Published in final edited form as:

Angew Chem Int Ed Engl. 2008 ; 47(50): 9653–9656. doi:10.1002/anie.200804634.

Facile Synthesis of Branched Au Nanostructures by Templating against a Self-Destructive Lattice of Magnetic Fe Nanoparticles**

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Abstract

This paper reports the demonstration of a reactive, self-destructive template for the facile synthesis of branched Au nanostructures. The template is a three-dimensionally porous lattice of uniform, magnetic Fe nanoparticles self-assembled *in situ* on the surface of a magnetic stir bar. Upon introduction of AuCl, Au atoms are formed in the voids among Fe nanoparticles due to the galvanic replacement reaction between Fe and Au⁺. The Au atoms then nucleate and grow into branched nanostructures under the confinement of Fe nanoparticles. As the replacement proceeds, Fe is consumed to gradually reduce the sizes and magnetic moments of the Fe nanoparticles. At a certain stage of the reaction, the template starts to fall apart to automatically release the branched Au nanostructures. We can routinely obtain Au multipods as pure samples via selective dissolution of the remaining Fe nanoparticles with sulfuric acid. The as-prepared Au multipods show strong absorption in the near infrared region and exhibit distinctive oxidative etching behaviors in different acidic solutions due to the presence of crystal defects and lattice distortions.

Keywords

gold; multipods; iron nanoparticles; galvanic replacement

Controlling the shape or morphology of metal nanostructures has attracted considerable attentions because it provides an effective means for tuning the electronic, optical, magnetic, and catalytic properties.[1] In particular, synthesis of Au nanostructures having controllable shapes has become a major subject of extensive research over the past decade owing to their unique optical properties known as localized surface plasmon resonance (LSPR).[2] Most of the published work, however, has focused on the synthesis of simple Au nanostructures such as spheres, cubes, plates, rods, and among others.[3] Only in recent years, there are some demonstrations on the chemical syntheses of complex, branched Au nanostructures.[4,5] Gold nanostructures with a branched morphology would be ideal for applications in areas such as catalysis, sensing, and flexible electronics. Calculations by the discrete dipole approximation (DDA) and finite difference time domain (FDTD) methods have shown that the tips of a branched Au nanostructure can exhibit strong enhancement of electromagnetic field, which is of great importance to applications such as surface-enhanced Raman scattering (SERS).[5] However, unlike semiconductor nanocrystals in which the branched, anisotropic growth can be naturally induced by polymorphism (i.e., switching between zinc blend and wurtzite structures),[6] formation of branched nanostructures from a face-centered cubic (*fcc*) metal has proven to be difficult and very sensitive to experimental conditions.

**This work was supported in part by research grants from the NSF (DMR, 0451788 and 0804088) and a Director's Pioneer Award from the NIH (5DP1OD000798). P.H.C.C. was supported in part by the Fulbright Program and the Brazilian Ministry of Education (CAPES).

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Although branched[4,5] or star-shaped[7] Au nanoparticles have been obtained through the overgrowth of Au nanocrystallite seeds, the cores are usually big and the branching tips are relatively short in most cases. To the best of our knowledge, it remains a grand challenge to develop a rational and effective method for preparing highly branched Au nanostructures in high yields.

Template-directed synthesis, a straightforward route to nanostructures with pre-defined shapes, has been widely used to generate various inorganic nanostructures in high yields.[8] In general, the template can serve as a scaffold, within (or around) which a different material is produced and shaped into a nanostructure with its shape or morphology complementary to that of the template. As limited by the availability of templates, this approach has mainly been applied to the preparation of nanostructures in a zero- or one-dimensional morphology. In many cases, the templates have to be removed by etching or calcination in order to harvest the final products. This last step is generally slow and difficult due to diffusion problems and often may cause damages to the desired nanostructures. In this communication, we demonstrate a reactive and self-destructive template that not only participates in the chemical reaction but also spontaneously falls apart at a certain point to release the products. The template is a three-dimensionally porous lattice consisting of uniform Fe nanoparticle self-assembled on a magnetic stir bar.[9] When AuCl is added, there will be a galvanic replacement reaction between Fe and Au⁺, leading to the formation of highly branched Au nanostructures in the void space of the lattice.[10] As the Fe nanoparticles are reduced in size due to the replacement reaction, their magnetic moments are also reduced accordingly and eventually the lattice falls apart to release the Au nanostructures. This approach is somewhat similar to those reported in previous studies that used the voids in crystalline lattices of latex spheres to produce inverse opals[11] or large anisotropic colloidal particles.[12] However, there are a number of major differences that deserve to be highlighted: *i*) the current system works on a scale almost 100 times smaller than those based on latex spheres; *ii*) the template itself is also directly involved in the reaction; *iii*) the template spontaneously disassembles during the synthesis; and *iv*) the final product shows a highly branched morphology.

