

Rapid synthesis of small silver nanocubes by mediating polyol reduction with a trace amount of sodium sulfide or sodium hydrosulfide

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Received 9 September 2006; in final form 20 October 2006

Available online 27 October 2006

Abstract

This Letter describes the fastest route to monodispersed silver nanocubes. By adding a trace amount of sodium sulfide (Na₂S) or sodium hydrosulfide (NaHS) to the conventional polyol synthesis, the reaction time was significantly shortened from 16–26 h to 3–8 min. By merely adjusting the reaction time, monodispersed silver nanocubes of 25–45 nm in edge length were rapidly and routinely produced on relatively large scales. These small nanocubes are of great interest for biomedical applications by way of generating gold nanocages with plasmon resonance peaks tunable to the near-infrared region through a galvanic replacement reaction.

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1. Introduction

The impact of metal nanostructures is continually increasing as we become more capable of producing them with well-controlled sizes and shapes for fine-tuning their properties and further development of emerging applications. It has been established that the optical and magnetic properties of a metal nanostructure are highly dependent not only on the size of the structure, but also on the shape [1–4]. Silver has been one of the most studied materials for nanostructures because of its superior performance in applications such as plasmonics and surface-enhanced Raman scattering (SERS). Silver nanostructures have been synthesized with a range of different shapes, including spheres, discs, rods, wires, stars, prisms, right bipyramids, and cubes [5–9]. Of these, single-crystal nanocubes appear to be the most exciting and useful structure particularly for the production of gold nanocages that hold great promise for biomedical applications such as optical imaging contrast enhancement and photothermal treatment [10]. In this case, silver nanocubes can serve as a sacrificial template to generate gold nanocages with tunable and controllable res-

onance peaks via a galvanic replacement reaction with chloroauric acid.

Our group has recently developed polyol synthesis as a simple, robust and versatile method for producing silver nanocubes as monodispersed samples [6]. In a typical polyol synthesis, silver atoms are formed by reducing AgNO₃ precursor with ethylene glycol through the following mechanism [11,12]:



Once the concentration of silver atoms has reached the supersaturation level, they will begin to nucleate and grow into silver nanostructures in the solution phase. Despite the demonstration of various methods for controlling polyol reduction [13–15,9,16], it is still a grand challenge to produce silver nanocubes on very large scales because of the length of time required for the formation of nanocubes from single-crystal seeds as well as the variation of reaction time between different batches. In general, a typical polyol synthesis may take anywhere from 16 to 26 h to form silver nanocubes.

In this work, we demonstrate that we can drastically improve the production rate of silver nanocubes by adding a trace amount of sodium sulfide (Na₂S) or sodium

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hydrosulfide (NaHS). Sulfide species are known to interact quite strongly with silver, such as the creation of Ag_2S when silver exists at concentrations above the μM level with trace sulfides in aqueous systems [17]. Furthermore, Ag_2S nanoparticles have been shown to catalyze the reduction of Ag^+ in a mechanism analogous to the autocatalytic reduction of silver clusters by drastically reducing the reduction potential compared to that of free Ag^+ [18,19]. At this enhanced rate, the evolution of silver nanocubes is dominated by the fast kinetic growth of single-crystal seeds. As a result, we were able to effectively limit the formation of twinned seeds and minimize the size distribution of resultant single-crystal cubes by creating a more simultaneous nucleation event, allowing all silver nanocubes to grow to the same size.

2. Experimental

2.1. Synthesis of silver nanocubes

In a typical synthesis, 6 mL ethylene glycol (EG, J.T. Baker, 9300-03) was heated under stirring with a Teflon-coated magnetic stirring bar for 1 h in a 24 mL glass vial. While the EG was heated, EG solutions containing AgNO_3 (48 mg/mL, Aldrich, 209139) and poly(vinyl pyrrolidone) (PVP, 20 mg/mL, MW \sim 55,000, Aldrich, 856568) were prepared. A 3 mM solution of Na_2S (Aldrich, 208043) or NaHS (Aldrich, 161527) in EG was also prepared 45 min prior to injection. Shortly after injecting 80 μL of the sulfide solution, 1.5 mL and 0.5 mL of the PVP and AgNO_3 solutions were sequentially injected (all with a micro-pipettor). As silver nitrate was added, the clear and colorless solution immediately turned purple-black, followed instantly by a transparent bright yellow color. The appearance of yellow color indicates the formation of small silver particles. After 2–3 min into the reaction, the solution darkened to an orange–yellow color and some silver nanoparticles were observed to deposit on the wall of the vial. After 6–8 min, the solution changed to an opalescent ruddy-brown and concurrently became opaque. If allowed to continue, the solution faded to a lighter, whitish-brown color but remained opaque. The final produce was diluted with acetone and collected by centrifugation, washed with water, and then suspended in water (4 mL) for future use. Since Na_2S and NaHS gave similar results, we will focus on Na_2S in the following discussion.

