Supporting Information

Isotopic Exchange of Atomically Precise Nanoclusters with Materials of Varying Dimensions: From Nanoscale to Bulk

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Table of contents

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental methods</td>
<td>S3-S6</td>
</tr>
<tr>
<td>Figure S1</td>
<td>ESI MS of $^{107}\text{Ag}<em>{25}(\text{DMBT})</em>{18}$ and $^{109}\text{Ag}<em>{25}(\text{DMBT})</em>{18}$</td>
<td>S7</td>
</tr>
<tr>
<td>Figure S2</td>
<td>TEM and UV characterization of AgNPs@DMBT of different sizes</td>
<td>S8</td>
</tr>
<tr>
<td>Figure S3</td>
<td>Raman spectra of AgNPs and pure DMBT ligand</td>
<td>S9</td>
</tr>
<tr>
<td>Figure S4</td>
<td>Time-dependent ESI MS showing the isotopic exchange in the cluster when reacted with -2 nm AgNP@DMBT at various NC:NP mixing ratios</td>
<td>S10</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>Time-dependent ESI MS showing the isotopic exchange in the cluster when reacted with 4 nm AgNP@DMBT at various NC:NP mixing ratios</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>Time-dependent ESI MS showing the isotopic exchange in the cluster when reacted with 11 nm AgNP@DMBT at various NC:NP mixing ratios</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>ESI MS showing the final equilibrated state of the clusters, after completion of the exchange reaction with 2 nm, 4 nm and 11 nm AgNP@DMBT, respectively, at various NC:NP mixing ratios</td>
<td></td>
</tr>
<tr>
<td>S8</td>
<td>UV-vis spectra for the products of reaction of NC with AgNPs of different sizes</td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>ESI MS of the product formed by reaction of $^{107}$Ag$<em>{25}$(DMBT)$</em>{18}^-$ and $^{109}$Ag$<em>{25}$(DMBT)$</em>{18}^-$ with normal Ag$<em>{25}$(DMBT)$</em>{18}^-$ (made from naturally abundant Ag)</td>
<td></td>
</tr>
<tr>
<td>S10</td>
<td>TEM image of Ag$<em>{25}$(DMBT)$</em>{18}^-$ cluster and particle size distribution</td>
<td></td>
</tr>
<tr>
<td>S11</td>
<td>TEM image of the final product of reaction of Ag$<em>{25}$(DMBT)$</em>{18}^-$ with 2 nm, 4 nm and 11 nm AgNPs@DMBT, respectively</td>
<td></td>
</tr>
<tr>
<td>S12</td>
<td>Time dependent ESI MS showing reaction of $^{107}$Ag$<em>{25}$(DMBT)$</em>{18}^-$ and $^{109}$Ag$<em>{25}$(DMBT)$</em>{18}^-$ with bare Ag foil</td>
<td></td>
</tr>
<tr>
<td>S13</td>
<td>Time dependent ESI MS showing reaction of $^{107}$Ag$<em>{25}$(DMBT)$</em>{18}^-$ and $^{109}$Ag$<em>{25}$(DMBT)$</em>{18}^-$ with 2,4-DMBT protected Ag foil</td>
<td></td>
</tr>
<tr>
<td>S14</td>
<td>Time dependent ESI MS showing reaction of the cluster with bulk Ag powder</td>
<td></td>
</tr>
</tbody>
</table>

S2
**Experimental methods**

**Instrumentation.** UV-vis studies were performed using a PerkinElmer Lambda 25 UV-vis spectrometer. ESI MS measurements were performed using a Waters Synapt G2Si high resolution mass spectrometer. Capillary voltage of 3 KV, cone voltage 20, source offset 20, source temperature 100 °C, desolvation temperature 150 °C and desolvation gas flow of 400 L/h was used for ESI MS studies. Transmission electron microscopy experiments were performed in a JEOL 3010 instrument. Raman measurements were carried out using a WITec GmbH alpha300S confocal Raman equipped with a 532 nm laser as the excitation source.

