Supporting Information

for

Hydration of Spherical PEO-Grafted Gold Nanoparticles: Curvature and Grafting Density Effect

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MD simulation details: Force Field Parameters for Au-PEO and Au-water interactions. As the gold substrate is electrically neutral, the interaction between gold and PEO or water is dictated by the Lennard-Jones potential with parameters listed in Table S1.

Table S1: Lennard-Jones interaction parameters for gold atoms (Au), PEO atoms (Carbon-CP, Oxygen-OP, Hydrogen-HP) and water oxygen (OW).

Atoms	$\boldsymbol{\sigma}$ **(nm)**	$\boldsymbol{\epsilon}$ $(\boldsymbol{kJ/mol})$
Gold (Au)	0.2737	3.2290
PEO carbon (CP)	0.3500	0.2761
PEO oxygen (OP)	0.2900	0.5858
PEO hydrogen (HP)	0.2500	0.1255
Water Oxygen (OW)	0.3166	0.6502
Au-CP	0.3095	0.9443
Au-OP	0.2817	1.3753
Au-HP	0.2616	0.6366
Au-OW	0.2943	1.4490

For OPLS-based force fields as we used the intermolecular LJ interaction parameters are determined using geometrical average as shown in equation S1:

$$\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}} \text{ and } \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad \text{(S1)}$$

In Table S1, Au-CP represents gold and PEO carbon interaction, Au-OP represents gold and PEO oxygen interaction, Au-HP represents gold and PEO hydrogen interaction and Au-OW represents gold and water oxygen interactions.

Figure S1, shows the Lennard-Jones potential energy as functions of the distance between the interacting atoms obtained using the LJ parameters listed in table S1.

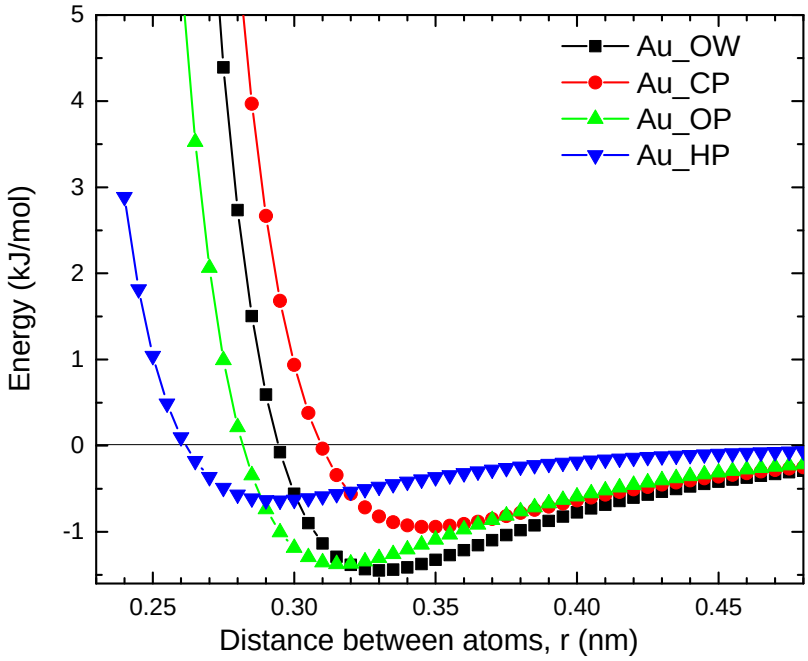

Figure S1: Lennard-Jones potential energy between gold (Au) and PEO atoms (carbon – CP, oxygen – OP, hydrogen –HP) as well as between gold and water oxygen (OW) as functions of the distance between atoms.