2.2. Synthesis of gold nanocages

In a typical synthesis, a fixed amount (100 μL) of the synthesized silver nanocubes was dispersed in 5 mL water containing 1 mg/mL PVP in a 50 mL flask under magnetic stirring and then heated to boil for 10 min. A specific amount (3 mL) of 0.2 mM HAuCl_4 aqueous solution was added to the flask through a syringe pump at a rate of 45 mL/h under magnetic stirring. The solution was heated for another 10 min until the color of the system was stable.

Once cooled down to room temperature, the sample was centrifuged and washed with saturated NaCl solution to remove AgCl and then with water several times to remove PVP and NaCl before characterization by SEM and TEM.

3. Results and discussion

The presence of sulfide anions greatly accelerated the polyol synthesis of silver nanocubes due to a dramatic increase in the reduction rate of silver ions. It is known that sulfide anions exist in three states in an aqueous medium depending on the pH of the solution as shown in Figure

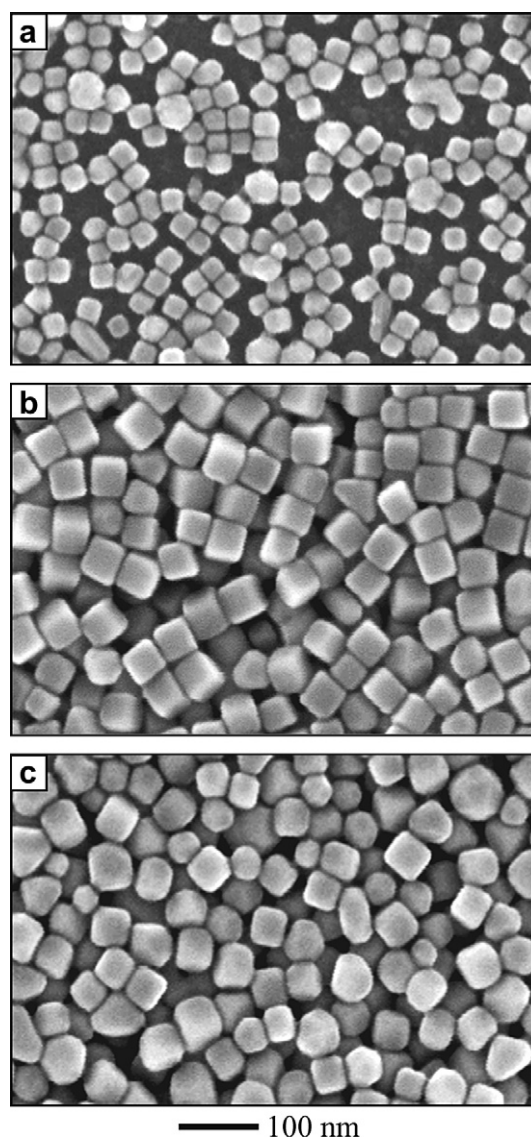


Fig. 1. SEM images of samples taken at different stages of a sulfide-assisted polyol synthesis: (a) 3 min after the injection of silver nitrate. The cubes had an edge length of 25 nm and the yellow solution had changed to darker orange-red. (b) The growth of the cubes peaks after 7 min into the reaction as the color changed to an opaque brown when the average edge length was increased to 45 nm. (c) If the reaction was allowed to continue (here after 30 min) etching would become dominant, stopping the growth and rounding the corners of the cubes and the color changed to a whitish-brown.