**Synthesis of $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$.** First, $^{107}\text{AgNO}_3$ and $^{109}\text{AgNO}_3$ salts were synthesized starting from isotopically pure $^{107}\text{Ag}$ and $^{109}\text{Ag}$ foils. Next, isotopically pure $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$ clusters were synthesized using the reported protocol for synthesis of $\text{Ag}_{25}(\text{DMBT})_{18}^-$ clusters.\(^1\)\(^2\) About 38 mg of AgNO\(_3\) was dissolved in 2 mL methanol and 90 µL of 2,4-DMBT thiol was added to it. Further, about 17 mL of DCM was added to it and the reaction mixture was kept for stirring at 0 °C. After about 15 mins, 6 mg of PPh\(_4\)Br in 1 mL methanol was added to it. About 5 mins later, 15 mg of NaBH\(_4\) in 0.5 mL water was added. The reaction was continued for 8 h and then stored in the refrigerator for
about 2 days. The sample was then centrifuged and insoluble materials were removed. The solvents were then evaporated using a rotary evaporator and the as-obtained crude cluster was repeatedly washed with methanol. The purified clusters were then extracted in DCM.

**Calculation of theoretical isotope patterns with varying composition of $^{107}\text{Ag}/^{109}\text{Ag}$:** We calculated the isotopic patterns of $[\text{Ag}_{25}(\text{DMBT})_{18}]^{-}$ with varying $^{107}\text{Ag}/^{109}\text{Ag}$ ratio by following our previous report. The abundance of each isotope ($^{107}\text{Ag}$ and $^{109}\text{Ag}$) in $[\text{Ag}_{25}(\text{DMBT})_{18}]^{-}$ cluster was varied such that the isotopic composition is (x,y) i.e., {(100,0), (99,1), (98,2)……(0,100)} where x and y are the abundance of $^{107}\text{Ag}$ and $^{109}\text{Ag}$, respectively. The experimental spectra were compared with the calculated spectra to find the best match and hence confirm the abundances of each isotope in the clusters.

**Biexponential fitting of the reaction kinetics.**

Equation used for fitting the kinetic plots of NC-NP reactions is:

$$Y(t) = A_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

where $Y(t)$ is the time-dependent property, i.e. abundance of the parent isotope (%) in this case, $\tau_1$ and $\tau_2$ are the timescales and $A_0$, $A_1$ and $A_2$ are the fitting parameters. $A_0$ corresponds to the value of $Y(t)$ when reaction reaches an equilibrium state.

The contribution, $a_1$ and $a_2$, of the timescales $\tau_1$ and $\tau_2$, respectively, to the overall process was evaluated using the following formula:

$$a_1 = \frac{A_1}{A_1 + A_2}, \quad a_2 = \frac{A_2}{A_1 + A_2}$$

The average timescale of the reaction, $\langle \tau \rangle$, was calculated as follows:

$$\langle \tau \rangle = a_1 \tau_1 + a_2 \tau_2$$
Calculation of no of particles/mL for:

a) Ag$_{25}$(DMBT)$_{18}$ cluster

Molecular weight = 5167

Mass of 1 Ag NC (m) = $\frac{5167 \times 10^3}{6.023 \times 10^{23}}$ mg = $8.58 \times 10^{-18}$ mg

Mass of Ag$_{25}$ NCs in 1 mL of the stock solution considered in the experiments (W) = 1 mg

No. of particles per mL of the stock solution = $\frac{W}{m} = 1.17 \times 10^{17}$

Size of the metal core of the NC (2R, from single crystal XRD) ~ 1 nm; this diameter is smaller than the core size from TEM (1.9 nm), which is slightly overestimated.

Surface area = $4\pi R^2 = 3.14$ nm$^2$

The surface of the NC is covered by 18 DMBT ligands.

So, 1 DMBT ligand is assumed to occupy a surface area of ~0.17 nm$^2$.

The ligand coverage for the ~2 nm, ~4 nm and ~11 nm plasmonic NPs are not known exactly.

So, the approximation that 1 DMBT ligand covers 0.17 nm$^2$ of the surface area of the particles is used to calculate the ligand coverage even for the other NPs, although the ligand packing is likely to be different.

Mass of 1 DMBT ligand (C$_8$H$_9$S) = $\frac{137 \times 10^3}{6.023 \times 10^{23}}$ mg = $22.75 \times 10^{-20}$ mg

b) ~ 2 nm AgNP

Average size of metal core of the Ag NP (HRTEM), 2R = 1.8 nm

Volume of 1 Ag NP metal core (sphere), $V = \frac{4}{3}\pi R^3 = 3.05$ nm$^3$

Density of Ag NPs, $\rho = 10.5 \frac{g}{cm^3} = 1.05 \times 10^{-17}$ mg/nm$^3$

Mass of metal core of 1 Ag NP = $V\rho = 3.2 \times 10^{-17}$ mg

Surface area of 1 AgNP = $4\pi R^2 = 10.17$ nm$^2$

No. of DMBT ligands covering the surface ~ 60

As mentioned before, this number is based on the TEM core size, which is likely to slightly overestimate the metal core dimension.