Figure 1 shows a schematic illustration of our strategy for generating branched Au nanostructures. The key component is a three-dimensional lattice of uniform magnetic Fe nanoparticles, which spontaneously forms on the surface of a magnetic stir bar. To increase the solubility of AuCl in the solvent, we complex it with oleyamine (OLA).[13] When the AuCl(OLA) complex is introduced into the reaction system, it quickly diffuses into the void space among the Fe nanoparticles and reacts with elemental Fe through the galvanic replacement reaction:

The resultant Au atoms then start to nucleate and gradually fill the voids as the reaction proceeds. As shown in eq.(1), consumption of one Fe atom can produce three Au atoms. So the volume of Au nanostructure inside each void is expected to expand much faster than the volume shrinkage associated with the Fe nanoparticles. This net expansion in volume is expected to push the Fe nanoparticles apart, weakening the magnetic attraction between the Fe nanoparticles. Meanwhile, the magnetic moments of the Fe nanoparticles are gradually reduced during the replacement reaction as a result of Fe consumption.[14] At a certain point, the lattice of Fe nanoparticles falls apart into the reaction solution, accompanied by releasing of the formed Au multipods. Samples of pure Au multipods could be obtained by

selectively dissolving the remaining Fe nanoparticles with H_2SO_4 , together with centrifugation.

Figure 2a shows a typical low-magnification TEM image of the as-prepared Au multipods, indicating that there was essentially no Fe nanoparticles left in the sample. TEM image at a higher magnification (Figure 2b) clearly indicates that most of the Au multipods had a complex, branched structure. The thicknesses of the arms were in the range of 8–10 nm, while the overall sizes of these multipods could vary from 30 to 100 nm due to the diversity of their geometries. High-resolution TEM images (Figure 1c and Figure S1) taken from a single multipod indicate that the Au multipod contained crystal defects and lattice distortions. Figure 1d shows an X-ray diffraction (XRD) pattern taken from the same sample of Au multipods, where all the peaks could be indexed to pure *fcc* Au (JCPDS 04-0784).

To experimentally decipher the formation mechanism for the Au multipods, we used TEM to check the intermediate products obtained at different stages of a typical synthesis. Before the addition of $\text{AuCl}(\text{OLA})$ complex, the Fe nanoparticles mainly existed as black aggregates on the magnetic stir bar as indicated by the photograph in the inset of Figure 3a. Figure 3a shows a TEM image of the Fe nanoparticles that were released from the stir bar by ultrasonic treatment for a few minutes, followed by quick drop-casting on a copper grid. The Fe nanoparticles were more-or-less spherical in shape and had a uniform diameter of 15 ± 1.6 nm. Note that the actual size of these Fe nanoparticles should be slightly smaller than the size measured from the TEM image because the surfaces of these nanoparticles were inevitably oxidized during TEM sample preparation. After adding $\text{AuCl}(\text{OLA})$ complex to the solution and stirring for 2 min, we observed that some black products started to disassemble from the stir bar and diffuse into the solution. The initially disassembled products were mainly made up of some small chunks (Figure S2), and each chunk was composed of Fe nanoparticles and Au multipods in a rather compact structure (Figure 3b). Obviously, the Au multipods were formed in the void space among Fe nanoparticles, suggesting that the Fe nanoparticles served as not only a reducing agent but also a template for the formation of Au multipods. After stirring the solution for another 20 min (Figure 3c), more black chunks were separated from the stir bar and most of them further disassembled into discrete Fe nanoparticles, resulting in the formation of isolated Au multipods. At the same time, the solution gradually changed into a deep black color (inset of Figure 3c) due to the complete disassembly of Fe nanoparticles. Figure 3d shows TEM image of the final product after washing with 1 M $\text{H}_2\text{SO}_4/\text{C}_2\text{H}_5\text{OH}$. The remaining Fe nanoparticles had been completely removed, leaving behind Au multipods with essentially the same branched morphology. These experimental observations agree well with the schematic illustration shown in Figure 1.