S1. In our experiments, the reaction medium was EG and the pH was close to 7 so both H_2S and HS^- species should be present independent of whether Na_2S or NaHS was used. The purple-black color developed upon injection of silver nitrate is indicative of Ag_2S nanoparticles, a catalyst for the reduction of Ag^+ ions [18,19]. During the synthesis, we could easily monitor the progress of the nanoparticle production through its color changes and then characterize the evolution of shape using scanning electron microscopy (SEM). Fig. 1 shows SEM images of samples taken at different stages of a typical Na_2S -mediated synthesis. The solution started darkening from a bright yellow to a deep orange after 3 min into the reaction due to the growth of small silver particles. Fig. 1a indicates that these particles were primarily cubic in profile with an average edge length of ~ 25 nm. Between 3 and 7 min, the cubes grow to 45 nm as shown in Fig. 1b, displaying a ruddy-brown color and opalescence. Once the cubes had reached 45 nm, most of the silver in the solution had been consumed and etching

overtook growth as the dominant force in this system, producing nanocubes with more rounded corners as shown in Fig. 1c. At the same time, the reaction solution turned into paler, whitish brown.

In order to better control the polyol synthesis for mass-production of monodispersed silver nanocubes, we also fine-tuned both the concentration of sulfide species and reaction temperature. Fig. 2 shows a series of SEM images of silver nanoparticles synthesized with different concentrations of Na_2S at various reaction temperatures demonstrating the delicate nature of reaction conditions. Balancing these two factors, we found that 28–30 μM was the ideal concentration of sulfide ions for the fast reduction of Ag^+ in the range of 150–155 $^\circ\text{C}$ with the optimal etching conditions (temperature dependent) to produce high quality, monodispersed silver nanocubes. The concentration of sulfide species available in the reaction is very important to the synthesis of high quality small nanocubes. If the concentration of sulfide species in the solution was under