Mass of the ligands = $60 \times 22.75 \times 10^{-20}$ mg = $1.36 \times 10^{-17}$ mg
Total mass of 1 Ag NP (m) = mass of metal core + mass of ligands = $4.56 \times 10^{-17}$ mg
Mass of AgNPs in 1 mL of the stock solution considered in the experiments (W) = 1 mg
No. of particles per mL of the stock solution = $\frac{W}{m} = 2.19 \times 10^{16}$

c)  ~ 4 nm AgNP

Average size of metal core of the Ag NP (HRTEM), $2R = 3.9$ nm
Volume of 1 Ag NP metal core (sphere), $V = \frac{4}{3}\pi R^3 = 31.04$ nm$^3$
Density of Ag NPs, $\rho = 10.5 \ \frac{g}{cm^3} = 1.05 \times 10^{-17} \ \frac{mg}{nm^3}$
Mass of metal core of 1 Ag NP = $V\rho = 3.2 \times 10^{-16}$ mg

Surface area of 1 AgNP = $4\pi R^2 = 47.76$ nm$^2$
No. of DMBT ligands covering the surface ~ 281
Mass of the ligands = $281 \times 22.75 \times 10^{-20}$ mg = $0.64 \times 10^{-16}$ mg
Total mass of 1 Ag NP (m) = mass of core + mass of ligands = $m = 3.84 \times 10^{-16}$ mg
Mass of AgNPs in 1 mL of the stock solution considered in the experiments (W) = 1 mg
No. of particles per mL of the stock solution = $\frac{W}{m} = 2.60 \times 10^{15}$

d)  ~ 11 nm AgNP

Average size of metal core of Ag NP (HRTEM), $2R = 11.2$ nm
Volume of 1 Ag NP metal core (sphere), $V = \frac{4}{3}\pi R^3 = 735.2$ nm$^3$
Density of Ag NPs, $\rho = 10.5 \ \frac{g}{cm^3} = 1.05 \times 10^{-17} \ \frac{mg}{nm^3}$
Mass of metal core of 1 Ag NPs, $m = V\rho = 7.72 \times 10^{-15}$ mg

