Electronic Supplementary Information (ESI)

One-step seeded growth of Au nanoparticles with widely tunable sizes

Chuanbo Gao, John Vuong, Qiao Zhang, Yiding Liu and Yadong Yin*

Department of Chemistry, University of California, Riverside, California 92521, USA

Correspondence: <u>yadong.yin@ucr.edu</u>

Experimental

Materials. Polyvinylpyrrolidone (PVP, Mw 29,000), hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O), and potassium iodide (KI) were purchased from Acros. Trisodium citrate dihydrate (TSC, 99%), L-ascorbic acid, and sodium borohydride (NaBH₄, 99%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Characterization. Transmission electron microscopy (TEM) images were taken with a Philips Tecnai 12 transmission electron microscope operating at 120 kV. Scanning electron microscopy (SEM) images were taken with an XL30 FEG microscope operating at 10 kV of accelerating voltage. Ultraviolet-visible-near IR (UV-vis-NIR) spectra were measured with a Cary 500 UV-Vis-NIR spectrophotometer. Dynamic light scattering (DLS) was performed on a Beckman Coulter Delsa Nano C particle analyzer.

Supporting Data



Fig. S1 TEM image of Au seeds (~3 nm). Due to their small sizes, the Au seeds tend to aggregate during deposition on TEM grids. Therefore they were stabilized by 16-mercaptohexadecanoic acid (MHA) before making TEM samples to decrease aggregation during drying. Black arrows indicate primary Au seeds without aggregation, while white arrows indicate Au seeds which aggregated in spite of MHA protection.



Fig. S2 Gaussian size distribution of Au nanoparticles in water measured by DLS measurements. The Au nanoparticles were synthesized by injecting different amounts of the seed solution, as indicated in the figure, to the Au growth solution. The samples correspond to those in the main text. The size measured by DLS is slightly larger than that measured by TEM due to the presence of surfactant and hydration layer around Au nanoparticles in an aqueous solution.



Fig. S3 Relationship between the size of the Au nanoparticles measured by DLS (Fig. S2) and the volume of seeds in the synthesis.



Fig. S4 Effect of the concentration of HAuCl₄ on the seeded growth of Au nanoparticles. The Au nanoparticles were obtained by varying the addition amount of HAuCl₄ (0.25 M) in a typical synthesis, as indicated in the figure. The size distributions were obtained by DLS. It can be inferred that uniform Au nanoparticles can be synthesized in a wide range of HAuCl₄ concentrations. However, too high concentration leads to self-nucleation, indicated by multimodal distribution, as a result of insufficient capping of the Au salt by PVP and KI.



Fig. S5 Effect of the concentration of KI on the seeded growth of Au nanoparticles. The Au nanoparticles were obtained by varying the addition amount of KI (0.2 M) in a typical synthesis, as indicated in the figure. It can be inferred that a certain concentration of KI is required for the formation of uniform Au nanoparticles. Severe self-nucleation occurs when the concentration of KI is too low, due to an insufficient coordination of the Au salt to Γ . On the other hand, too high concentration of KI can also cause multimodal distribution of the particle size, which might result from inappropriate kinetics of the reduction reaction.



Fig. S6 Effect of the concentration of PVP on the seeded growth of Au nanoparticles. The Au nanoparticles were obtained by varying the addition amount of PVP (5 *wt.*%) in a typical synthesis, as indicated in the figure, and the amount of water was adapted to make the same volume of the reaction system. It can be inferred that an appropriate range of the concentration of PVP is required for the formation of uniform Au nanoparticles. Self-nucleation occurs when the concentration of PVP is too low, due to insufficient capping of the Au salt to PVP. On the other hand, PVP can act as a weak reducing agent, and therefore when its concentration is high enough it accelerates the reduction reaction of Au, leading to unfavorable reaction kinetics and the consequent self-nucleation.



Fig. S7 Electron diffraction (ED) patterns of different parts of a Au nanoparticle (190 nm). High crystallinity of the Au nanoparticle can be inferred. All the ED patterns show the feature of a polycrystalline structure, as diffractions from multiple sets of lattices can be observed from each ED pattern, which stem from the inherent polycrystalline nature of the initial Au seeds. However, it also shows that a common set of electron diffraction spots are shared by ED patterns obtained from different positions, indicating the presence of one dominantly large crystal domain and a lattice plane shared by multiple domains.