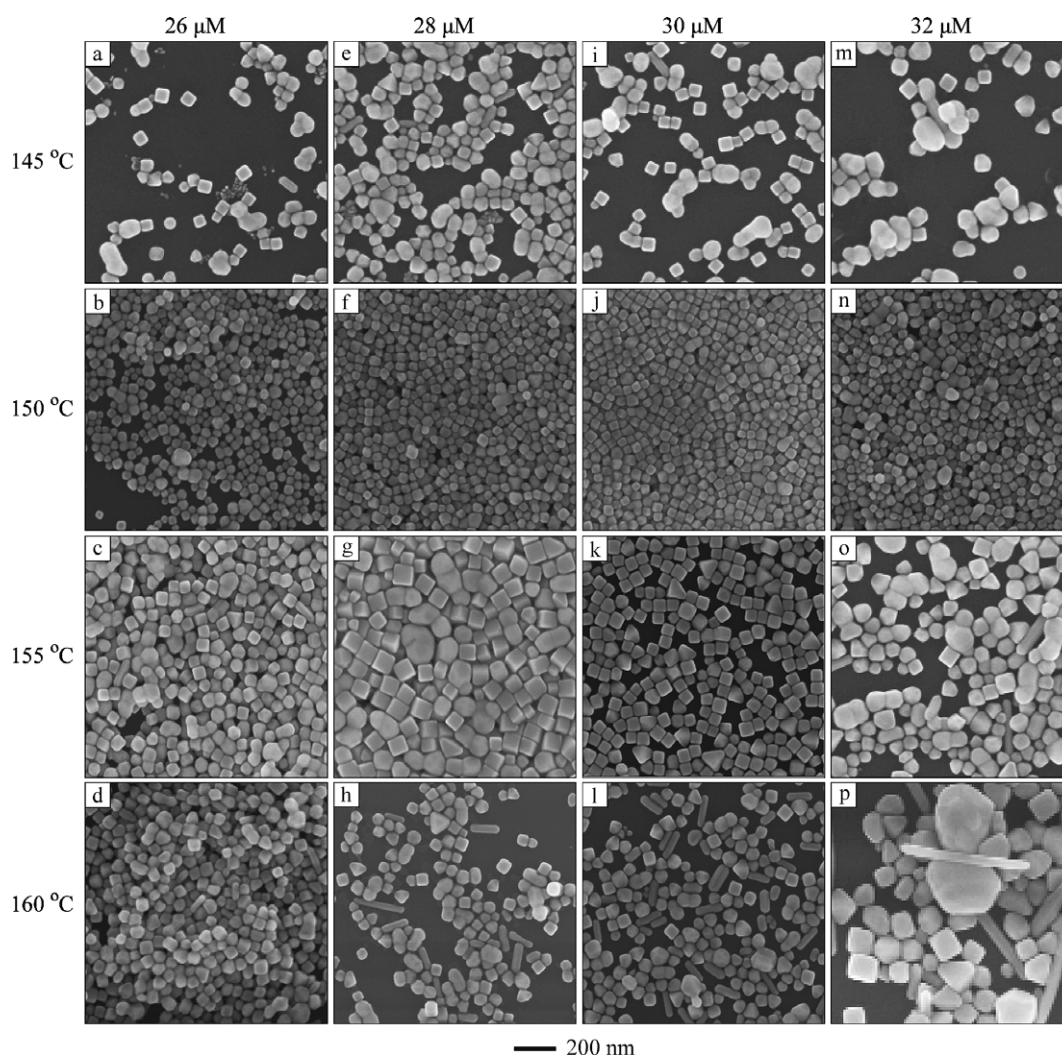


Fig. 2. SEM images showing a series of sodium sulfide concentrations at different temperatures (145–160 $^\circ\text{C}$). Each row shows reactions that were conducted in the same bath at the same temperature, side-by-side, and with the same precursor solutions. Each column was performed with the same sodium sulfide concentration (26–32 μM).

28 μM , the reduction was not fast enough to produce only the single-crystal nanocubes as there would be some round and twinned particles as seen in the images of Fig. 2a–d. When the concentration is higher than 30 μM , the rate of reduction was increase beyond that of etching, favoring the production of multiply-twinned particles, wires, and agglomerated particles along with some nanocubes (Fig. 2m–p). Above 40 μM , a significant portion of the Ag^+ ions would form complexes with the sulfur ions to create stable and insoluble silver sulfide species before rapid reduction could take place.

The sulfide-assisted synthesis was further optimized by adjusting the molar ratio between the repeating unit of PVP and silver. The series of reactions in Fig. 3 show a range of molar ratios from 0.75:1 to 2.7:1 for the repeating unit of PVP to silver nitrate. In our previous study, PVP has been shown to preferentially adsorb onto the $\{100\}$ surface of silver particles both stabilizing and protecting the small single-crystal seeds [20]. When there was not enough PVP to lower the $\{100\}$ surface energy of the small seeds sufficiently, the higher surface energy allowed for the production of twin defects [21], which can be seen as single-twinned bipyramids depicted in Fig. 3a. Conversely, if there was too much PVP in the system, it would indiscriminately protect all facets of the initial seeds including the thermodynamically favored multiply-twinned, quasi-spherical seeds. These twinned species would end up as dominant products as the ratio of PVP to silver atoms became

larger, see Fig. 3f. Therefore the ratio of PVP in the system is critical, and must be balanced in order to lower the surface energy of $\{100\}$ facets without overwhelming the seeds with a blanket layer that would prevent etching. In this system, the ratio of 1.9 repeating units of PVP to each silver nitrate yielded the most uniform nanocubes without appreciable twinned particles, see Fig. 3d.

In addition to scanning electron microscopy (Fig. 4a), the silver nanocubes were analyzed with transmission electron microscopy (TEM), electron diffraction, X-ray diffraction (XRD), and UV–Vis spectroscopy. Fig. 4b shows a TEM image, confirming that the particles are single-crystal cubes and the electron diffraction pattern in the inset indicates that the surface is bounded by $\{100\}$ planes as expected for a cube on a flat substrate. In addition, the XRD pattern (Fig. 4c) also suggests highly crystalline silver. Note that the (200) peak is significantly stronger relative to the (111) that dominates the JCPDS pattern mainly because the cubes were bound by $\{100\}$ facets and the powder standard were overwhelmed by the lower energy $\{111\}$ facets. This is expected and indicative that most nanocubes were aligned flat on the substrate with their $\{100\}$ planes being oriented upward. The UV–Vis spectra (Fig. 4d) of cubes produced via the sulfide-assisted synthesis are also in agreement with previous studies [13,14]: there was a blue-shift as the edge length of the cubes decreased and became closer to spherical.

