup>56–58</sup> If  $d \gg L$  (e.g., when a particle is transferred to a different solvent so that  $d \rightarrow \infty$ ), the peak shift becomes a linear function of the refractive index change  $\Delta\lambda_{\max} = m \Delta n$ . Our Mie theory calculations confirm this relationship with  $m = 64.5 \pm 0.6$  nm per refractive index unit (RIU) for our bare AuNPs with  $R_{\text{NP}} = 7$  nm over the range of  $n$  spanned by mixtures of THF and toluene (Figure 3b). For the larger AuNPs, the corresponding Mie-predicted RIS is  $m = 125.5 \pm 1.5$  nm/RIU over the same range of  $n$  (Supporting Information). We cannot experimentally measure the peak shift of bare particles over the same range of  $n$  because the particles are unstable in organic solvents without PS functionalization, but we do experimentally confirm this linear relationship in aqueous solutions (Supporting Information). Therefore, we use the Mie-predicted RIS  $m$  for each AuNP core size as a reference to interpret the different shift magnitudes of PGNPs. We expect that differences in the RIS  $m$  with polymer  $M_n$  arise from changes in  $\sigma$ .

To relate peak shifts to  $\sigma$ , we develop a physical model schematically illustrated in Figure 4. In this model, we relate the macromolecular conformation of the grafted polymer chains, controlled by  $\sigma$ , to the radially dependent polymer volume fraction  $\varphi(z)$  surrounding the particle, where  $z$  is the radial distance from the AuNP surface. We then use  $\varphi(z)$  to calculate the distance-dependent refractive index  $n(z)$ , which can be appropriately weighted to result in an effective refractive index  $n_{\text{eff}}$  controlling the peak shift  $\Delta\lambda_{\max}$ . When implementing this model, we iterate over different  $\sigma$  so that the RIS  $m$  as a function of  $n_{\text{eff}}$  for the PGNPs converges to that of the corresponding bare AuNP core size. With this approach, we



**Figure 4.** Schematic illustration of the important length scales of the PGNP model for predicting optical shifts: nanoparticle core radius  $R_{\text{NP}}$ , decay length  $L$ , cross over radius  $R_C$ , hydrodynamic radius  $R_H$ , and effective cross-sectional diameter of a polymer chain  $b$ .

quantitatively extract the PGNP  $\sigma$  from peak shifts in solvent mixtures. We now provide more specifics on this approach.

First, we build an analytical estimate of polymer density in the grafted corona as a function of  $\sigma$ . Near surfaces, grafted polymers<sup>41,59</sup> exhibit extended conformations<sup>60–62</sup> in which the polymer backbone orients normal to the surface. A concentrated polymer brush (CPB) regime exists at sufficiently high  $\sigma$ , in which the chain conformation can be approximated as a cylinder normal to the surface with a diameter  $b$ .<sup>63</sup> Farther from the surface, the polymer density decreases and the chains enter a semidilute polymer brush (SDPB) regime with a more coiled conformation.<sup>40,64,65</sup> The crossover radius between these two regimes is given by

$$R_C = R_{\text{NP}}\sigma^{*1/2}\nu^{*-1} \quad (2)$$

where  $\nu^* = (4\pi)^{1/2} \nu$  is a normalized excluded volume parameter with  $\nu \approx 0.588$  for a good solvent condition<sup>66</sup> and  $\sigma^* = 4\pi b^2 \sigma$  normalizes the grafting density by the cross-sectional diameter  $b$  of the grafted chain. Typically, this diameter is assumed to be equivalent to the Kuhn length, but to achieve quantitative agreement in our model, we use an experimentally measured value  $b = 0.95$  nm for polystyrene.<sup>67</sup> For simplicity, we assume that the polymer chains exist primarily within the CPB regime, allowing us to approximate the polymer volume fraction as a function of radial distance  $z$  according to the ratio of the differential volume pervaded by the grafted chains to the differential volume of a spherical shell. Mathematically, this ratio is given by

$$\varphi(z) = \begin{cases} \frac{\sigma\pi b^2 R_{\text{NP}}^2}{4(R_{\text{NP}} + z)^2}, & 0 < z \leq h \\ 0, & z > h \end{cases} \quad (3)$$

where  $h$  is the thickness of the polymer corona calculated from the difference between the hydrodynamic radius  $R_H$  of the PGNP and  $R_{\text{NP}}$  in water. We validate this assumption and identify its limiting conditions further in the text. Using this approach, the  $\varphi(z)$  profiles exhibit a dense polymer region

near the particle surface that monotonically decays toward zero at large  $z$ , consistent with literature findings.<sup>68</sup>

Second, we convert  $\varphi(z)$  into a spatially varying refractive index profile  $n(z)$  through the Lorentz–Lorenz relationship,<sup>69</sup> which considers the dielectric effects of both polymer and solvent, given by

$$\frac{n(z)^2 - 1}{n(z)^2 + 2} = \varphi(z) \frac{n_{\text{poly}}^2 - 1}{n_{\text{poly}}^2 + 2} + [1 - \varphi(z)] \frac{n_{\text{solv}}^2 - 1}{n_{\text{solv}}^2 + 2} \quad (4)$$

where  $n_{\text{poly}} = 1.5993$  and  $n_{\text{solv}}$  are the refractive indices of polystyrene<sup>70,71</sup> and solvent, respectively. The resulting profiles are shown in Figure 5b. Because changes in index farther from the particle surface cause weaker peak shifts (eq 1), we follow an approach from literature<sup>55</sup> to calculate an effective index  $n_{\text{eff}}$  controlling the LSPR peak position by integrating  $n(z)$  with respect to a normalized weighting function  $w(z) = \frac{2}{L} \exp(-2z/L)$ , according to