PEO volume fraction distribution for gold nanoparticles with R=1nm and R=3nm:

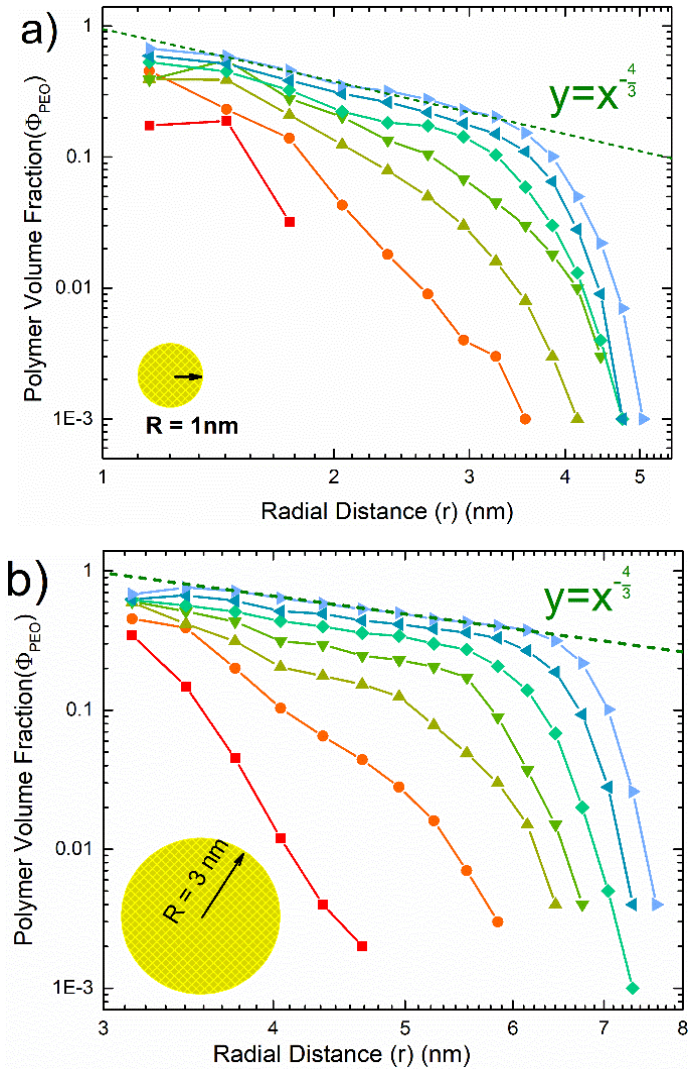

Figure S2: Log-log plot of PEO volume fractions as functions of radial distance from nanoparticle center, r, showing Daoud and Cotton scaling behavior (dashed lines) for gold nanoparticles of a) 1nm and b) 3nm in radius. Different symbols indicate the grafting density as in Figure 2 of the main text.

PEO aspect ratio and PEO chain orientation.

We calculated the average end-to-end distance for PEO in a spherical polymer brush attached to gold nanoparticles of different sizes at different grafting densities and calculated the ratio of this value to the end-to-end distance of PEO in aqueous solutions. The results are shown in Figure S3a.

