Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2016

Supporting Information

Direct Synthesis of Au Nanocrystals in Micro-droplets by Spray-Assisted Method

Hairui Fang,[a] Keke Huang,[a] Long Yuan,[a] Xiaofeng Wu,[a] Dong Wang,[c] Huanwen Chen,[a,b] and Shouhua Feng*[a]

[a] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.*
Email: shfeng@jlu.edu.cn; Fax: +86-431-85168624; Tel.: +86-431-85168661
[b] *Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology,Nanchang 330013, P. R. China*
[c] *Department of Chemical Engineering, Northeast Dianli University, NO.169 Changchun Road, Jilin City 132012, P.R. China.*

1. Experimental section

1.1. Regents

Gold chloride acid ($HAuCl_4$) was purchased from Sinopharm Chemical Reagent Co., Ltd.. The solution was prepared using ultrapure water from a PL5121 system (PALL, USA).

1.2. Mothed

Preparing of precursors:

1): 1000 ppm concentration of precursor: 10mg chloroauric acid (HAuCl4) was dissolved into 10 g ultrapure water to prepared the concentration of 1000ppm precursor.

2): Other concentrations of precursor: Other concentrations of precursor were attenuated from 1000 ppm concentration of precursor. Such as, 1 g of the 1000 ppm precursor was attenuated by 1 g ultrapure water for preparing 500 ppm concentration of precursor. Then the other concentrations of precursor were prepared with the same mothed.

Explain our self-made equipment

The Au nanocrystals were synthesized using our self-made equipment (shown in Fig. S-1, ESI†), mainly including the sample injection system (including injection pump (Kent Scientific Corporation, USA)), high voltage

system (including high voltage source (Boher High Voltage Power Supplies Co., Ltd, China)) and reaction system (including plate heater, three-dimensional operation platform and self-made spray nozzle). The sample injection system is used to control the volume and flux speed of the precursor during the injection process. By adjusting the flux speed and concentration of precursor, we could accurately control the amount of reactant in the unit time. In order to make a temperature field between the sample receptor and spray nozzle, a plate heater controlled by program was employed in the reaction system.

Through the coordination control of the reaction system and sample injection system, we could meticulously control the energy obtained by reactants. A high voltage was applied to a micro-syringe (Hamilton company, USA) using a high-voltage source and the earthed line was also connected to a silicon wafer (Hefei Kejing Materials Technology Co., Ltd, China) placed on the top of plate heater for collecting samples. The silicon wafer receptor was positioned at a distance of 15 mm from the nozzle. In order to get smaller droplets and increase the evaporation rate of the solvent during the flying process of droplets, the nitrogen was introduced. The nitrogen gas bottle and spray port were connected through pipe, thus high-speed jet of nitrogen between quartz capillary (inside diameter is 100μm) and spray nozzle has been happened. The N_2 flow rate was 90 ml/min, and nitrogen pressure was 0.6MPa. The solution of gold precursor was prepared using ultrapure water. A certain volume of solution was extracted with micro-syringe, then adjusting the parameter of injection pump to make sure that 100μl solution of gold precursor was injected into quartz capillary with the flux speed of 10μl/min.

The precursor, gold chloride acid, was dissolved in ultrapure water without adding any surfactants and inorganic ligands. We used the spray-assisted method to manufacture microdroplets. In this way, the process of controlling gold nanocrystals was limited within the microdroplets, separated from each other. In our experiment, we adjusted and optimized several key parameters (applied voltage, concentration of gold chloride acid, and temperature) to achieve shape control of the Au NPs.

1.3. Material characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a JEOL JEM 2200FS electron microscope operating at 200 kV. X-ray Powder diffraction patterns were accumulated on a Japan Regaku Ultima Ⅳ X-ray diffractometer using graphite monochromatized Cu K radiation (λ=1.5418 Å). The scanning electron microscopy (SEM) and the energy-dispersive X-ray (EDS) spectroscopic measurements were performed with a FEI Helios Nanolab 600i double beam scanning electron microscopy.