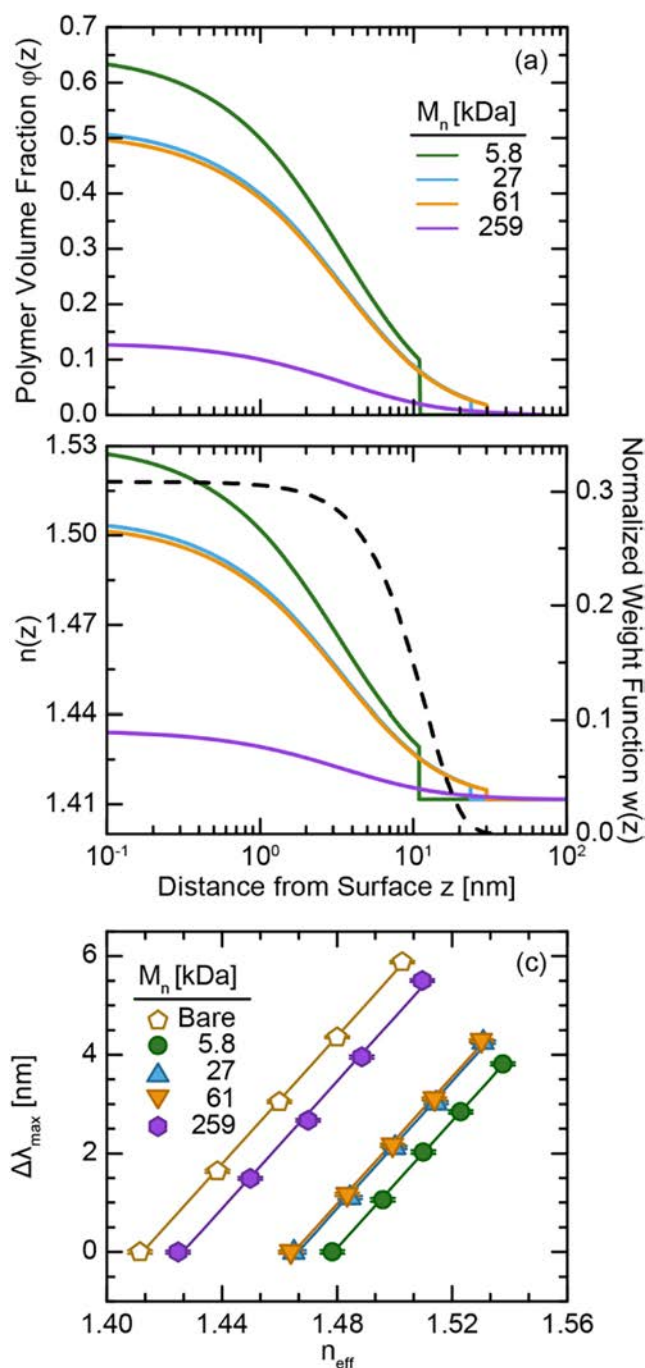
$$n_{\text{eff}} = \frac{2}{L} \int_0^\infty n(z) \exp(-2z/L) dz \quad (5)$$

where  $L = 6.5 \pm 0.1$  nm and  $L = 31.6 \pm 0.4$  nm for the small and large AuNPs, respectively, determined from Mie theory calculations (Supporting Information). These values are consistent with those reported in literature.<sup>13,54</sup> With this weighting, grafted chains near the particle surface contribute more significantly to peak shifts than those farther from the surface.

Finally, we use these estimates of  $\varphi(z)$  and  $n(z)$  to quantify  $\sigma$  through iterative calculations until the RIS of the PGNPs as a function of  $n_{\text{eff}}$  agrees with that of the corresponding bare AuNP core sizes. For PGNPs with  $R_{\text{NP}} = 7$  nm, we find unique numerical convergence to  $m = 64.5 \pm 0.6$  nm/RIU for all  $M_n$ , resulting in identical slopes of  $\Delta\lambda_{\text{max}}$  as a function  $n_{\text{eff}}$  at the converged graft density (Figure 5c). The PGNPs with  $R_{\text{NP}} = 31$  nm similarly converge to the corresponding bare-particle RIS of  $m = 125.5 \pm 1.5$  nm/RIU (Supporting Information). For each solvent mixture,  $n_{\text{eff}}$  varies with  $M_n$  due to changes in  $\sigma$ , with higher  $\sigma$  shifting  $n_{\text{eff}}$  toward the polymer refractive index and lower  $\sigma$  yielding values closer to those of the pure solvent. For example, we find that PGNPs with  $R_{\text{NP}} = 7$  nm with 5.8 kDa grafted polymer experience a higher  $n_{\text{eff}}$  than PGNPs with 259 kDa polymer because of a higher grafting density, consistent with the TGA results (Figure 2). This observation is consistent with our expectations that larger polymer chains experience more significant steric hindrances during “grafting-to” synthesis, resulting in lower  $\sigma$ .<sup>72–74</sup>

So far, we have established an analytical framework to quantitatively relate shifts in LSPR peaks to  $\sigma$ . We verify the accuracy of this approach by comparing the  $\sigma$  values extracted using this UV–vis method with those determined independently using TGA analysis, as shown in Figure 6. We find excellent agreement over a wide range of functionalization conditions for both AuNP core sizes. Specifically, the UV–vis and TGA estimates correlate with each other across an order of magnitude in  $\sigma$  and two orders in  $M_n$ . This high degree of correlation between the methods indicates that the optical method accurately quantifies  $\sigma$  for plasmonic nanoparticles.

While most of the UV–vis measurements are consistent with TGA results, the open symbols in Figure 6 deviate noticeably from this trend and correspond to functionalizations performed with low concentrations of high  $M_n = 259$  kDa PS-



**Figure 5.** (a) Polymer volume fraction  $\varphi(z)$  as a function of distance  $z$  from the nanoparticle surface for PGNPs with  $R_{\text{NP}} = 7$  nm with various  $M_n$ . (b) Corresponding local refractive index  $n(z)$  as a function of distance, with the dashed line indicating the normalized near-field electromagnetic decay weighting function  $w(z)$ . (c) Mie theory predictions for bare AuNPs with  $R_{\text{NP}} = 7$  nm (open symbols) as a function of the refractive index of THF–toluene mixtures, and peak shift  $\Delta\lambda_{\text{max}}$  as a function of  $n_{\text{eff}}$  for PGNPs with  $R_{\text{NP}} = 7$  nm (closed symbols) with different  $M_n$ . The solid and dashed lines indicate linear fits showing a constant slope with  $m = 64.5 \pm 0.6$ .

SH on both core sizes. Specifically, we find that the UV–vis approach significantly overestimates  $\sigma$  for these samples so that the data points sit well above the measured values from TGA. To understand this deviation, we investigate the role of PGNP length scales underlying the assumptions of our model (Figure

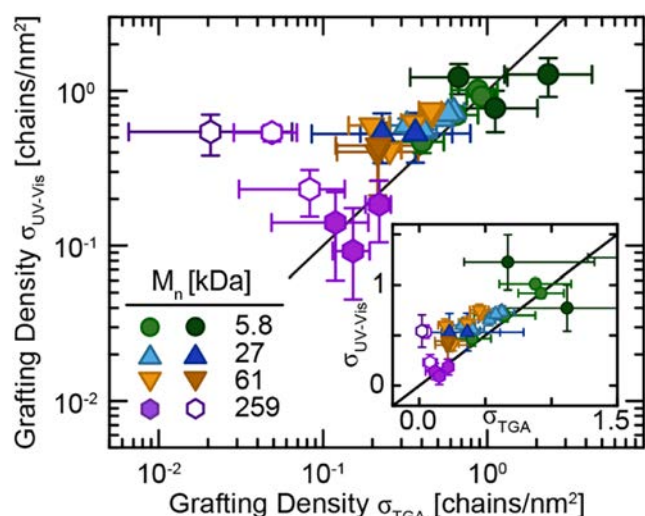


Figure 6. Comparison of  $\sigma$  obtained from the UV-vis method and traditional TGA. Light- and dark-colored symbols represent PGNPs with  $R_{NP} = 7$  and  $31$  nm, respectively. The solid line  $y = x$  represents perfect quantitative agreement between the two methods. Open symbols represent experimental conditions that do not satisfy the assumptions of our model. Inset: The same comparison of  $\sigma$  obtained through both methods, plotted on a linear scale.