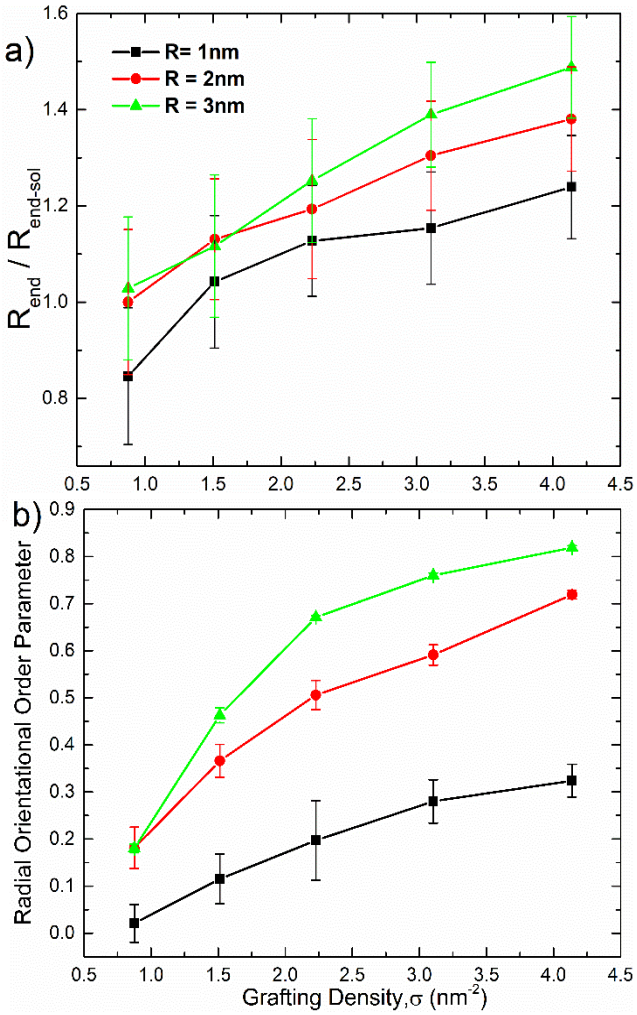

Figure S3: a) The ratio of the end-to-end distances (R_{end}) for PEO grafted to gold nanoparticles of 1nm, 2nm or 3nm in radius to that in homogeneous aqueous solution, characterizing the chain extension and b) the orientational order parameter for the end-to-end vector with respect to the radial direction as functions of grafting density σ.

To characterize chain orientation, we calculated the orientational order parameter of PEO end-to-end vector with respect to the radial direction (normal to spherical surface):

$$S = \frac{1}{2}\langle(3\,Cos^2\theta - 1)\rangle\,, \tag{S2}$$

where θ is the angle between the end-to-end vector of PEO chain and the radial direction from the center of gold nanoparticle to the grafting point of the chain. The orientational order parameter as a function of grafting density for gold nanoparticles of varying sizes is shown in Figure S3b.

Brush Height:

The average height for PEO chains grafted to gold nanoparticles can be obtained from the volume fraction profile Φ(r) (shown in Figure 2 and Figure S2) by calculating the second moment using the equation,

$$H^2 = \frac{\int r^2\,\Phi(r)\,(r-R_c)^2 dr}{\int r^2\,\Phi(r) dr} \tag{S3}$$

or can be estimated from the end-group distribution. Figure S4 shows in a logarithmic scale the spherical brush heights H for different nanoparticle sizes as functions of grafting density σ for five highest values of σ.

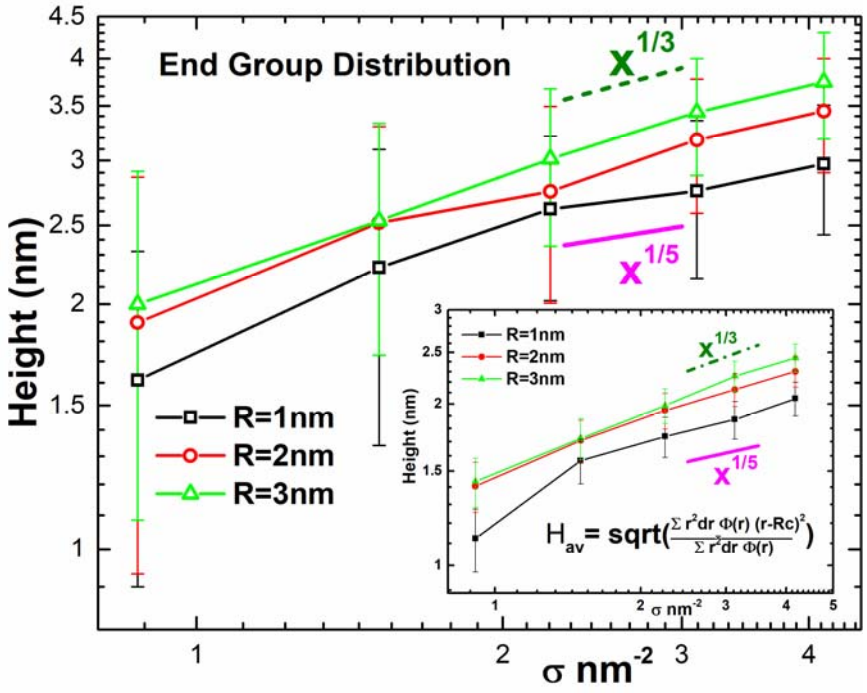

Figure S4: Log-log plot for the brush height obtained from the maximum of end-group distributions as a function of grafting density, σ, for gold nanoparticles of radii 1nm, 2nm and 3nm. The inset plot shows the average height of spherical PEO brush obtained using eq. S3 above as a function of polymer grafting density for gold nanoparticles of radius 1nm (squares), 2nm (circles) and 3nm (triangles). Slopes corresponding to the scaling dependences for spherical $H \sim \sigma^{1/5}$ and planar brushes $H \sim \sigma^{1/3}$ are shown. We note that at low grafting densities partial or complete polymer adsorption distorts the scaling.

