Supporting Information – A simple method for the quantification of molecular decorations on silica particles

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Figures S1 – S3 suggest that the fit in Figure 1 is appropriate to measure the hydrodynamic radius of the nanoparticles synthesised in this paper.

**Figure S1**: Correlation data for the DLS measurements of thiol terminated SiNPs presented in Figure 2.
**Figure S2:** Raw correlation data for the DLS measurements of thiol terminated SiNPs presented in Figure 2.

**Figure S3:** Data fit for thiol terminated SiNPs presented in Figure 2.
The following calculations support the attachment density calculated for the TGA analysis of the particles synthesised in the paper for the case study.

As we know the surface area of each particle and the number of moles of attaching agent added directly to the nanoparticle powder, we can estimate the grafting density of attachments per unit area of particle present using ATR-FTIR.

From DLS and SEM results presented in Figure 2 an average particle is 170 nm in size. By knowing the volume and the density of the particle we can work out the average mass per particle.

\[
\text{Volume of a Particle} = \frac{4}{3} \pi r^3 \quad \text{(where } r = 85 \times 10^{-7} \text{ cm)}
\]

\[
= 2.6 \times 10^{-15} \text{ cm}^3 \text{ per particle}
\]

\begin{equation}
\text{Particle density of 2g.cm}^{-3}
\end{equation}

\[
d = \frac{m}{v}
\]

\[
\text{Mass of a Particle} = 5.14 \times 10^{15} \text{ grams per particle, which is equivalent to } 1.95 \times 10^{14} \text{ particles per gram}
\]

Theoretically, surface area (SA) of 170nm particle is expected to be \(4\pi r^2 = 91,000 \text{ nm}^2\) per particle, which gives a corresponding 18 m\(^2\) of surface area per gram.
BET Isotherm yielded an available surface area of 21.7 m$^2$ per gram which corresponds to 110,000 nm$^2$ per particle. This value is used and carried through these calculations as the experimental value for attachment density.

The BET isotherm shows behaviour similar to type III and type V isotherms (using the B.D.D.T isotherm classification system), which suggests a weak adsorbate-adsorbent interaction, and, given the adsorption and slight hysteresis at higher relative pressures, infers a level of ordered meso or macro porosity. Due to the nature of the drying process, these particles irreversibly agglomerate quickly when not solvated which results a high level of clustering. Given that AFM, SEM and TEM images of the particles alone resemble a solid sphere, it is inferred that the high adsorption of gas in the higher relative pressure region is the filling of the void volume due to spherical packing within the particle clusters.

TGA shows 4.4% of 5.046 mg due to 10-bromodecane which corresponds to 0.22 mg of 10-bromo-1-decane
\[
\frac{0.22 \times 10^{-3} \text{g}}{\text{221 g per mol}} = 1.0 \times 10^{-6} \text{ moles}
\]

\[
1.0 \times 10^{-6} \text{ moles} \times 6.022 \times 10^{23} \text{ particles per mole} = 6.0 \times 10^{17} \text{ attachments present}
\]

\[
\text{Attachments per particle} = \frac{\text{# of attachments}}{\text{# of particles}}
\]

\[
\frac{6.0 \times 10^{17}}{9.4 \times 10^{11}} = 640,000 \text{ attachments per particle}
\]

Attachments per square nanometre = \[
\frac{640,000 \text{ attachments}}{110,000 \text{nm}^2} = 5.8 \text{ attachments per nm}^2
\]

The following calculations support the attachment density calculated for the ATR-FTIR analysis of the particles synthesised in the paper for the case study.

Ratio of A/B is 0.23

\[Y = 0.020x + 0.12\text{ from Figure 5}\]

Where x is the number of molecules of 11-bromo-1-undecene in the matrix per \(\text{nm}^2\) of surface area on silica nanoparticles

This is for 9 CH\(_2\) carbons, given it measures 11-bromo-1-undecene

For attachment we multiply the slope by 11/9 (two new CH\(_2\) carbons formed during the click process due to loss of double bond), then multiply by 10/11 in order to accommodate for the use of 10-bromo-1-undecene.

This corresponds to multiplying the slope by a factor of 1.11

Thus, \(y = 0.022x + 0.12\)

\(x = 4.9 \text{ attachments per nm}^2\)

It should also be mentioned that 13mg of thiol terminated particles were used to create the attachment density given in the ATR-FTIR. This corresponds to 25mL of nanoparticle solution, which is used in each functionalization process.