7). The optical sensitivity of PGNPs is governed by the decay length  $L$ , and our model assumes that the polymer maintains a cylindrical structure over this length scale. If the crossover radius  $R_c$  between SDPB and CPB is smaller than  $R_{NP} + L$ , however, the cylindrical chain approximation no longer holds because the chains adopt an SDPB structure near the particle surface.<sup>19,75</sup> With this more coiled structure, the polymer chain

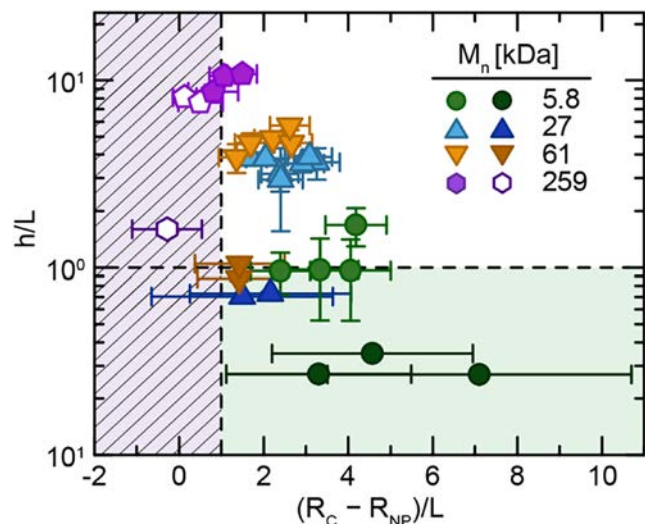


Figure 7. State diagram identifying regions in which UV-vis provides accurate estimates of  $\sigma$ . Light- and dark-colored symbols represent PGNPs with  $R_{NP} = 7$  and  $31$  nm, respectively. Normalized polymer thickness  $h/L$  as a function of the normalized distance between the crossover radius and nanoparticle core size  $(R_c - R_{NP})/L$  for PGNPs with varying  $M_n$ . The green shaded region indicates when the piecewise description of  $n_{eff}$  becomes important. The purple cross-hatched region indicates when the polymer can no longer be accurately approximated through a cylindrical assumption, resulting in overestimates of  $\sigma$ .

will pass through a differential shell at a distance  $z$  from the particle surface multiple times, thereby contributing multiplicatively to the local dielectric properties. To explicitly identify this limit to our analytical approximation, we construct a state diagram using the TGA measurements of  $\sigma$  (Figure 7). We find that the deviating data points lie in the region in which  $(R_c - R_{NP})/L < 1$ , indicating that for these PGNPs, the SDPB transition occurs within the electromagnetic field decay length  $L$ . This state diagram therefore confirms the limits of our analytical approach in determining low grafting densities where the grafted polymer structure can no longer be reasonably described through the cylindrical approximation. Additionally, the state diagram identifies a second region in which the grafted layer thickness  $h$  is smaller than  $L$ . In this region, the pure solvent mixture beyond the grafted layer would contribute significantly to the peak shift. For the samples within this region, the UV-vis method remains in good quantitative agreement with TGA because the piecewise description of the polymer density profile  $\varphi(z)$  in eq 3 accurately captures the optical properties of the neat solvent beyond the polymer shell.

We end by noting that the choice of solvents used to vary  $n$  is critical for quantitative determination of  $\sigma$ . Because changes in solvent quality will change the conformation of the grafted polymer chains, it is imperative to maintain solvent quality while changing  $n$ . For solvent mixtures in which both are good solvents for the grafted polymer, such as THF-toluene and THF-anisole, we find nearly identical RIS values for PGNPs of both sizes. By contrast, when a mixture is formed by one good solvent and one  $\theta$ -solvent, such as 2-butanone,<sup>76,77</sup> we measure a significantly lower RIS (Supporting Information). We attribute this difference to conformational changes in the grafted polymer corona as we vary the solvent composition. DLS measurements of PGNPs in four different solvents support this interpretation, showing a smaller hydrodynamic size in 2-butanone than in the good solvents (Supporting Information). This reduction in hydrodynamic size in 2-butanone indicates that polymer chains are more contracted, invalidating the cylindrical polymer approximation, and therefore overestimating  $\sigma$ . These results highlight the importance of using solvent mixtures that maintain good-solvent conditions to minimize changes in polymer conformation during characterization.

### 3. CONCLUSION

In this work, we introduce a nondestructive method to measure polymer grafting density  $\sigma$  from the optical response of plasmonic nanoparticles. This method accurately quantifies  $\sigma$  across orders of magnitude in polymer  $M_n$ , an order of magnitude in  $\sigma$ , and across multiple AuNP core sizes, in excellent agreement with standard TGA measurements. Our approach assumes that the polymer maintains an approximately cylindrical conformation across the electromagnetic decay length around the particle. If the polymer transitions into the SDPB regime and adopts a more coil-like conformation, our model overestimates  $\sigma$ . Additionally, our model requires good solvent quality across the studied refractive index range to achieve quantitatively accurate estimates. Despite these minor limitations, our optical method provides a new framework for determining  $\sigma$  on plasmonic nanoparticles, offering an affordable and straightforward alternative to conventional techniques. Notably, this method uses non-destructive technology widely available in most facilities that work with plasmonic nanoparticles. Unlike conventional

techniques such as TGA, NMR, or ellipsometry, this approach does not require polymer cleavage to determine polymer  $M_n$ , specialized instrumentation, or large sample quantities, and instead preserves the sample for further characterization and applications.

To facilitate reproducibility and broader use by the plasmonic nanoparticle community, the model and analysis code developed in this paper are made openly available.<sup>78</sup> The model takes as input the LSPR peak positions  $\lambda_{\max}$  for PGNPs measured across solvents of known refractive index  $n_{\text{solvent}}$ , the polymer shell thickness  $h$ , and key physical parameters including nanoparticle radius  $R_{\text{NP}}$ , decay length  $L$ , cross sectional polymer diameter  $b$ , and polymer refractive index  $n_{\text{poly}}$ . From these inputs, the code constructs the spatial polymer density profile  $\varphi(z)$ , converts it to a refractive index profile  $n(z)$ , and computes an effective refractive index  $n_{\text{eff}}$  using near-field weighting. The  $\sigma$  is obtained by iteratively matching the calculated RIS as a function of  $n_{\text{eff}}$  to the RIS of the nanoparticle core. This approach allows users to extract quantitative estimates of  $\sigma$  directly from routine UV–vis data, providing a rapid and nondestructive alternative to conventional methods.