Curvature dependence of PEO volume fraction at $\sigma = 1.5\ nm^{-2}$:

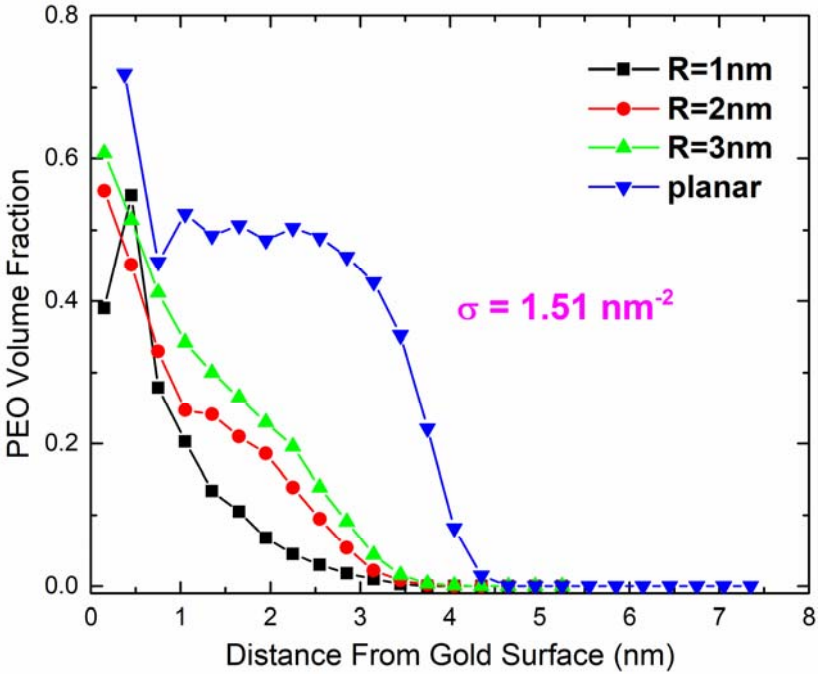

Figure S5: Polymer volume fraction as a function of radial distance from the nanoparticle surface for $\sigma = 1.5\ nm^{-2}$ for r=1nm, 2nm, 3nm and planar brush.

Curvature dependence of PEO hydration at $\sigma = 4.17\ nm^{-2}$

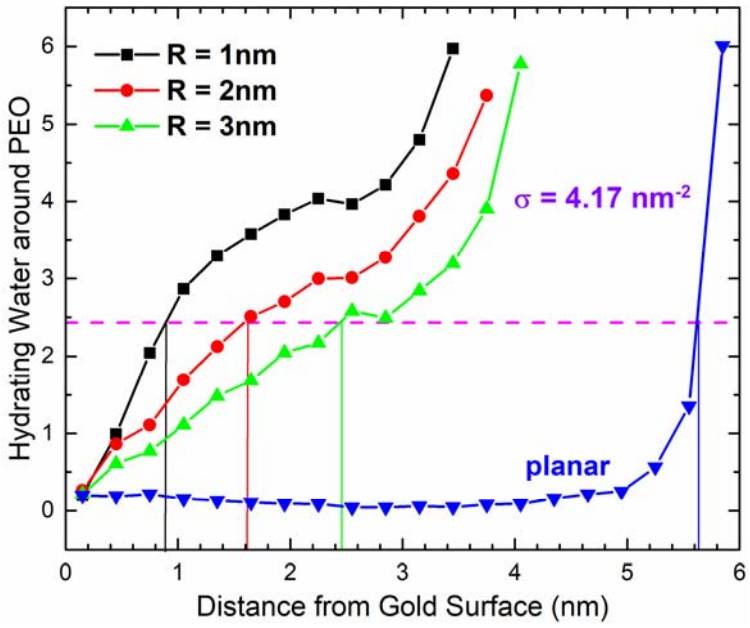

Figure S6: The average number of water molecules within 3.5 Å from the PEO backbone, hydration number, per repeat unit of PEO as a function of the distance from the surface of gold nanoparticles for radii 1nm, 2nm, 3nm and a planar surface for the highest grafting density $\sigma = 4.17\ nm^{-2}$. The horizontal dashed line at 2.5 indicates the boundary of low hydration zone (hydration number ≤2.5) and vertical lines show the dehydration zone thickness.