Both the aggregate state of Fe nanoparticles and the oxidation state of Au ions played critical roles in the formation of Au multipods. In the synthesis of Fe nanoparticles, some of them ($\sim 10\%$ by wt.) remained in the solution and did not aggregate on the stir bar (Figure S3), presumably due to their smaller sizes. When these non-aggregate Fe nanoparticles were used as a reactant and mixed with $\text{AuCl}(\text{OLA})$ complex under the same condition as the synthesis of Au multipods, only Au nanoparticles were obtained and no branched structures were observed (Figure S4). This result confirmed that only the Fe nanoparticles in an aggregated state could act as a template to generate Au multipods. Otherwise, Au nanoparticles were produced via direct galvanic replacement of suspended Fe nanoparticles and the Au^+ ions in the solution. In another experiment, when AuCl was replaced with the same molar amount of HAuCl_4 to react with a three-dimensional lattice of Fe nanoparticles, some small Au nanoparticles and L-shaped bipods were obtained (Figure S4). In this case, the oxidation of one Fe atom to Fe^{3+} only generated one Au atom so that the net volume expansion for the system should be negligible. As a result, the Au nanostructures formed in the voids could

not effectively push and loosen the surrounding Fe nanoparticles and grow into a multipod shape. The L-shaped bipods might be formed through the galvanic replacement between Au^{3+} and Fe along the surface of some active Fe nanoparticles. Except for the aggregate state of Fe nanoparticles and the oxidation state of Au ions, other variables such as solvent did not have much influence on the formation of Au multipods. In fact, Au multipods could be readily obtained when tetrahydrofuran (THF) or dichloromethane (DCM) was used as the solvent, respectively (Figure S5).

Because the as-synthesized Au multipods contained defects and lattice distortions, they were found to show different oxidative etching behaviors in various acids. Figures 4a and 4b show TEM images of Au multipods after they had been washed with 1 M $\text{HNO}_3/\text{C}_2\text{H}_5\text{OH}$ and 1 M $\text{HCl}/\text{C}_2\text{H}_5\text{OH}$ for 5 min, respectively. No obvious morphological change was observed when the multipods were washed by H_2SO_4 (Figure 3d) or HNO_3 (Figure 4a), indicating that these two acids could not be combined with oxygen (from air) to form etchants for the Au multipods. However, the Au multipods could be etched by 1 M $\text{HCl}/\text{C}_2\text{H}_5\text{OH}$ to become nanoparticles (Figure 4b). The same result was also obtained by replacing HCl with a mixture of equal molar amounts of HNO_3 and NaCl. The different etching behaviors of Au multipods in different acids can be attributed to the fact that Cl^- can act as a ligand to form complexes with Au ions (e.g., AuCl_2^- or AuCl_4^-), while both NO_3^- and SO_4^{2-} ions have no such capacity. Previous studies have shown that multiply twinned metal nanostructures are susceptible to oxidative etching due to the high density of defects on the surface and thus high reactivity. To observe oxidative etching, a ligand is generally required to enhance the etching power of oxygen.[15] Since the Au multipods synthesized using the present method contained defects and lattice distortions, they are expected to exhibit higher reactivity than the single crystalline Au nanostructures. High-resolution TEM imaging indicates that the Au nanoparticles left behind from HCl etching were single crystals (Figure S6), confirming that the oxidative etching mainly attacked the defect zones on the Au multipods. The Au nanoparticles were spherical in shape and their average diameters were a little bigger than the sizes of the pods, suggesting that an Ostwald ripening process might be involved during the oxidative etching process.

Figure 4c shows the extinction spectra taken from Au multipods dispersed in hexane after washing with different acids. The spectral profile of the Au multipods washed by HNO_3 was similar to that washed by H_2SO_4 . The peak around 520 nm could be ascribed to the transverse mode while the broad peak in the near-infrared (NIR) region was due to the longitudinal mode of the rod-like arms of the multipods.[16] When the multipods were washed by HCl, only the 520 nm peak appeared, indicating the formation of Au spherical nanoparticles. The vis-NIR spectra were consistent with our TEM observations of the corresponding samples. The morphological changes of Au multipods in different acids, coupled with the variations of their absorption spectra, could also be easily appreciated from their colors, as shown by the photographs in Figure 4d.

In summary, we have demonstrated a simple, template-directed method for generating Au multipods. The template is a three-dimensional lattice self-assembled *in situ* from magnetic Fe nanoparticles on a magnetic stir bar. When reacted with a $\text{AuCl}(\text{OLA})$ complex, the void spaces among the Fe nanoparticles were gradually filled with Au due to the galvanic replacement reaction between Fe and Au^+ . During this reaction, both the volume expansion associated with Au/Fe replacement and the consumption of Fe gradually weakened the attraction between the Fe nanoparticles. As a result, the lattice of Fe nanoparticles spontaneously fell apart at a certain stage of the reaction to automatically release the Au multipods. The remaining Fe nanoparticles could be readily removed by washing the samples with acids such as H_2SO_4 or HNO_3 . Unlike the star-shaped gold nanoparticles reported in previous publications, these Au multipods were mainly composed of branched

arms and showed a broad absorption peak in the NIR region. This interesting optical property suggests that these Au multipods might have potential use in applications such as NIR-based photothermal therapy, chemical sensing, and fabrication of flexible and conductive composite materials.