## 4. MATERIALS AND METHODS

### 4.1. Materials

Sodium citrate tribasic dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ , 99%), gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.9%), silver nitrate ( $\text{AgNO}_3$ , 99%), tris(hydroxymethyl)aminomethane ( $((\text{HOCH}_2)_3\text{CNH}_2$ , 99.9%), glycerol (99.5%), anisole (99%), and 2-butanone (99%) were purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, 99.8%), tetrahydrofuran (THF, 99.0%) and toluene (99.5%) were obtained from VWR, Inc. Thiol-terminated polystyrene (PS-SH) with number-average molecular weight  $M_n$  of 5.8 kDa (dispersity  $\text{Đ} = M_w/M_n = 1.1$ ), 27 kDa ( $\text{Đ} = 1.07$ ), 61 kDa ( $\text{Đ} = 1.08$ ), and 259 kDa ( $\text{Đ} = 1.11$ ) was purchased from Polymer Source and denoted as PS5.8, PS27, PS61, and PS259, respectively. Ultrapure water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ) was obtained from a Millipore Direct-Q5 UV-R system.

### 4.2. Synthesis and Functionalization of Gold Nanoparticles (AuNPs)

AuNPs with an average radius of  $R_{\text{NP}} = 7 \pm 1 \text{ nm}$  were synthesized using a modified Turkevich method<sup>79,80</sup> according to our previously reported protocol.<sup>42</sup> Briefly, an aqueous solution of gold(III) chloride was reduced with sodium citrate while stirring at  $95^\circ\text{C}$ , resulting in an aqueous suspension of stable AuNPs. AuNPs with an average radius of  $R_{\text{NP}} = 31 \pm 4 \text{ nm}$  were synthesized using the Tris-assisted premixing method.<sup>81</sup> Briefly, aqueous solutions of gold(III) chloride, sodium citrate, and silver nitrate were premixed at room temperature using a citrate-to-gold molar ratio of 1.1. After 4 min of premixing, the solution was added to boiling water containing Tris under vigorous stirring. The final concentrations of gold(III) chloride, citrate, silver ion, and Tris in the reaction mixture were 0.25 mM, 0.27 mM, 5.05  $\mu\text{M}$ , and 4 mM, respectively. Representative TEM images and the corresponding extinction spectrum of these larger AuNPs are provided in the Supporting Information.

AuNPs of both core sizes were functionalized with PS-SH by transferring dropwise into a DMF solution with varying amounts of PS-SH. This suspension was allowed to react under strong stirring at room temperature for 24 h.<sup>42</sup> The PS-SH concentration serves as a key parameter for tuning the  $\sigma$  at each  $M_n$ . The functionalized PGNPs were purified twice by repeated centrifugation–redispersion cycles in THF to remove unreacted polymer chains.

### 4.3. Transmission Electron Microscopy (TEM)

PGNPs were diluted in THF, pipetted directly onto Formvar/carbon-coated 400-mesh copper grids (Electron Microscopy Sciences), and allowed to dry under ambient conditions. PGNP nanostructures were

then analyzed using transmission electron microscopy (TEM, JEOL JEM-F200) at an accelerating voltage of 200 kV. The TEM images were segmented based on pixel intensity using ImageJ<sup>82</sup> to identify individual particles and quantify particle size. Particle size  $R_{\text{NP}}$  is determined from the major Feret diameter of the segmented areas.

### 4.4. Thermal Gravimetric Analysis (TGA)

PGNPs suspended in THF ( $\sim 3.5 \mu\text{L}$ ) were carefully pipetted onto a clean platinum pan and subsequently dried in a vacuum oven to facilitate solvent evaporation, resulting in approximately 1 mg of dried PGNPs. TGA was then performed using a TA Instruments TGA 55 under a nitrogen flow of  $25 \text{ mL min}^{-1}$ . Samples were heated from ambient temperature to  $600^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$ . The polymer  $\sigma$  was calculated according to

$$\sigma_{\text{TGA}} = \frac{m_{\text{polymer}} \rho_{\text{NP}} R_{\text{NP}} N_A}{m_{\text{NP}} 3M_n} \quad (6)$$

where  $m_{\text{polymer}}$  and  $m_{\text{NP}}$  are the polymer and AuNP core masses respectively,  $\rho_{\text{NP}}$  is the core mass density, and  $N_A$  is Avogadro's number.<sup>19,83</sup> The  $m_{\text{polymer}}$  was determined by the mass loss at  $280^\circ\text{C}$  to eliminate any contributions from residual THF and thiol ligands. The  $m_{\text{NP}}$  was determined by the remaining mass at  $600^\circ\text{C}$ .

### 4.5. UV–Visible (UV–Vis) Spectroscopy

UV–vis extinction spectra of PGNP suspensions at low concentrations ( $0.02\text{--}0.04 \text{ mg mL}^{-1}$ ) were acquired using a Shimadzu UV-2600i spectrophotometer at a scanning rate of  $225 \text{ nm min}^{-1}$  over a range of 400 to 900 nm. All measurements were performed at a constant temperature of  $25^\circ\text{C}$  in glass cuvettes with a 1 cm optical path length. The dielectric environment surrounding the particles was varied by preparing solvent mixtures with distinct refractive indices. For bare AuNPs, water–glycerol mixtures were used to span a refractive index range of 1.3342 to 1.4400. For PGNPs, mixtures of THF and toluene were used to achieve refractive indices ranging from 1.4116 to 1.5027. The refractive index of each mixture was calculated using the volume fractions and refractive indices of the pure solvents based on the Lorentz–Lorenz equation,<sup>69,84,85</sup> The LSPR peak wavelength  $\lambda_{\max}$  was quantified from the extinction spectra by fitting the data to a Gaussian peak function.

### 4.6. Dynamic Light Scattering (DLS)

DLS analysis was performed on PGNP samples in good solvents (THF) to measure the hydrodynamic radius  $R_H$  at room temperature using a Brookhaven BI-200SM instrument with a wavelength of  $\lambda = 640 \text{ nm}$ , and a 40 mW diode laser as the light source. All measurements were conducted at a  $90^\circ$  scattering angle to measure the scattered light intensity at  $25^\circ\text{C}$ . The intensity autocorrelation function  $G_2$  was fit to a single stretched exponential function given by

$$G_2(q, \tau) = A + B \exp[-(\Gamma\tau)^\beta] \quad (7)$$

where  $\tau$  is the delay time,  $\Gamma$  is the relaxation rate, and  $\beta$  is a stretching exponent.  $A$  and  $B$  are constants that characterize the signal noise at long times and the signal amplitude at short times, respectively. The PGNP diffusivity was then obtained by  $D = \Gamma/q^2$ , where  $q = 4\pi n \sin(\theta/2)/\lambda$  is the wavevector, and  $n$  is the index of refraction of THF. The corresponding hydrodynamic radius  $R_H$  was calculated by applying the Stokes–Einstein equation  $R_H = k_B T / 6\pi \eta D$  where  $\eta$  is the temperature-dependent solvent viscosity with values of 0.46 mPa  $\cdot$  s for THF and 0.89 mPa  $\cdot$  s for water at  $25^\circ\text{C}$ ,  $T$  is the temperature, and  $k_B$  is the Boltzmann constant.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.6c11390>.

