

Supporting Information

***In Situ* Formation and Ordered Assembly of Gold Nanoclusters to Nano-ribbons at Oil/Water Interface**

FuKe Wang, Xinhai Zhang, Zheng Zhang, and Chaobin He

Synthesis and Integration, Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 3 Research Link, Singapore, 117602; Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543; Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576

Experimental Section

To a vial was added 100 μl of 0.5 g/ml of HAuCl_4 aqueous solution, 6 ml hexane, and 500 μl of the 1-dodecanethiol. The mixture was ultrasonicated at room temperature for 30 min until all the aqueous solution became colorless. Yellow precipitate were obtained, which were separated by centrifugation and washing with water and hexane. The composition was analyzed with elemental analysis (EA), which shows C, 35.9883; H, 6.3338; S, 7.6104. Based on EA analysis, we can calculate that the mole composition of Au to SC_{12} is nearly to 1:1. 60 mg of the obtained precipitates were re-dispersed into 6 ml of octadecene (ODE) and heated up to 80 $^\circ\text{C}$ with vigorous stirring. During stirring, 500 μl of 37% formaldehyde aqueous solution was quickly added. The solution became cloudy at the beginning which may be due to the formation of O/W system, but it became transparent after 30 min. Continue stirring and heating at 80 $^\circ\text{C}$ for 6 hours, and then stopped the stirring and heating. With cooling, the solution became cloudy and finally became yellow gel. To separate the gold nanoclusters, hexane (20 ml) was added to the gel and light yellow precipitates were obtained. The gold nanoclusters were collected by centrifuge and washing with hexane.

UV-vis spectra were recorded on a Shimadzu 3600 UV-VIS-NIR Spectrophotometer while excitation and emission spectra were recorded on a spectrofluorophotometer. For the time-resolved photoluminescence (PL) measurements, the samples were excited using the 2.5 MHz pulse train of 405 nm from a pulsed diode laser (PicoQuant, PDL 800-B). The PL was dispersed in a monochromator (Acton, SpectraPro 2300i) and then recorded using a conventional time-correlated single-photon counting (TCSPC) setup (PicoQuant, Picoharp 300).

The X-ray diffraction (XRD) pattern measurement was done on a Bruker D8 General Area Detector Diffraction System with $\text{Cu K}\alpha$ radiation. Samples for XRD measurement was prepared

by press the powder of Au NCs into a small pellet. The Au NCs deposited on silicon wafer was imaged using a JEOL FESEM JSM6700F field-emission scanning electron microscope (FESEM) at 5 kV acceleration voltage. The chemical compositions of nano-ribbon were analyzed using an energy dispersive X-ray spectroscopy in a scanning electron microscope (EDX-equipped SEM). TEM micrographs were obtained using a JEOL 2100TEM operating at an accelerating voltage of 200 kV. A drop of sample solution in hexane was cast onto a 200-mesh carbon-coated copper grid. The samples were dried at room temperature prior to measurement.

The surface analysis of the samples has been carried out using the Thermo Scientific Theta Probe XPS. A monochromatic Al $K\alpha$ (1486.6 eV) x-ray source was employed for analysis with photoelectron take-off angle of 50° respect to surface normal. Charge compensation was performed by means of low-energy electron flooding and further correction was made based on adventitious C1s at 285.0 eV. For chemical state analysis, a spectral deconvolution was performed by a curve-fitting procedure based on Lorentzians broadened by a Gaussian using the manufacturer's standard software. The error of binding energy is within $\pm 0.2\text{eV}$.

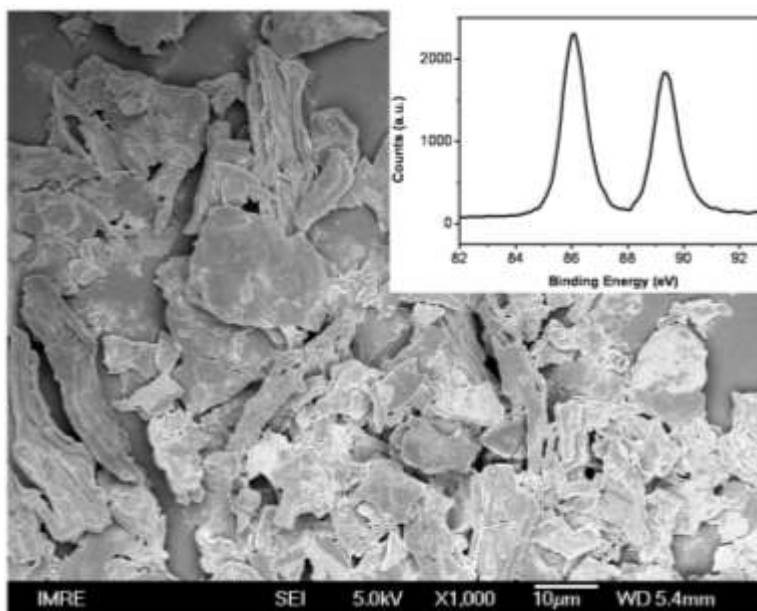


Figure S1. SEM image of the Au(III)-SC₁₂ which was used as precursors for preparation of Au NCs. Inset shows the XPS results of the Au(III)-SC₁₂, displaying the Au 4f_{7/2} (Au 4f_{5/2}) peaks at 86.0 eV (89.3 eV), assigned to Au³⁺ species.