Experimental Section

The Fe nanoparticles were synthesized via thermal decomposition of $\text{Fe}(\text{CO})_5$ in octadecene (ODE) with OLA as a capping agent.[9b] Most of the Fe nanoparticles (~90% wt.) were attached to the magnetic stir bar used for the synthesis, and they were transferred to a 10 mL glass vial which contained 3 mL of chloroform (see Supporting Information for details). In a typical synthesis of Au multipods, a 10 mL stock solution of 0.01 M $\text{AuCl}(\text{OLA})$ complex was prepared by dissolving 0.0233 g AuCl powder in a mixture of 9.67 mL of chloroform and 0.33 mL of OLA.[13] 2 mL of this solution was slowly injected into the 10 mL glass vial that contained aggregates of Fe nanoparticles on the stir bar. After adding the $\text{AuCl}(\text{OLA})$ solution, the stir bar started to stir at a rate of 300 rpm and maintained for 20 min. During this process, the Fe nanoparticles were gradually released from the stir bar and the chloroform solution gradually became black. A mixture of Au multipods and suspended Fe nanoparticles was collected by centrifuging after adding an equal volume of acetone. The product was then dispersed in 5 mL of hexane and treated with an equal volume of 1 M H_2SO_4 solution in absolute $\text{C}_2\text{H}_5\text{OH}$ to remove Fe nanoparticles for three times. Pure Au multipods were collected by centrifugation and subsequently dispersed in hexane for further characterization.

References

- Recent reviews: a) Xia Y, Xiong Y, Lim B, Skrabalak SE. *Angew Chem Int Ed*. 2008 in press. b) Tao AR, Habas S, Yang P. *Small*. 2008; 4:310. c) Jun YW, Choi JS, Cheon JW. *Angew Chem*. 2006; 37:32. *Angew Chem Int Ed*. 2006; 45:3414. d) Burda C, Chen X, Narayanan R, El-Sayed MA. *Chem Rev*. 2005; 105:1025. [PubMed: 15826010]
- Recent reviews: a) Hu M, Chen J, Li ZY, Au L, Hartland GV, Li X, Marquez M, Xia Y. *Chem Soc Rev*. 2006; 35:1084. [PubMed: 17057837] b) Eustis S, El-Sayed MA. *Chem Soc Rev*. 2006; 35:209. [PubMed: 16505915] c) Daniel MC, Astruc D. *Chem Rev*. 2004; 104:293. [PubMed: 14719978] d) Liz-Marzán LM. *Mater Today*. 2004; 7:26. e) El-Sayed MA. *Acc Chem Res*. 2001; 34:257. [PubMed: 11308299]
- See, for example, Murphy CJ, Sau TK, Gole A, Orendorff CJ. *MRS Bull*. 2005; 30:349.
- a) Kuo CH, Huang MH. *Langmuir*. 2005; 21:2012. [PubMed: 15723503] b) Wu HY, Liu M, Huang MH. *J Phys Chem B*. 2006; 110:19291. [PubMed: 17004782] c) Zou X, Ying E, Dong S. *Nanotechnology*. 2006; 17:4758. d) Xie J, Lee JY, Wang DIC. *Chem Mater*. 2007; 19:2823.
- a) Hao E, Bailey RC, Schatz GC, Hupp JT, Li S. *Nano Lett*. 2004; 4:327. b) Bakr OM, Wunsch BH, Stellacci F. *Chem Mater*. 2006; 18:3297.
- See, for example, a) Manna L, Milliron DJ, Meisel A, Scher EC, Alivisatos AP. *Nat Mater*. 2003; 2:382. [PubMed: 12764357] b) Milliron DJ, Hughes SM, Cui Y, Manna L, Li J, Wang LW, Alivisatos AP. *Nature*. 2004; 430:190. [PubMed: 15241410] c) Mokari T, Rothenberg E, Popov I, Costi R, Banin U. *Science*. 2004; 304:1787. [PubMed: 15205530] d) Peng ZA, Peng X. *J Am Chem Soc*. 2002; 124:3343. [PubMed: 11916419]
- a) Nehl CL, Liao H, Hafner JH. *Nano Lett*. 2006; 6:683. [PubMed: 16608264] b) Yamamoto M, Kashiwagi Y, Sakata T, Mori H, Nakamoto M. *Chem Mater*. 2005; 17:5391. c) Sau TK, Murphy CJ. *J Am Chem Soc*. 2004; 126:8648. [PubMed: 15250706] d) Chen S, Wang ZL, Ballato J, Foulger SH, Carroll DL. *J Am Chem Soc*. 2003; 125:16186. [PubMed: 14692749]
- See, for example, a) Hulteen JC, Martin CR. *J Mater Chem*. 1997; 7:1075. b) Martin CR. *Acc Chem Res*. 1995; 28:61.
- See, for example, a) Dumestre F, Chaudret B, Amiens C, Renaud P, Fejes P. *Science*. 2004; 303:821. [PubMed: 14764874] b) Peng S, Wang C, Xie J, Sun S. *J Am Chem Soc*. 2006;