2. Figures

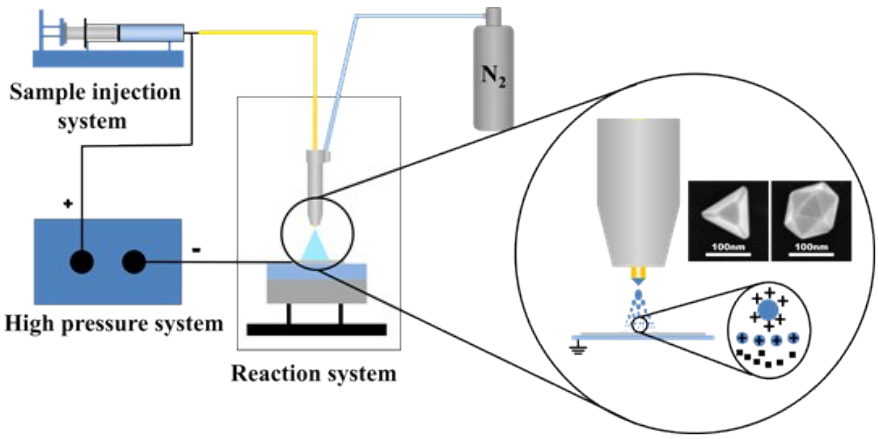

Figure S-1 The schematic of our self-made equipment used in experiments. The self-made equipment is mainly composed by three parts, the sample injection system, high pressure system and reaction system.