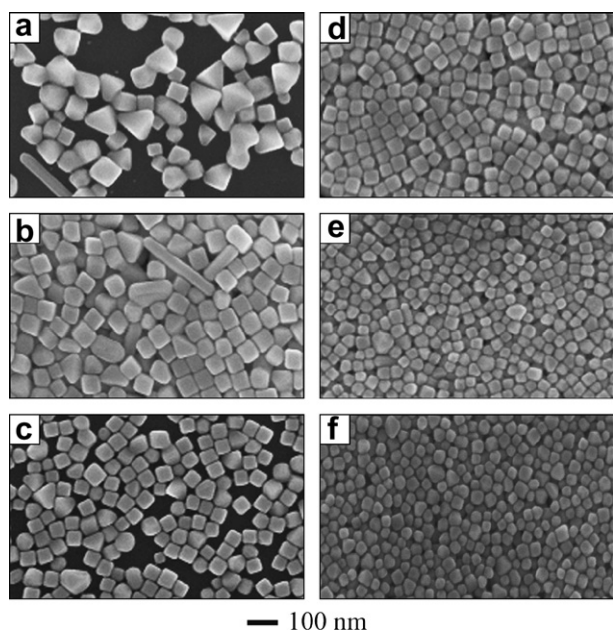


Fig. 3. SEM images of reactions containing increasing molar ratios between the repeating unit of PVP and silver nitrate. The ratios of PVP to silver nitrate were (a) 0.77, (b) 1.15, (c) 1.5, (d) 1.9, (e) 2.3, and (f) .7. We can see (a) single-twinned particles are produced by a lower ratio but at a much higher ratio (f), PVP indiscriminately protects all surfaces and produces multiply-twinned, quasi-spherical particles are synthesized along with cubes. (d) The ratio of 1.9 repeating units of PVP to each silver atom is ideal for the production of the 45 nm single-crystal cubes.

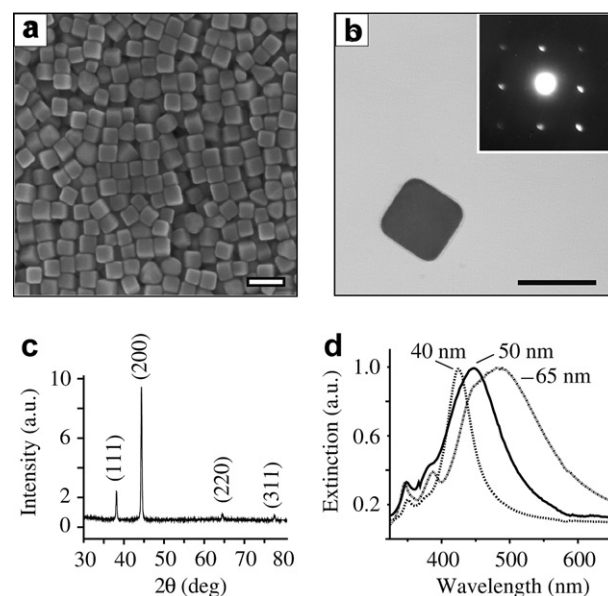


Fig. 4. (a) SEM image of silver nanocubes synthesized under the mediation of sodium sulfide (scale bar is 100 nm). (b) TEM image and electron diffraction pattern (inset) taken from a single nanocube, indicating that it is single crystal and enclosed by $\{100\}$ facet (scale bar is 50 nm). (c) XRD pattern taken from the same batch of silver nanocubes. All peaks can be indexed to face-centered cubic (fcc) silver, and the abnormal ratio of (200) peak to (111) peak can be ascribed to the texturing effect of these nanocubes on a flat substrate. (d) UV–Vis spectra taken from silver nanocubes of different sizes that were all synthesized under the mediation of sodium sulfide. The main peak blue-shifted as the size was reduced.