Surface area of 1 AgNP = $4\pi R^2 = 393.88$ nm$^2$
No. of DMBT ligands covering the surface ~ 2317
Mass of the ligands = $2317 \times 22.75 \times 10^{-20}$ mg = $0.53 \times 10^{-15}$ mg
Total mass of 1 Ag NP (m) = mass of core + mass of ligands = $m = 8.25 \times 10^{-15}$ mg
Mass of AgNPs in 1 mL of the stock solution considered in the experiments (W) = 1 mg
No. of particles per mL of the stock solution = $\frac{W}{m} = 1.21 \times 10^{14}$
**Figure S1.** ESI MS of A) $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and B) $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$. Insets show the comparison of the experimental and theoretical isotopic patterns. The slight mismatches in the patterns may be attributed to some impurity present in the sample from the other isotope as the isotopic enrichment was 98%. However, this small discrepancy in the patterns may be neglected for further interpretation of the results.
**Figure S2.** Characterization of AgNPs@DMBT of size A) \(\approx 2\) nm, B) \(\approx 4\) nm and C) \(\approx 11\) nm, respectively. TEM images are shown in (a) and particle size distribution of the NPs are shown in (b). UV-vis spectra of the respective NPs are presented in the insets of (a) for each set.
Figure S3. Raman spectra of 11 nm AgNP, 4 nm AgNP, 2 nm AgNP protected with DMBT and pure DMBT ligand.
Figure S4. Time-dependent ESI MS showing the isotopic exchange in the cluster when reacted with 2 nm AgNP@DMBT at NC:NP mixing ratios of A) 1:1, B) 1:2, C) 1:3 and D) 1:5, respectively. In each of A), B), C) and D), (a) denotes the case where $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ was used and (b) denotes the case where $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$ was used as the isotopically labelled cluster for reaction with AgNP@DMBT, respectively.
Figure S5. Time-dependent ESI MS showing the isotopic exchange in the cluster when reacted with 4 nm AgNP@DMBT at NC:NP mixing ratios of A) 1:1, B) 1:2, C) 1:3 and D) 1:5, respectively. In each of A), B), C) and D), (a) denotes the case where $^{107}\text{Ag}_{25}\text{(DMBT)}_{18}^-$ was used and (b) denotes the case where $^{109}\text{Ag}_{25}\text{(DMBT)}_{18}^-$ was used as the isotopically labelled cluster for reaction with AgNP@DMBT, respectively.
Figure S6. Time-dependent ESI MS showing the isotopic exchange in the cluster when reacted with 11 nm AgNP@DMBT at NC:NP mixing ratios of A) 1:1, B) 1:2, C) 1:3 and D) 1:5, respectively. In each of A), B), C) and D), (a) denotes the case where $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ was used and (b) denotes the case where $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$ was used as the isotopically labelled cluster for reaction with AgNP@DMBT, respectively.
Figure S7. ESI MS showing the final equilibrated state of the clusters, after completion of the exchange reaction with A) 2 nm, B) 4 nm and C) 11 nm AgNP@DMBT, respectively, at various NC:NP mixing ratios. Panel (a) refers to the reaction with $^{107}$Ag$_{25}$(DMBT)$_{18}$ and panel (b) refers to the reaction with $^{109}$Ag$_{25}$(DMBT)$_{18}$. The NC:NP mixing ratio is indicated beside each spectrum. The mass spectrum of the final equilibrated state shown here are actually the data at 60 min of reaction of the respective cases, presented in Figures S4-S6. Those data are recombined in this figure to increase the clarity in understanding the extent of exchange with NC:NP mixing ratios, for a given size of AgNP.
**Figure S8.** UV-vis spectra for the products of reaction of NC with AgNPs of sizes A) ~2 nm, B) ~4 nm and C) ~11 nm, at different NC:NP mixing ratios.

**Figure S9.** ESI MS of the product formed by reaction of A) $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and B) $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$ with normal $\text{Ag}_{25}(\text{DMBT})_{18}^-$ (made from naturally abundant Ag). The reaction was rapid, so the ESI MS was measured within 1 min of mixing the reactants. The NC ($^{107/109}\text{Ag}_{25}(\text{DMBT})_{18}^-$) : NC (normal $\text{Ag}_{25}(\text{DMBT})_{18}^-$) mixing ratio is indicated for each of the spectra.
Figure S10. A) TEM image of Ag25(DMBT)18− cluster and B) particle size distribution of the clusters.

Figure S11. TEM image of the final product of reaction of Ag25(DMBT)18− with A) 2 nm, B) 4 nm and C) 11 nm AgNPs@DMBT, respectively. The areas containing the larger sized NPs are marked and the smaller particles represent the NCs.
Figure S12. Time dependent ESI MS showing reaction of A) $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and B) $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$ with bare Ag foil.

Figure S13. Time dependent ESI MS showing reaction of A) $^{107}\text{Ag}_{25}(\text{DMBT})_{18}^-$ and B) $^{109}\text{Ag}_{25}(\text{DMBT})_{18}^-$ with 2,4- DMBT protected Ag foil.
Figure S14. Time dependent ESI MS showing reaction of the cluster with A) ~80 mg, B) ~40 mg and C) ~20 mg bulk Ag powder. In each of A), B) and C), (a) denotes the case where $^{107}$Ag$_{25}$(DMBT)$_{18}^-$ was used and (b) denotes the case where $^{109}$Ag$_{25}$(DMBT)$_{18}^-$ was used as the isotopically labelled cluster for reaction with Ag powder, respectively.

Figure S15. Time dependent UV-vis study of the reaction of Ag$_{25}$(DMBT)$_{18}^-$ NCs with A) 20 mg, B) 40 mg and C) 80 mg of bulk Ag powder.
Table S1. Timescales of reaction of NCs with NPs of different sizes and at different mixing ratios

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<th>Size of AgNPs</th>
<th>NC:NP mixing ratio</th>
<th>(a_1)</th>
<th>(\tau_1) (min)</th>
<th>(a_2)</th>
<th>(\tau_2) (min)</th>
<th>(&lt;\tau&gt;) (min)</th>
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References