Details of the characterization of the large core PGNPs, the effect of different solvent qualities, experimental determination of the refractive-index sensitivity of

AuNPs, the Mie-theory prediction of the refractive-index sensitivity of AuNPs, and the electromagnetic near-field decay-length calculation are provided (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

**Irene Andreu** – Department of Chemical, Biomolecular, and Materials Engineering, University of Rhode Island, Kingston, Rhode Island 02881, United States; [orcid.org/0000-0001-7689-2269](https://orcid.org/0000-0001-7689-2269); Email: [iandreu@uri.edu](mailto:iandreu@uri.edu)

**Ryan Poling-Skutvik** – Department of Chemical, Biomolecular, and Materials Engineering, University of Rhode Island, Kingston, Rhode Island 02881, United States; [orcid.org/0000-0002-1614-1647](https://orcid.org/0000-0002-1614-1647); Email: [ryanps@uri.edu](mailto:ryanps@uri.edu)

### Author

**Masoud Abdi** – Department of Chemical, Biomolecular, and Materials Engineering, University of Rhode Island, Kingston, Rhode Island 02881, United States; [orcid.org/0009-0005-8047-7451](https://orcid.org/0009-0005-8047-7451)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsnano.6c11390>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank Dr. Sumanta Das for access to the TGA instrument. We also thank Dr. Benjamin McDonald and Hana Tabit for conducting GPC measurements of polymer molecular weights. This work was partially supported by grants CBET-2339052 (R.P.-S.) and CBET-2301790 (I.A.) from the National Science Foundation and Cottrell Scholar Award #CS-CSA-2025-033 from Research Corporation for Science Advancement (R. P.-S.). TEM data were acquired at the RI Consortium for Nanoscience and Nanotechnology, a URI College of Engineering core facility, and was supported by the National Science Foundation Major Research Instrumentation grant #1919588.

## REFERENCES

- (1) Palani, S.; Kenison, J. P.; Sabuncu, S.; Huang, T.; Civitci, F.; Esener, S.; Nan, X. Multispectral Localized Surface Plasmon Resonance (msLSPR) Reveals and Overcomes Spectral and Sensing Heterogeneities of Single Gold Nanoparticles. *ACS Nano* **2023**, *17*, 2266–2278.
- (2) Nusz, G. J.; Curry, A. C.; Marinakos, S. M.; Wax, A.; Chilkoti, A. Rational Selection of Gold Nanorod Geometry for Label-Free Plasmonic Biosensors. *ACS Nano* **2009**, *3*, 795–806.
- (3) Luo, Y.-L.; Shiao, Y.-S.; Huang, Y.-F. Release of Photoactivatable Drugs from Plasmonic Nanoparticles for Targeted Cancer Therapy. *ACS Nano* **2011**, *5*, 7796–7804.
- (4) Skinner, W. H.; Salimi, M.; Moran, L.; Blein-Dezayes, I.; Mehta, M.; Mosca, S.; Vaideanu, A.-G.; Gardner, B.; Palombo, F.; Schätzlein, A. G.; Matousek, P.; Harries, T.; Stone, N. Plasmonic Nanoparticles for Photothermal Therapy: Benchmarking of Photothermal Properties and Modeling of Heating at Depth in Human Tissues. *J. Phys. Chem. C* **2025**, *129*, 1864–1872.
- (5) Yang, J.; You, J.; Chen, C.-C.; Hsu, W.-C.; Tan, H.-R.; Zhang, X. W.; Hong, Z.; Yang, Y. Plasmonic Polymer Tandem Solar Cell. *ACS Nano* **2011**, *5*, 6210–6217.
- (6) Cortés, E.; Besteiro, L. V.; Alabastri, A.; Baldi, A.; Tagliabue, G.; Demetriadou, A.; Narang, P. Challenges in Plasmonic Catalysis. *ACS Nano* **2020**, *14*, 16202–16219.
- (7) Mantri, Y.; Jokerst, J. V. Engineering Plasmonic Nanoparticles for Enhanced Photoacoustic Imaging. *ACS Nano* **2020**, *14*, 9408–9422.
- (8) Nadeem, A.; Rahmani, M.; Wang, Y.; Yari, S.; Lopez, R. M.; Kim, M.; Roxbury, D. Spectral Fingerprinting of Engineered Nanomaterials for Precision Biosensing. *ACS Nano* **2026**, *20*, 3921–3943.
- (9) Langer, J.; Jimenez de Aberasturi, D.; Aizpurua, J.; Alvarez-Puebla, R. A.; Auguie, B.; Baumberg, J. J.; Bazan, G. C.; Bell, S. E. J.; Boisen, A.; Brolo, A. G.; Choo, J.; Cialla-May, D.; Deckert, V.; Fabris, L.; Faulds, K.; García de Abajo, F. J.; Goodacre, R.; Graham, D.; Haes, A. J.; Haynes, C. L.; et al. Present and Future of Surface-Enhanced Raman Scattering. *ACS Nano* **2020**, *14*, 28–117.
- (10) Kaur, K.; Forrest, J. A. Influence of Particle Size on the Binding Activity of Proteins Adsorbed onto Gold Nanoparticles. *Langmuir* **2012**, *28*, 2736–2744.
- (11) Englebienne, P.; Van Hoonacker, A.; Verhas, M. High-Throughput Screening Using the Surface Plasmon Resonance Effect of Colloidal Gold Nanoparticles. *Analyst* **2001**, *126*, 1645–1651.
- (12) Englebienne, P. Use of Colloidal Gold Surface Plasmon Resonance Peak Shift to Infer Affinity Constants from the Interactions between Protein Antigens and Antibodies Specific for Single or Multiple Epitopes. *Analyst* **1998**, *123*, 1599–1603.
- (13) Dileseigres, A. S.; Prado, Y.; Pluchery, O. How to Use Localized Surface Plasmon for Monitoring the Adsorption of Thiol Molecules on Gold Nanoparticles? *Nanomaterials* **2022**, *12*, 292.
- (14) Liu, L.; Legg, B. A.; Smith, W.; Anovitz, L. M.; Zhang, X.; Harper, R.; Pearce, C. I.; Rosso, K. M.; Stack, A. G.; Bleuel, M.; Mildner, D. F. R.; Schenter, G. K.; Clark, A. E.; De Yoreo, J. J.; Chun, J.; Nakouzi, E. Predicting Outcomes of Nanoparticle Attachment by Connecting Atomistic, Interfacial, Particle, and Aggregate Scales. *ACS Nano* **2023**, *17*, 15556–15567.
- (15) Hassan, S. A. Computational Study of the Forces Driving Aggregation of Ultrasmall Nanoparticles in Biological Fluids. *ACS Nano* **2017**, *11*, 4145–4154.
- (16) Gillich, T.; Acikgöz, C.; Isa, L.; Schlüter, A. D.; Spencer, N. D.; Textor, M. PEG-Stabilized Core–Shell Nanoparticles: Impact of Linear versus Dendritic Polymer Shell Architecture on Colloidal Properties and the Reversibility of Temperature-Induced Aggregation. *ACS Nano* **2013**, *7*, 316–329.
- (17) Grzelczak, M.; Vermant, J.; Furst, E. M.; Liz-Marzán, L. M. Directed Self-Assembly of Nanoparticles. *ACS Nano* **2010**, *4*, 3591–3605.
- (18) Lin, H.; Singh, M.; Musard, K. K.; Kumar, S. K.; Benicewicz, B. C. Particle Dispersion Controls the Gas-Separation Properties of Polymer-Grafted Nanoparticle Membranes. *ACS Macro Lett.* **2025**, *14*, 872–877.
- (19) Chancellor, A. J.; Seymour, B. T.; Zhao, B. Characterizing Polymer-Grafted Nanoparticles: From Basic Defining Parameters to Behavior in Solvents and Self-Assembled Structures. *Anal. Chem.* **2019**, *91*, 6391–6402.
- (20) Xu, M.; Tan, Z.; Baek, G.; Stein, G. E.; Yun, H.; Kim, B. J. 3D Assembly of Polymer-Grafted Nanoparticles: Soft Confinement for Structural Diversity. *Macromolecules* **2025**, *58*, 2178–2191.
- (21) LaNasa, J. A.; Hickey, R. J. Surface-Initiated Ring-Opening Metathesis Polymerization: A Method for Synthesizing Polymer-Functionalized Nanoparticles Exhibiting Semicrystalline Properties and Diverse Macromolecular Architectures. *Macromolecules* **2020**, *53*, 8216–8232.
- (22) Kang, M.; Lin, P.-A.; Bunch, J. A.; Lipomi, D. J.; Arya, G.; Cohen, S. M. Impact of Grafting Density on the Assembly and Mechanical Properties of Self-Assembled Metal–Organic Framework Monolayers. *J. Am. Chem. Soc.* **2025**, *147*, 6966–6973.
- (23) Wen, X.; Su, Y.; Shui, Y.; Zhao, W.; Müller, A. J.; Wang, D. Correlation between Grafting Density and Confined Crystallization Behavior of Poly(Ethylene Glycol) Grafted to Silica. *Macromolecules* **2019**, *52*, 1505–1516.