- 128:10676. [PubMed: 16910651] c) Park SJ, Kim S, Lee S, Khim ZG, Char K, Hyeon T. J Am Chem Soc. 2000; 122:8581.
10. Au L, Lu X, Xia Y. Adv Mater. 2008; 20:2517. [PubMed: 18725963]
11. See, for example, a) Velev OD, Jede TA, Lobo RF, Lenhoff AM. Nature. 1997; 389:447. b) Holland BT, Blanford CF, Stein A. Science. 1998; 281:538. [PubMed: 9677191] c) Wang Y, Angelatos AS, Caruso F. Chem Mater. 2008; 20:848.
12. Li F, Wang ZY, Stein A. Angew Chem. 2007; 119:1917. Angew Chem Int Ed. 2007; 46:1885.
13. Lu X, Tuan HY, Korgel BA, Xia Y. Chem Eur J. 2008; 14:1584.
14. Huber DL. Small. 2005; 1:482. [PubMed: 17193474]
15. a) Wiley B, Herricks T, Sun Y, Xia Y. Nano Lett. 2004; 4:1733. b) Xiong Y, Chen J, Wiley B, Xia Y. J Am Chem Soc. 2005; 127:7332. [PubMed: 15898780] c) Zettsu N, McLellan JM, Wiley B, Yin Y, Li ZY, Xia Y. Angew Chem. 2006; 118:1310. Angew Chem Int Ed. 2006; 45:1288.
16. See, for example, a) Nehl CL, Hafner JH. J Mater Chem. 2008; 18:2415. b) Link S, Mohamed MB, El-Sayed MA. J Phys Chem B. 1999; 103:3073.

Figure 1.

Schematic detailing four major steps involved in the formation of Au multipods by templating against a self-destructive lattice of Fe nanoparticles: a) Au nucleates in the voids of aggregated Fe nanoparticles through a replacement reaction between Fe and Au^+ ; b) the Au evolves into multipods under the confinement of Fe nanoparticles as the reaction proceeds; c) the lattice of Fe nanoparticles falls apart at a certain point as the volume of Au structures expand and the magnetic moments of individual Fe nanoparticles are reduced; and d) Au multipods are harvested and purified by dissolving the remaining Fe nanoparticles with H_2SO_4 .

Figure 2.

a, b) TEM images of the as-prepared Au multipods at two different magnifications; c) high-resolution TEM image of a typical Au multipod (see Figure S1 for details); and d) XRD pattern taken from the Au multipods.

Figure 3.

TEM images of samples obtained at different stages of the replacement reaction: a) Fe nanoparticles before the reaction that were released from the stir bar by sonication; b) a black chunk initially disassembled from the stir bar after adding AuCl(OLA) and stirring for 2 min; c) completely disassembled Fe nanoparticles and Au multipods after continuous stirring for 20 min; and d) Au multipods purified by washing the sample with 1 M H₂SO₄/C₂H₅OH solution to selectively dissolve the remaining Fe nanoparticles.

Figure 4.

a, b) TEM images of the Au multipods after washing with 1 M $\text{HNO}_3/\text{C}_2\text{H}_5\text{OH}$ and 1 M $\text{H}_2\text{SO}_4/\text{C}_2\text{H}_5\text{OH}$, respectively. c, d) Extinction spectra and digital photos of Au multipods dispersed in hexane after washing with 1 M $\text{H}_2\text{SO}_4/\text{C}_2\text{H}_5\text{OH}$, 1 M $\text{HNO}_3/\text{C}_2\text{H}_5\text{OH}$ and 1 M $\text{HCl}/\text{C}_2\text{H}_5\text{OH}$. Note that the spectra in Figure 4c were vertically shifted for display purpose, so the peak height did not match with the absorbance.