Metal Nanoparticles of Various Shapes

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Abstract

Metal nanoparticles have received considerable attention due to their unusual properties and promising applications in electronics, photonics and biochemical sensing and imaging. This review presents an introduction to the synthesis of metal nanoparticles, especially the gold nanoparticles in shape of rod. The growth mechanism of gold nanorods and optical properties of metallic nanoparticles is also discussed.

1. Introduction

The physical and chemical properties of materials are mostly determined by the motion of electrons. When the motion of electrons is confined in nanometer length scale (1-100nm), which happens in nanomaterials, unusual effects are observed [1]. As of fine metal particles, gold nanospheres of diameter ~100 nm or smaller appear red when suspended in transparent media [2] and gold nanoparticles of diameter less than ~3 nm can catalyze chemical reactions [3,4]. In addition, the optical properties of silver and gold nanoparticles are tunable throughout the visible and near-infrared region of spectrum as a function of nanoparticle size, shape, aggregation state and local environment [2]. Additionally, gold nanoparticles also show intense surface plasmon resonance absorption, leading to an absorption coefficient orders of magnitude larger than strongly absorbing dyes and thus higher detection sensitivity. However, the absorption strength of metal nanospheres only is weakly dependent on its size, which limits its application in sensing. When anisotropy is added to the nanoparticles, such as nanorods, the surface plasmon resonance absorption is not only enhanced but also strongly dependent on the size of such rods (tunable as a function of aspect ratio). [5]
This makes gold nanorods potentially useful as sensors.\textsuperscript{[1]}

There are many different ways to synthesize metal nanoparticles and can be categorized into two general strategies\textsuperscript{[6]}: Bottom up method and top down method. Bottom up method means that the atoms are assembled to nanostructures, and top down method means that materials are “cut” into small pieces in nanoscale. Common top down techniques are photolithography and electron beam lithography. Photolithography is limited by the diffraction limit of the wavelength of lasers. Electron beam lithography is not limited by such diffraction limit and recent instrument can produce nanostructures smaller than 10 nm. Both of these two methods can only create a 2-dimensional structure in a single step. Common bottom up method are nanosphere lithography, templating, chemical, electrochemical, sonochemical, thermal and photochemical reduction techniques.

A useful way to make gold and silver nanorods and nanowires of controllable aspect ratio is seed-mediated growth method. This method includes two steps: growth of “seed” particles and growth of such seed into rods. When changing some crucial growth parameters in such seed-mediated growth method, nanoparticles of shapes other than sphere and rod can be easily got. This indicates this method is a possible option to synthesize gold nanoparticles of other shapes.

2. Synthesis of Metal Nanoparticles (Gold)

2.1 Nanosphere lithography\textsuperscript{[7]}

This method is an inexpensive synthetic procedure to generate arrays of noble metal nanoparticles. Polystyrene nanospheres are drop-coated onto piranha-cleaned and base-treated glass substrates and are allowed to dry, forming a hexagonal closed-packed monolayer or spheres. Such monolayer can act as a template or deposition mask for metal deposition. Metal is then deposited onto and in between the spheres by thermal evaporation, creating particles in the voids of the polystyrene spheres. Following metal deposition, the samples are sonicated in ethanol to remove
the polystyrene nanosphere mask, leaving an array of triangular shaped metal nanoparticles on the substrate, as shown in Fig. 1. This generates monodisperse, uncapped nanoparticles in geometric arrays over a large surface area of the substrate. Also, it is possible to release the triangular nanoparticles into solution by adding surfactant and sonicating the sample to remove the particles from the substrate to form isolated particles. [8]

![Deposition of polystyrene spheres on substrate, thermal evaporation of bulk gold and removal of polystyrene spheres to leave triangular gold nanoparticles (ref. 9)](image)

**2.2 Citrate Reduction Method** [10]

This method is first reported by Turkevitch in 1951 and is popularly used to generate spherical gold nanoparticles. Simply put, gold salt, reducing agent and citrate are stirred in water and metal nanospheres are reduced. During the process, the temperature, the ratio of gold to citrate, and the order of addition of the reagents control the size distribution of gold nanospheres. The most popular one for a long time has been that using sodium citrate reduction of HAuCl₄ in water.