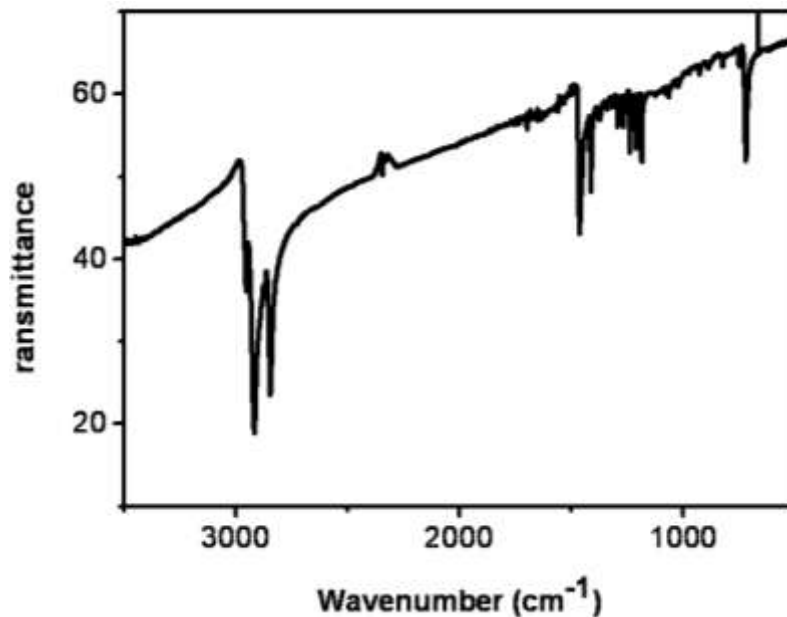


Figure S2. FT-IR spectra of the formed gold nanocluster. The sample was prepared by ground the sample with KBr.

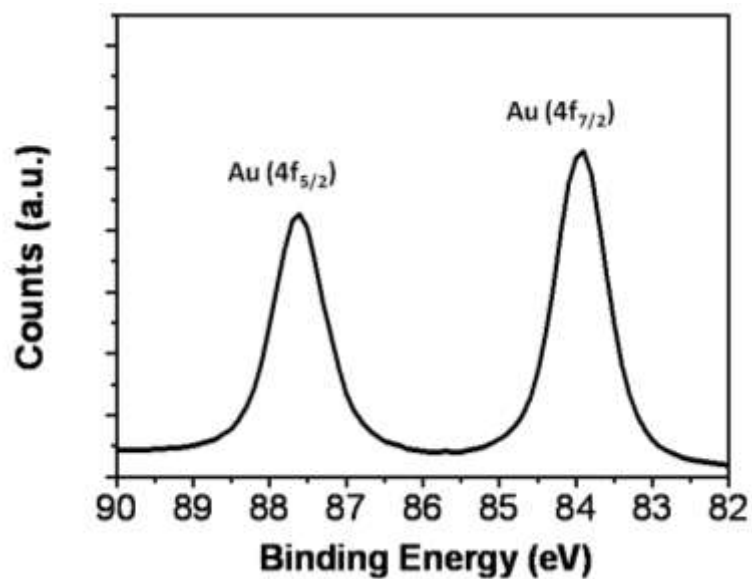


Figure S3. Au 4f binding energy (BE) of gold nanoparticles prepared by using sodium citrate as reducing agent, as reference for Au (0).

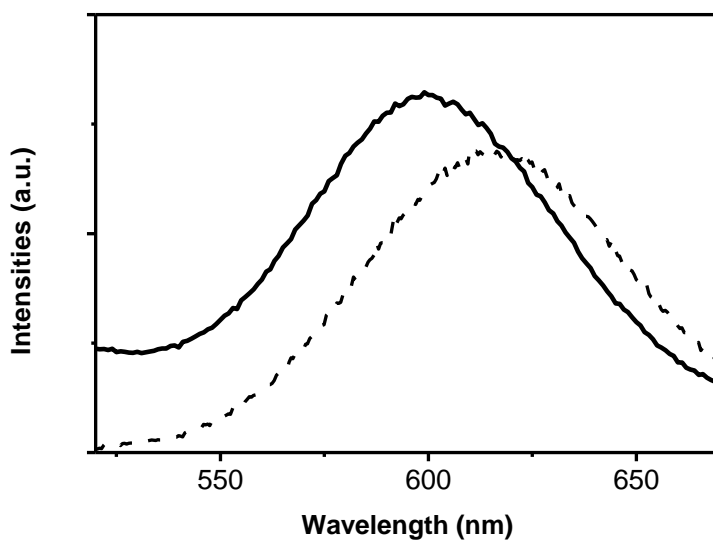


Figure S4. Comparison of the fluorescence spectra of ordered (solid line) and randomly (dash line) aligned gold nanoclusters upon excitation at $\lambda_{ex} = 365$ nm.