- (24) Barcus, K.; Lin, P.-A.; Zhou, Y.; Arya, G.; Cohen, S. M. Influence of Polymer Characteristics on the Self-Assembly of Polymer-Grafted Metal–Organic Framework Particles. *ACS Nano* **2022**, *16*, 18168–18177.
- (25) Shen, X.; He, H.; Zheng, D.; Cao, W.; Sang, Y.; Nie, Z. Engineering the Electrostatic Interactions between Oppositely Charged Polymer-Grafted Nanoparticles for Constructing Colloid Molecules on Substrates. *ACS Nano* **2024**, *18*, 20999–21008.
- (26) Kubiak, J. M.; Li, B.; Suazo, M.; Macfarlane, R. J. Polymer Grafted Nanoparticle Composites with Enhanced Thermal and Mechanical Properties. *ACS Appl. Mater. Interfaces* **2022**, *14*, 21535–21543.
- (27) Tawade, B. V.; Singh, M.; Apatha, I. E.; Veerasamy, J.; Pradhan, N.; Karim, A.; Douglas, J. F.; Raghavan, D. Polymer-Grafted Nanoparticles with Variable Grafting Densities for High Energy Density Polymeric Nanocomposite Dielectric Capacitors. *JACS Au* **2023**, *3*, 1365–1375.
- (28) Babu, K.; Dhamodharan, R. Synthesis of Polymer Grafted Magnetite Nanoparticle with the Highest Grafting Density via Controlled Radical Polymerization. *Nanoscale Res. Lett.* **2009**, *4*, 1090.
- (29) Chávez, M.; Sánchez-Obrero, G.; Madueño, R.; Sevilla, J. M.; Blázquez, M.; Pineda, T. Electrochemical Evaluation of the Grafting Density of Self-Assembled Monolayers of Polyethylene Glycol of Different Chain Lengths Formed by the Grafting to Approach under Conditions Close to the Cloud Point. *J. Electroanal. Chem.* **2022**, *913*, 116294.
- (30) Porter, C. J.; Werber, J. R.; Ritt, C. L.; Guan, Y.-F.; Zhong, M.; Elimelech, M. Controlled Grafting of Polymer Brush Layers from Porous Cellulosic Membranes. *J. Membr. Sci.* **2020**, *596*, 117719.
- (31) Benoit, D. N.; Zhu, H.; Lilierose, M. H.; Verm, R. A.; Ali, N.; Morrison, A. N.; Fortner, J. D.; Avendano, C.; Colvin, V. L. Measuring the Grafting Density of Nanoparticles in Solution by Analytical Ultracentrifugation and Total Organic Carbon Analysis. *Anal. Chem.* **2012**, *84*, 9238–9245.
- (32) Zhou, H.; Fan, Z.; Li, P. Y.; Deng, J.; Arhontoulis, D. C.; Li, C. Y.; Bowne, W. B.; Cheng, H. Dense and Dynamic Polyethylene Glycol Shells Cloak Nanoparticles from Uptake by Liver Endothelial Cells for Long Blood Circulation. *ACS Nano* **2018**, *12*, 10130–10141.
- (33) Niwa, R.; Aoki, D.; Taniguchi, T. Controlled Grafting Density of Zwitterionic Polymer Brushes for Enhanced Antifouling Properties of Polymer Particles. *Langmuir* **2025**, *41*, 27957–27967.
- (34) Li, X.; Liu, Y.; Wong, N. E. C.; Winnik, M. NMR Studies of PEG Chain Dynamics on Mesoporous Silica Nanoparticles for Minimizing Non-Specific Binding. *Nanoscale* **2025**, *17*, 14759–14771.
- (35) Hofmaier, M.; Flemming, P.; Guskova, O.; Münch, A. S.; Uhlmann, P.; Müller, M. Swelling and Orientation Behavior of End-Grafted Polymer Chains by In Situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy Complementing In Situ Ellipsometry. *Langmuir* **2023**, *39*, 16219–16230.
- (36) Sakulaue, P.; Lertvanithphol, T.; Eiamchai, P.; Siriawatwechakul, W. Quantitative Relation between Thickness and Grafting Density of Temperature-Responsive Poly(N-isopropylacrylamide-co-acrylamide) Thin Film Using Synchrotron-Source ATR-FTIR and Spectroscopic Ellipsometry. *Surf. Interface Anal.* **2021**, *53*, 268–276.
- (37) Dokukin, M. E.; Kuroki, H.; Minko, S.; Sokolov, I. AFM Study of Polymer Brush Grafted to Deformable Surfaces: Quantitative Properties of the Brush and Substrate Mechanics. *Macromolecules* **2017**, *50*, 275–282.
- (38) Csányi, E.; Hammond, D. B.; Bower, B.; Johnson, E. C.; Lishchuk, A.; Armes, S. P.; Dong, Z.; Leggett, G. J. XPS Depth-Profiling Studies of Chlorophyll Binding to Poly(Cysteine Methacrylate) Scaffolds in Pigment–Polymer Antenna Complexes Using a Gas Cluster Ion Source. *Langmuir* **2024**, *40*, 14527–14539.
- (39) Gibson, M. I.; Danial, M.; Klok, H.-A. Sequentially Modified, Polymer-Stabilized Gold Nanoparticle Libraries: Convergent Synthesis and Aggregation Behavior. *ACS Comb. Sci.* **2011**, *13*, 286–297.
