Structure and characterisation of hydroxyethylcellulose-decorated nanoparticles

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Figure SI1 Exemplar TEM images of nanoparticles
TGA analysis

To calculate the grafting density, the weight of polymer in the sample was divided by the surface area of the raw silica particle (based on the size determined by TEM/SANS analysis; 2827 nm$^2$). It should be noted that due to the presence of free HEC in the sample, there may be some error in this calculation.

Small Angle Neutron Scattering

Following collection and data reduction, all SANS data was modelled using the SASview software package (www.sasview.org).

Initially, data were modelled to a spherical form factor (Equation S1), however the results yielded a poor fit at higher q-values, suggesting a core-shell type structure. The likely reason for this is the presence of either free HEC or a shell consisting of HEC.

\[ I(q) = \frac{\text{scale}}{V} \left[ \frac{3V(\Delta \rho)(\sin(qr) - qrcos(qr))^2}{(qr)^3} \right] + bkg \]  
\[ \text{Equation S1} \]

Where scale is volume fraction, V is the volume of the scattering object, r is the radius, bkg is the background, and \( \Delta \rho \) is the scattering length density contrast factor (i.e. difference in SLD between the sphere and surrounding solvent).

To account for this addition, a core-shell sphere model was used (Equation S2).

\[ P(q) = \frac{\text{scale}}{V_s} \left[ \frac{3V_c(\rho_c - \rho_s)\sin(qr_c) - qrcos(qr_c)}{(qr_c)^3} + 3V_s(\rho_s - \rho_{solv})\sin(qr_s) - qrcos(qr_s)}{(qr_s)^3} \right] + bkg \]  
\[ \text{Equation S2} \]

Where scale is a scaling factor, \( V_s \) is the volume of the outer shell, \( V_c \) is the volume of the core, \( r_s \) is the radius of the shell, \( r_c \) is the radius of the core, \( \rho_c \) is the SLD of the core, \( \rho_s \) is the SLD of the shell, \( \rho_{solv} \) is the SLD of the solvent, and bkg is the background. The fits for this model can be found in Fig S12, and a table for the parameters in Table S11. Given the uncertainty of how the HEC is interacting with the silica nanoparticles, the SLD parameter for the core and shell were left as floating variables, and SLD for solvent was fixed at 6.35x10^{-6} Å$^2$. 
Fig S12 Fitting to a core-shell model for HEC-silica nanoparticles.  A) shows unfunctionalised silica, B) 0.1% HEC-silica, C) 0.5% HEC-silica, D) 1% HEC-silica, and E) 2% HEC-silica.

Table S1. Fitting parameters for Y1 to Y5 for the fits indicated in Fig S13

|                     | Y1     | Y2     | Y3     | Y4     | Y5     |
|---------------------|--------|--------|--------|--------|--------|
| Scale               | 0.014  | 0.03   | 0.057  | 0.06   | 0.07   |
| Background (cm⁻¹)   | 0.065  | 0.069  | 0.065  | 0.068  | 0.07   |
| Radius (Å)          | 152    | 172    | 179    | 146    | 175    |
| Thickness (Å)       | 4.8    | 5.1    | 30     | 30     | 34     |
| SLD core (Å²)       | 1.38x10⁻⁶ | 4.6x10⁻⁶ | 4.6x10⁻⁶ | 3.7x10⁻⁶ | 1.38x10⁻⁶ |
| SLD shell (Å²)      | 1.38x10⁻⁶ | 7.9x10⁻⁶ | 6.7x10⁻⁶ | 6.0x10⁻⁶ | 5.2x10⁻⁶ |
| SLD solvent (Å²)    | 6.35x10⁻⁶ | 6.35x10⁻⁶ | 6.35x10⁻⁶ | 6.35x10⁻⁶ | 6.35x10⁻⁶ |
Estimation of number of particles per aggregate.

Using the aggregate size from DLS which includes the hydration shell around all of the particles in the aggregate, the volume of the hydrated aggregate can be calculated.

To estimate the number of particles in each aggregate, the hydrated aggregate volume from DLS is simply divided by the hydrated particle volume. Individual particle size data for each HEC concentration is available from the SANS or TEM diameters; SANS data was selected. However, SANS provides the sizes of the particle cores and so 20 nm (as the mean hydration layer thickness) was added to the SANS size data to account for the hydration shell we expect around each particle in the aggregate. From this, the volume of each hydrated particle was calculated. Dividing the hydrated aggregate volumes by hydrated particle volumes gave an estimate of the number of particles in the aggregate.

Clearly there are numerous assumptions in this approach. We assume the hydration shells of the particles within the aggregates remain at 20 nm thick and that the particles don’t “share” the layer in the aggregates (i.e. the hydration shells may not be 20 nm between particles), we assume perfect dense packing and have taken SANS values rather than sizes from TEM which could provide some minor discrepancies. Not withstanding these caveats, the estimates illustrate that the higher HEC concentrations allows greater number of particles to aggregate.
Table S12. Estimation of number of particles per aggregate

| HEC concentration (%) | Aggregate Hydrodynamic radius by DLS (nm) | Aggregate Hydrodynamic volume by DLS (nm$^3$) | Particle diameter SANS (nm) | Estimated Hydrated Particle diameter SANS + 20 (nm) | Hydrated particle volume (nm$^3$) | Number of hydrated particles per aggregate |
|-----------------------|------------------------------------------|---------------------------------------------|-----------------------------|-----------------------------------------------|---------------------------------|---------------------------------------------|
| 0                     | 25                                       | 65450                                       | 31                          | 51                                           | 69556                           | 1                                           |
| 0.1                   | 27                                       | 82448                                       | 35                          | 55                                           | 87114                           | 1                                           |
| 0.5                   | 54                                       | 659584                                      | 41                          | 61                                           | 118847                          | ~6                                          |
| 1                     | 97                                       | 3822996                                     | 35                          | 55                                           | 87114                           | 44                                          |
| 2                     | 190                                      | 28730912                                    | 42                          | 62                                           | 124799                          | 230                                         |