Growth of Supported Gold Nanoparticles in Aqueous Phase Studied by In Situ Transmission Electron Microscopy

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III. Supporting Movie Descriptions

Movie M1 (M1_unimodal_Au_TiO₂_H₂O): The unimodal sample being scanned for 1 hour in H₂O, with only a limited number of particles disappearing and most other particles hardly growing. During the movie, some very dark spots appear, seem to grow to quite large proportions (typically >25 nm) and then disappear quickly. These are likely partially the result of some form of TiO₂ charging from the electron beam and partially from overlapping TiO₂ crystals, but not Au particles since they also appear in the pristine TiO₂ in H₂O and are very rare if NaCl is present in solution. Furthermore, the gold particles are somewhat mobile, moving small distances, more so than in NaCl (see Movie M2). This also suggests that charging of the support might take place when the conductivity of the liquid is insufficient to dissipate the charging, weakening the Au-TiO₂ interactions.

Movie M2 (M2_unimodal_Au_TiO₂_NaCl): The unimodal sample being scanned for 1 hour in 10 mmol/L NaCl in H₂O. As can be seen, more particles disappear (and most do
so rapidly) than in movie M1, while many others grow significantly. The only large dark spots observed are the result of overlapping crystals and Au particles are far less mobile. This movie also illustrates the limited influence of Au size on their sintering, with one of the larger particles disappearing during the experiment.

**Movie M3 (M3_bimodal_Au_TiO2_H2O):** The bimodal sample being scanned for 1 hour in H$_2$O. Again, large dark spots appearing, growing and disappearing quickly and higher Au particle mobility can be observed, likely for the same reason as discussed above (see description of movie M1). But again, only few Au particles disappear and the other particles show very limited growth.

**Movie M4 (M4_bimodal_Au_TiO2_NaCl):** The bimodal sample being scanned for 1 hour in 10 mmol/L NaCl in H$_2$O. As with the unimodal sample in movie M2, a significant portion of the particles disappears, but this time growth of the other particles is far more limited. Furthermore, one of the ~20 nm Au particles in the field of view disappears as well. There seem to be a few small dark spots that appear and disappear quickly in this
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Figure S1. Nitrogen physisorption isotherms and X-ray diffraction patterns of P25 TiO$_2$ (a and c respectively) and the Au/TiO$_2$ catalyst with an unimodal particle size distribution (b and d respectively). For the nitrogen physisorption, a significantly finer powder was used for the Au/TiO$_2$ sample, resulting in the higher adsorption at high $P/P_0$. The BET surface area was very similar for the two samples (45 m$^2$/g).
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nm. (b) The second area followed during the heating LP-TEM experiment, with the arrow showing the initially largest particle disappearing after the first 5 minutes. The scale bar corresponds to 100 nm in both images.

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irradiated area is the area inside the square visible in the center of the image after one hour. The scale bars in the top two images correspond to 200 nm and the scale bars in the bottom two images correspond to 50 nm.

**Table S1.** Calculations of equilibrium concentrations of the \([\text{AuCl}_4^-]\) complex in water for various concentrations/pressures at 25 °C.

| pH | Concentration Cl\textsuperscript{-} (mol/L) | \(\text{O}_2\) partial pressure (bar) | Resulting equilibrium concentration [AuCl\textsubscript{4}\textsuperscript{-}] (mol/L) |
|----|---------------------------------------------|----------------------------------|-----------------------------------|
| Bulk Au | 7 | 0.01 | 0.2 | 9.9E-19 |
| Nanoparticles* | 7 | 0.01 | 0.2 | 1.4E-08 |
| Bulk Au | 4 | 0.01 | 0.2 | 9.9E-10 |
| Nanoparticles | 4 | 0.01 | 0.2 | 1.4E+01** |
| Bulk Au | 7 | 0.01 | 0.001 | 1.9E-20 |
| Nanoparticles | 7 | 0.01 | 0.001 | 2.6E-10 |
| Bulk Au | 7 | 0.001 | 0.2 | 9.9E-23 |
| 7 | 0.01 | 0.2 | 9.9E-19 |
| Nanoparticles | 7 | 0.1 | 0.2 | 9.9E-15 |
|--------------|---|-----|-----|--------|
|              | 7 | 0.001 | 0.2 | 1.4E-12 |
|              | 7 | 0.01  | 0.2 | 1.4E-08 |
|              | 7 | 0.1   | 0.2 | 1.4E-04 |

*Considered to have a reduction potential shift of -200 mV

**Not considering solubility limits of the complex