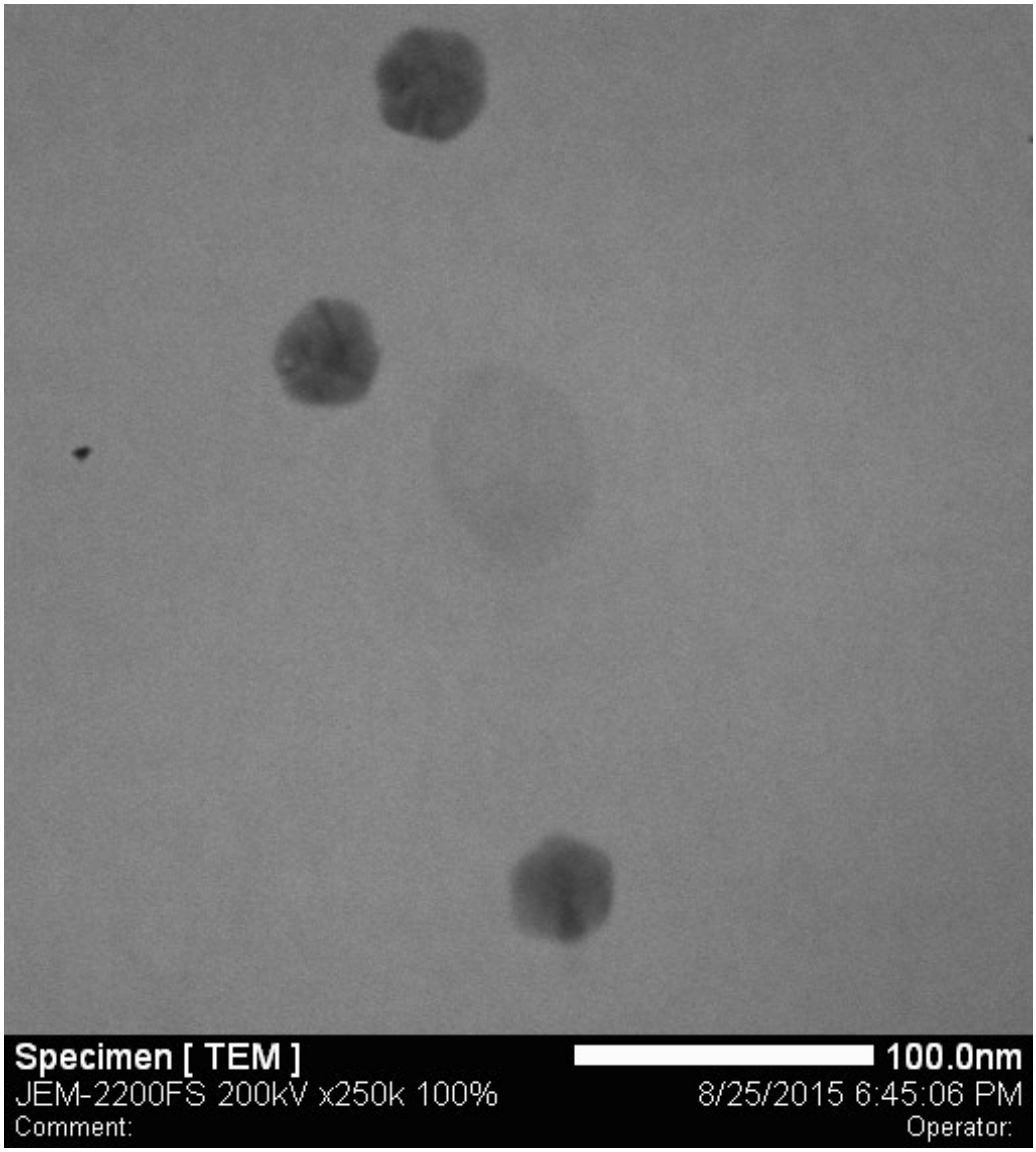

Figure S-2 The TEM of Au nanocrystals (360°C, 0 kV, 100 ppm) collected by the holey support film (special carrier for transmission electron microscope) at the position of silicon wafer receiver. The nanocrystals with hexagonal outlines were found. This was the projection of the icosahedron under the transmission electron microscope test.

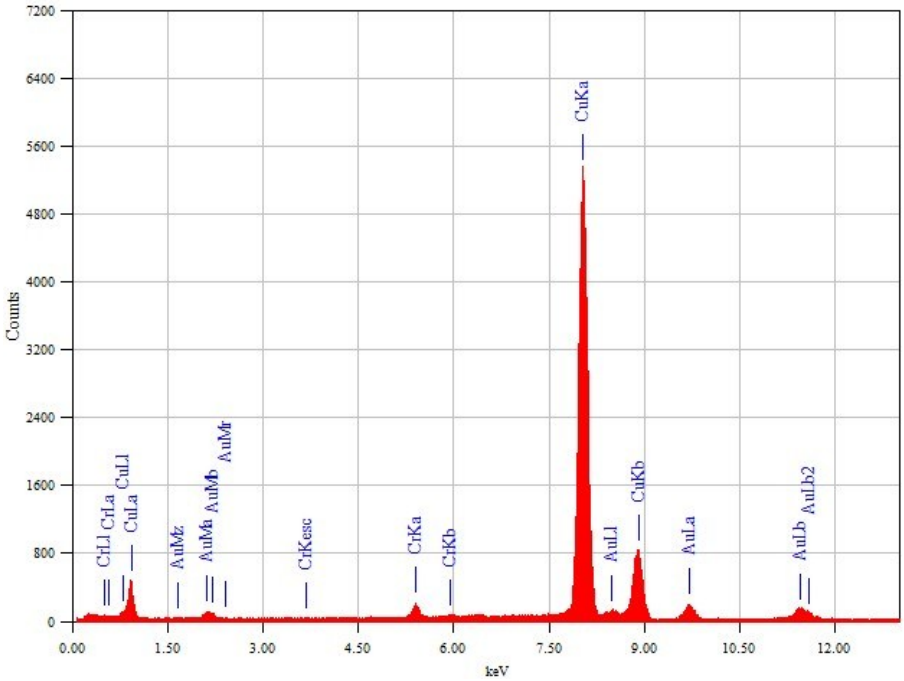

Figure S-3 The EDS analysis of Au nanocrystals (360 ^{o}C, 0 kV, 100 ppm) collected by the holey support film (special carrier for transmission electron microscope) at the position of silicon wafer receiver. Only gold element appeared in the sample, without chlorine element. The Cu and Cr belongs to the holey carbon support film we used for collecting samples.