We further demonstrated the use of these silver nanocubes as sacrificial template to generate gold nanocages [6]. Although some sulfur ions likely to adsorb to the surface of as-synthesized cubes due to strong binding between sulfur and silver, this sulfur did not interfere with the galvanic replacement reaction between Ag and HAuCl_4 :

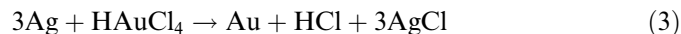


Fig. 5a shows typical SEM and TEM (inset) images of gold nanocages produced by reacting the as-prepared Ag nanocubes with HAuCl_4 in an aqueous medium. Similar to silver nanocubes synthesized using other methods, we were able to precisely tune the surface plasmon resonance (SPR) peaks of the hollow nanostructures to any position in the visible and near-infrared regions by controlling the volume of HAuCl_4 added to the reaction system. Fig. 5b shows the spectra taken from a set of samples, where the SPR peak had been tuned to 900 nm. As described in a number of recent studies [10,22,23], gold nanocages are emerging as a novel class of materials with great potential

as contrast enhancement agents and thermal therapeutic agents for cancer detection and treatment.

4. Summary

In this Letter, we report a new method that utilizes low concentrations of sulfide anions to manipulate the polyol process and thus increase both the rate of production and importantly the yield of monodispersed nanocubes of 25–45 nm in size. This synthesis is a stride toward the increased production of practical quantities of silver nanocubes without further processing or filtering for potential industrial applications. These small silver cubes are also significant for developing new biomedical technologies that employ gold nanocages. In addition, this work may help study some of the fundamental processes that can be manipulated to produce metal nanocrystals with well-controlled sizes and shapes that can fuel future developments in nanotechnology.

Acknowledgement

This work was supported in part by a TGIF grant from the UW, a research grant from the NIH (R01 CA120480-01), a subcontract from GEMSEC, Genetically Engineered Materials Science and Engineering Center, an NSF-funded MRSEC program at the UW, and a fellowship from the David and Lucile Packard Foundation. Y.X. is a Camille Dreyfus Teacher Scholar (2002–2007). Instrumentation was provided by the Nanotech User Facility (NTUF), a member of the National Nanotechnology Infrastructure Network (NNIN) supported by the NSF.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2006.10.095](https://doi.org/10.1016/j.cplett.2006.10.095).

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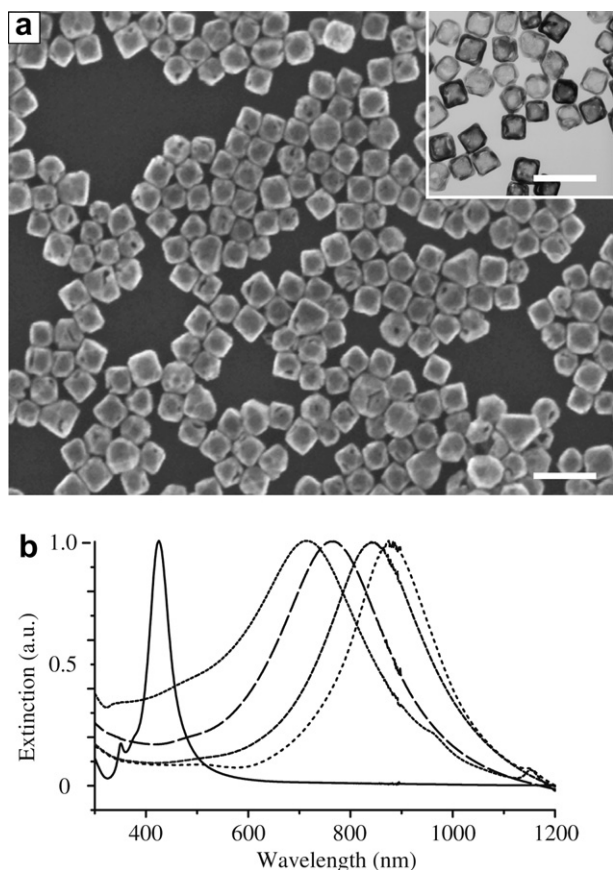


Fig. 5. (a) SEM and TEM (inset) images of a sample of gold nanocages produced from silver nanocubes that were, in turn, synthesized under the mediation of sodium sulfide (scale bars are 100 nm for both images). (b) UV-Vis extinction spectra taken from the silver nanocubes and gold nanocages. Note that silver nanocubes prepared using the sulfide-mediated route also yield high-quality gold nanocages with their surface plasmon resonance peaks tunable throughout the visible and near infrared regions by varying the volume of HAuCl_4 titrated (from left to right, 0, 1.2, 1.5, 2.0, and 2.5 mL, respectively).

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