

## SUPPORTING INFORMATION

### **Inclusion-Water-Cluster in a Three-Dimensional Superlattice of Gold Nanoparticles**

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#### **Experimental Procedures**

##### **1. Preparation of Au-MSA powders<sup>1</sup>**

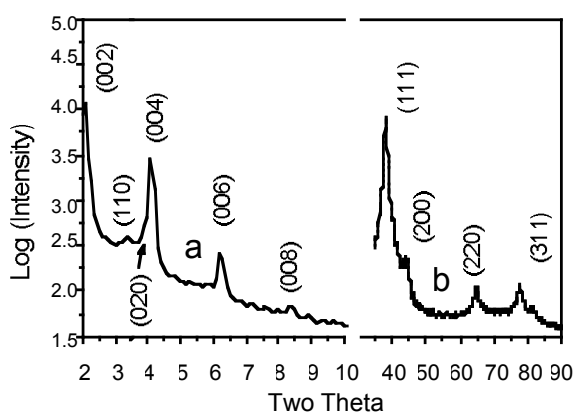
Under vigorous stirring with 100W-ultrasonic irradiation, 80mL freshly prepared 0.3M sodium borohydride aqueous solution was added to a water-methanol mixed solution containing 1g of  $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$  and 0.73g of mercaptosuccinic acid (MSA). After reduction, a flocculent precipitate was collected by decantation and centrifugation, and then washed three times with a water-methanol mixture by repeating re-suspension and re-centrifugation process. This process was repeated an additional three times with 99.8% methanol to remove unbound MSA and Au-MSA complex. The suspension was dried by lyophilization followed by evacuating the sample powders for 24h. This is the as-prepared sample B in the form of sodium salt. The protonated sample C was obtained by dissolving sample B in dilute hydrochloric acid solution and then purified/dried by the same manner as in the case of as-prepared sample.

##### **2. Preparation of Au Nanoparticle Superlattices for IR Measurement**

The gold particle crystals (Sample D) were produced by the procedures described in literature.<sup>1-3</sup> 7.2mg of Au-MSA powder was dispersed in 4mL of distilled water and the pH value of the dispersion was adjusted with 6M HCl solution. The solution was filtered through a syringe-driven micro-filter with 0.22-mm pore size immediately before storing in a sealed vial. It took 3-5 days at room temperature to form numerous faceted particle crystals with micrometer sizes in a wide range of HCl concentration from 0.5 to 0.1M. As-prepared crystals formed at an air/water interface were transferred onto KBr plate several times to accumulate enough amount of crystals on the plate for FTIR observation and stored in vacuum before IR measurement in order to remove physisorbed water from the crystals. Fourier transform infrared spectra were recorded with a Horiba FT-IR spectrophotometer using KBr disc method otherwise noted. An EDAX DX-4 system attached to the Philips XL-20 scanning electron microscope operated under an acceleration voltage of 6kV was used to analyze the elements in the sample. EDX showed no trace of sodium and chlorine elements in both samples C and D, indicating the purity of the samples.

### 3. X-ray diffraction (XRD)

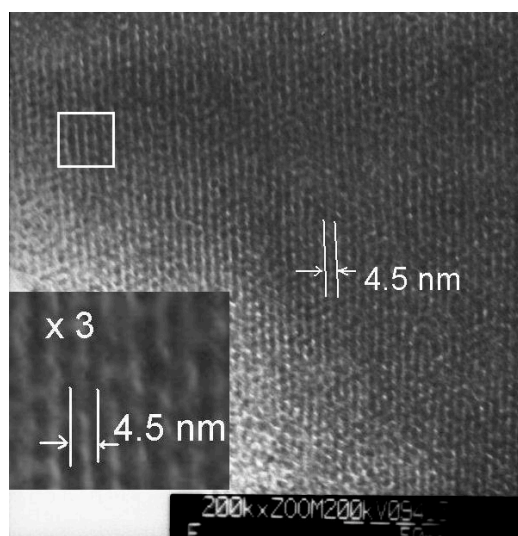
Powder X-ray diffraction measurements were performed by using Rigaku RINT-2000 with CuK $\alpha$  tube attaching a graphite monochromator. Sample crystals were mounted on a Si single crystal. Comparing SAXRD patterns with those of SATD, we can successfully index all of Miller indices by hexagonal-close-packing structure.<sup>1</sup> Observed lattice spacing 4.5nm from HRTEM image gives particle diameter of 5.2 nm (gold core: 3.7 nm, MSA shell: 0.75 nm). Hence spheres smaller than 1.78 or 0.97 can be incorporated in the O<sub>h</sub> or T<sub>d</sub> cavity of the superlattices, respectively.



**Figure S1.** XRD of small-angle region (a: left) and wide-angle region (b: right). Miller indices are for superlattice a and for atomic arrangement b.

### 4. High resolution TEM (HRTEM)

A Hitachi-8100 transmission electron microscope operated at 200kV was used to observe lattice image as well as small-angle transmission electron diffraction (SATD) with camera length 2m.



**Figure S2.** High resolution TEM (HRTEM) image for a quality superlattice of  $\{100\}$  in the hcp system. The inset stands for the enlargement of the boxed area

### References

- (1) Wang, S.H.; Sato, S.; Kimura, K. *Chem. Mater.* **2003**, *15*, 1075.
- (2) Wang, S.H.; Sato, S.; Kimura, K. *Trans. Mater. Res. Soc. Jpn.* **2003**, *28*, 903.
- (3) Kimura, K.; Sato, S.; Yao, H. *Chem. Lett.* **2001**, 372.