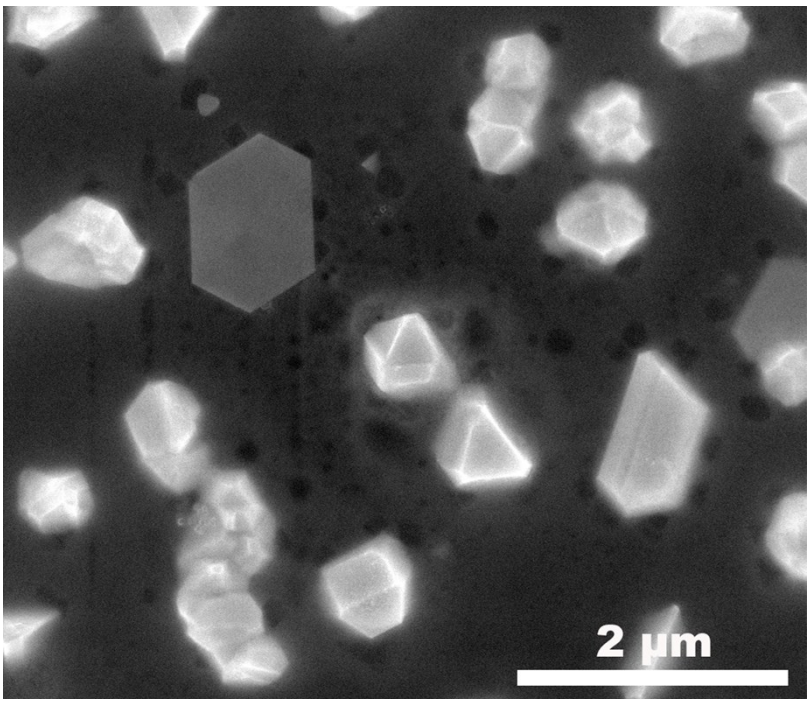

Figure S-4 SEM images of Au nanocrystals prepared with concentrations of 1000 ppm (360°C, 0 kV).

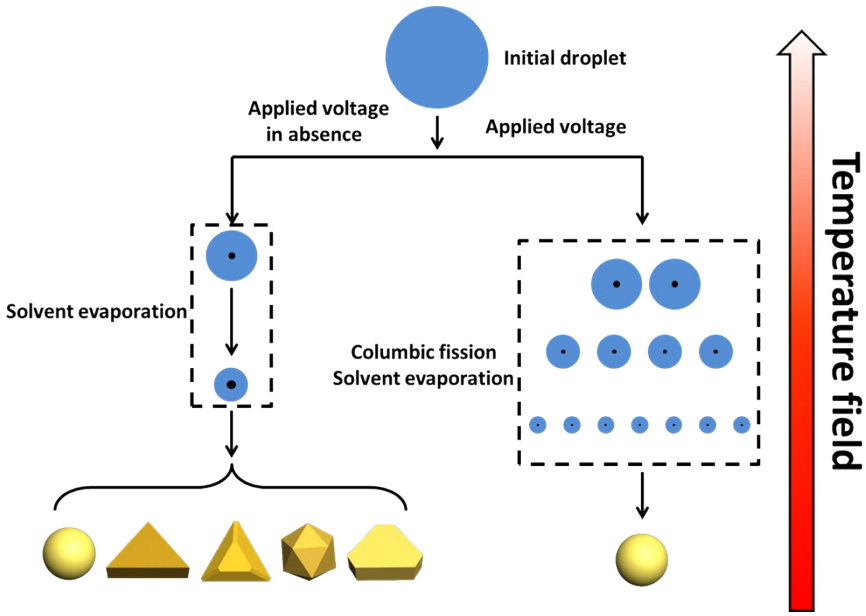

Figure S-5 Simple forming process of Au NCs.