- (40) Wei, Y.; Xu, Y.; Faraone, A.; Hore, M. J. A. Local Structure and Relaxation Dynamics in the Brush of Polymer-Grafted Silica Nanoparticles. *ACS Macro Lett.* **2018**, *7*, 699–704.
- (41) Midya, J.; Rubinstein, M.; Kumar, S. K.; Nikoubashman, A. Structure of Polymer-Grafted Nanoparticle Melts. *ACS Nano* **2020**, *14*, 15505–15516.
- (42) Abdi, M.; Amirsadri, D.; Andreu, I.; Poling-Skutvik, R. Stability and Anomalous Aggregation in Suspensions of Polymer-Grafted Nanoparticles. *Macromolecules* **2025**, *58*, 12154–12162.
- (43) Dong, A.; Zhang, Q.; Wang, T.; Wang, W.; Liu, F.; Gao, G. Immobilization of Cyclic N -Halamine on Polystyrene-Functionalized Silica Nanoparticles: Synthesis, Characterization, and Biocidal Activity. *J. Phys. Chem. C* **2010**, *114*, 17298–17303.
- (44) Lee, S. W.; Jeong, S.-J.; Hidajat, M. J.; Kim, B.-S.; Hwang, D. W.; Yun, G.-N. Sustainable Chemical Recycling of Waste Polystyrene via Catalytic Pyrolysis over Waste Shell-Derived Calcium Oxide Catalysts. *ACS Omega* **2025**, *10*, 51406–51418.
- (45) Zawada, K.; Tomaszewski, W.; Megiel, E. A Smart Synthesis of Gold/Polystyrene Core–Shell Nanohybrids Using TEMPO Coated Nanoparticles. *RSC Adv.* **2014**, *4*, 23876–23885.
- (46) Izor, S.; Schantz, A.; Jawaid, A.; Grabowski, C.; Dagher, T.; Koerner, H.; Park, K.; Vaia, R. Coexistence and Phase Behavior of Solvent–Polystyrene-Grafted Gold Nanoparticle Systems. *Macromolecules* **2021**, *54*, 10435–10446.
- (47) Mie, G. Beiträge Zur Optik Trüber Medien, Speziell Kolloidaler Metallösungen. *Ann. Phys.* **1908**, *330*, 377–445.
- (48) Khoury, C. G.; Norton, S. J.; Vo-Dinh, T. Plasmonics of 3-D Nanoshell Dimers Using Multipole Expansion and Finite Element Method. *ACS Nano* **2009**, *3*, 2776–2788.
- (49) Lermé, J.; Bonnet, C.; Lebeault, M.-A.; Pellarin, M.; Cottancin, E. Surface Plasmon Resonance Damping in Spheroidal Metal Particles: Quantum Confinement, Shape, and Polarization Dependences. *J. Phys. Chem. C* **2017**, *121*, 5693–5708.
- (50) Laven, P. Simulation of Rainbows, Coronas and Glories Using Mie Theory and the Debye Series. *J. Quant. Spectrosc. Radiat. Transfer* **2004**, *89*, 257–269.
- (51) Laven, P. MiePlot: A Computer Program for Scattering of Light from a Sphere Using Mie Theory. <http://www.philiplaven.com/mieplot.htm> (accessed 15 April 2026).
- (52) McPeak, K. M.; Jayanti, S. V.; Kress, S. J. P.; Meyer, S.; Iotti, S.; Rossinelli, A.; Norris, D. J. Plasmonic Films Can Easily Be Better: Rules and Recipes. *ACS Photonics* **2015**, *2*, 326–333.
- (53) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J. Phys. Chem. B* **2003**, *107*, 668–677.
- (54) Jain, P. K.; Huang, W.; El-Sayed, M. A. On the Universal Scaling Behavior of the Distance Decay of Plasmon Coupling in Metal Nanoparticle Pairs: A Plasmon Ruler Equation. *Nano Lett.* **2007**, *7*, 2080–2088.
- (55) Jung, L. S.; Campbell, C. T.; Chinowsky, T. M.; Mar, M. N.; Yee, S. S. Quantitative Interpretation of the Response of Surface Plasmon Resonance Sensors to Adsorbed Films. *Langmuir* **1998**, *14*, 5636–5648.
- (56) Bukasov, R.; Ali, T. A.; Nordlander, P.; Shumaker-Parry, J. S. Probing the Plasmonic Near-Field of Gold Nanocrescent Antennas. *ACS Nano* **2010**, *4*, 6639–6650.
- (57) Chen, H.; Kou, X.; Yang, Z.; Ni, W.; Wang, J. Shape- and Size-Dependent Refractive Index Sensitivity of Gold Nanoparticles. *Langmuir* **2008**, *24*, 5233–5237.
- (58) Bonyár, A. Label-Free Nucleic Acid Biosensing Using Nanomaterial-Based Localized Surface Plasmon Resonance Imaging: A Review. *ACS Appl. Nano Mater.* **2020**, *3*, 8506–8521.
- (59) Wang, C.; Zhao, H. Polymer Brushes and Surface Nanostructures: Molecular Design, Precise Synthesis, and Self-Assembly. *Langmuir* **2024**, *40*, 2439–2464.
- (60) Li, T.-H.; Yadav, V.; Conrad, J. C.; Robertson, M. L. Effect of Dispersity on the Conformation of Spherical Polymer Brushes. *ACS Macro Lett.* **2021**, *10*, 518–524.
- (61) Wei, Y.; Chen, Q.; Zhao, H.; Duan, P.; Zhang, L.; Liu, J. Conformation and Dynamics along the Chain Contours of Polymer-Grafted Nanoparticles. *Langmuir* **2023**, *39*, 11003–11015.

- (62) Yun, H.; Lee, Y. J.; Xu, M.; Lee, D. C.; Stein, G. E.; Kim, B. J. Softness- and Size-Dependent Packing Symmetries of Polymer-Grafted Nanoparticles. *ACS Nano* **2020**, *14*, 9644–9651.
- (63) Ohno, K.; Morinaga, T.; Takeno, S.; Tsujii, Y.; Fukuda, T. Suspensions of Silica Particles Grafted with Concentrated Polymer Brush: Effects of Graft Chain Length on Brush Layer Thickness and Colloidal Crystallization. *Macromolecules* **2007**, *40*, 9143–9150.
- (64) Mukherjee, S.; Liesen, N. T.; Milner, S. T.; Hall, L. M.; DeLongchamp, D. M. Reconciling Chain Orientation in Polymer-Grafted Nanoparticles between Coarse-Grained Models and Resonant Soft X-ray Scattering. *ACS Nano* **2025**, *19*, 15638–15650.
- (65) Kotkar, S. B.; Howard, M. P.; Nikoubashman, A.; Conrad, J. C.; Poling-Skutvik, R.; Palmer, J. C. Confined Dynamics in Spherical Polymer Brushes. *ACS Macro Lett.* **2023**, *12*, 1503–1509.
- (66) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: Oxford, NY, 2003.
- (67) Privalko, V. P. Chain Thickness and Polymer Conformation in the Crystalline State. *Macromolecules* **1980**, *13*, 370–372.
- (68) Tagliazucchi, M.; Blaber, M. G.; Schatz, G. C.; Weiss, E. A.; Szleifer, I. Optical Properties of Responsive Hybrid Au@Polymer Nanoparticles. *ACS Nano* **2012**, *6*, 8397–8406.
- (69) Lorentz, H. A. *The Theory of Electrons and Its Applications to the Phenomena of Light and Radiant Heat*; G. E. Stechert & Co.; B. G. Teubner: New York; Leipzig, 1916.
- (70) McGrory, M. R.; King, M. D.; Ward, A. D. Using Mie Scattering to Determine the Wavelength-Dependent Refractive Index of Polystyrene Beads with Changing Temperature. *J. Phys. Chem. A* **2020**, *124*, 9617–9625.
- (71) Miles, R. E. H.; Rudić, S.; Orr-Ewing, A. J.; Reid, J. P. Influence of Uncertainties in the Diameter and Refractive Index of Calibration Polystyrene Beads on the Retrieval of Aerosol Optical Properties Using Cavity Ring Down Spectroscopy. *J. Phys. Chem. A* **2010**, *114*, 7077–7084.
- (72) Yun, H.; Yu, J. W.; Lee, Y. J.; Kim, J.-S.; Park, C. H.; Nam, C.; Han, J.; Heo, T.-Y.; Choi, S.-H.; Lee, D. C.; Lee, W. B.; Stein, G. E.; Kim, B. J. Symmetry Transitions of Polymer-Grafted Nanoparticles: Grafting Density Effect. *Chem. Mater.* **2019**, *31*, 5264–5273.
- (73) Avdeev, M. M.; Shibaev, A. V.; Maslakov, K. I.; Dvoryak, S. V.; Lokshin, B. V.; Gorshkova, Y. E.; Tropin, T. V.; Philippova, O. E. Polymer Brushes Synthesized by the “Grafting-through” Approach: Characterization and Scaling Analysis. *Langmuir* **2024**, *40*, 23918–23929.
- (74) Murad Bhayo, A.; Yang, Y.; He, X. Polymer Brushes: Synthesis, Characterization, Properties and Applications. *Prog. Mater. Sci.* **2022**, *130*, 101000.
- (75) Conrad, J. C.; Robertson, M. L. Shaping the Structure and Response of Surface-Grafted Polymer Brushes via the Molecular Weight Distribution. *JACS Au* **2023**, *3*, 333–343.
- (76) Terao, K.; Morihana, N.; Ichikawa, H. Solution SAXS Measurements over a Wide Temperature Range to Determine the Unperturbed Chain Dimensions of Polystyrene and a Cyclic Amylose Derivative. *Polym. J.* **2014**, *46*, 155–159.
- (77) Lewis, M. E.; Nan, S.; Yunan, W.; Li, J.; Mays, J. W.; Hadjichristidis, N. Analysis of Solution Properties of Polystyrene in 2-Butanone in the Framework of the Hard-Sphere Model. *Macromolecules* **1991**, *24*, 6686–6689.
- (78) Abdi, M.; Poling-Skutvik, R.; Andreu, I. *GraftCal: A GUI Application for Optical Estimation of Polymer Grafting Density on Gold Nanoparticles*. <https://github.com/RPSLabURI/GraftCal> 2026. (accessed 19 September 2026).
- (79) Turkevich, J.; Stevenson, P. C.; Hillier, J. A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discuss. Faraday Soc.* **1951**, *11*, 55.
- (80) Oliveira, A. E. F.; Pereira, A. C.; Resende, M. A. C.; Ferreira, L. F. Gold Nanoparticles: A Didactic Step-by-Step of the Synthesis Using the Turkevich Method, Mechanisms, and Characterizations. *Analytica* **2023**, *4*, 250–263.
- (81) Xia, H.; Xiahou, Y.; Zhang, P.; Ding, W.; Wang, D. Revitalizing the Frens Method to Synthesize Uniform, Quasi-Spherical Gold Nanoparticles with Deliberately Regulated Sizes from 2 to 330 nm. *Langmuir* **2016**, *32*, 5870–5880.
- (82) Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W. NIH Image to ImageJ: 25 Years of Image Analysis. *Nat. Methods* **2012**, *9*, 671–675.
- (83) Yin, R.; Wu, H.; Hu, X.; Kim, K.; Lorandi, F.; D’hooge, D. R.; Benetti, E. M.; Bockstaller, M. R.; Matyjaszewski, K. Effect of Initiator Density, Catalyst Concentration, and Surface Curvature on the Uniformity of Polymers Grafted from Spherical Nanoparticles. *Macromolecules* **2026**, *59*, 689–701.
- (84) An, N.; Zhuang, B.; Li, M.; Lu, Y.; Wang, Z.-G. Combined Theoretical and Experimental Study of Refractive Indices of Water–Acetonitrile–Salt Systems. *J. Phys. Chem. B* **2015**, *119*, 10701–10709.
- (85) Heller, W. Remarks on Refractive Index Mixture Rules. *J. Phys. Chem.* **1965**, *69*, 1123–1129.