**2.3 Two Phase Reactions** [5, 10]

This method has been widely used to produce small nanoparticles (1-5 nm) with
narrow dispersity. A gold-thiol bond is used to stabilize these particles. Samples generated with this method are stable for long periods of time when dry and can be repeatedly isolated and redissolved in common organic solvents without irreversible aggregation or decomposition. In synthesis, the gold salt is first transferred to the organic phase using a suitable surfactant. Then sodium borohydride (NaBH₄) is added to the aqueous phase. The formation of nanoparticles is monitored by the generation of the orange to deep brown color in the organic phase:

\[
\text{AuCl}_4^- (aq) + N(C_8H_{17})_4^+ (C_6H_5Me) \rightarrow \text{N}(C_8H_{17})_4^+ \text{AuCl}_4^- (C_6H_5Me)
\]

\[
m\text{AuCl}_4^- (C_6H_5Me) + nC_{12}H_{25}SH (C_6H_5Me) + 3m e^- \rightarrow 4m Cl^- (aq) + [\text{Au}_{n/m}(C_{12}H_{25}SH)]_{n/m} (C_6H_5Me)
\]

(ref. 10)

### 2.4 Inverse Micelles

This method can be used to generate many different sizes and shapes of nanoparticles. Inverse micelles use surfactants to create small pockets of a water phase in an organic solvent, where the surfactant has a polar group that faces the aqueous phase, and the tail faces the organic phase. The most important part to generating single crystal, monodisperse nanoparticles using this method is to use a metal salt conjugated to the surfactant prior to the addition of the reducing agent. Exchange between different water volumes, generating good monodispersity of nanoparticles, is permitted if using this method. Furthermore, this method can also be used for many other materials.

### 3. Synthesis of Metallic Nanorods

A popular method to make metallic nanorods is seed-mediated growth method. The following will describe how to synthesize gold nanorods with tunable aspect ratio. In this seed-mediated growth procedure, metal salts are reduced initially with a strong reducing agent to seed particles. Subsequent reduction of more metal salt with a weak reducing agent, with the presence of structure-directing additives results in the
controlled formation of nanorods of specific aspect ratio.

The first step is to produce seed particles. Metal salts are reduced in water, in air, at room temperature, with strong reducing agent (sodium borohydride) to yield 3.5-4 nm spherical “seed” particles. Such seed particles, in shape of faceted nanospheres, are single crystalline [11] and can be capped with several surface groups, such as citrate, surfactants, etc., which can be present during the reaction. As the seeds “age”, growth solutions containing more metal salt, a structure-directing agent, and a weak reducing agent are prepared in a separate flask. The weak reducing agent is usually ascorbic acid (vitamin C), and it is not capable of fully reducing the metal salt to elemental metal at room temperature. However, upon addition of the seeds the reaction probably takes place on the surface of the seed and can be autocatalytic, thus producing larger nanoparticles. The structure-directing agent is crucial to obtaining nanorods. Murphy etc. found that cetyltrimethylammonium bromide (CTAB) is uniquely suited to produce rods and gold nanorods starting from ~3.5-4 nm spherical seeds can grow out to 20-30 nm wide and up to 600 nm long, resulting in the aspect ratio ranging from ~2 to ~25.. The basic approach is shown in Fig. 2. More details are described in ref. 16.

Some synthetic parameters on nanorod production can greatly influence the result of the growth. The smaller seeds produce higher-aspect ratio nanorods. [12] (Fig. 3) The concentration of CTAB is critical for nanorod growth: 0.1 M concentrations are required. Additive metal ions are also important for nanorod growth. For instance, the presence of ~5% Ag+ raises the yield of gold nanorods to nearly 100% and the yield is only ~20-40% in the absence of Ag+. [13] However, the presence of Ag+ can reduce the highest aspect ratio that can be obtained. The highest aspect ratio gold nanorods obtainable with silver ion is about 6, compared to ~25 in the absence of silver. Therefore, there is a trade-off under the presence of Ag+. Moreover, the slight changes in reaction conditions lead to other shapes of gold nanoparticles, such as blocks, cubes and tetrapods. [14] This might be a possible way to synthesize gold nanoparticles of different shapes other than rods. (Fig. 4)
I. Synthesis of seed

\[ 2.5 \times 10^{-4} \text{ M HAuCl}_4 + 2.5 \times 10^{-4} \text{ M Na-citrate} \]

\[ \text{Gold nanoparticle seeds} \quad (\sim 4 \text{nm diameter}) \]

II. Stock solution

\[ \text{Stock solution} \quad 2.5 \times 10^{-4} \text{ M HAuCl}_4 + 0.1 \text{ M CTAB} = \]

\[ \text{Addition of Ascorbic acid} \]

\[ \text{Reduction of Au}^{3+} \text{ to Au}^{1+} \text{ results in disappearance of color} \]

II. Three step protocol for nanorod synthesis

1. **Step A**
   - Add 1 mL of A to 1 mL seed + 9 mL of stock solution

2. **Step B**
   - 1 mL A + 9 mL of stock solution

3. **Step C**
   - 10 mL B + 90 mL stock

Fig. 2 Seed-mediated growth approach to making gold nanorods of controlled aspect ratio. Bottom right is the transmission electron micrograph of gold nanorods that are an average of 500 nm long. (ref. 2)

Fig. 3 Experimental dependence of nanorod aspect ratio on seed size (data from ref 12)
4. Growth Mechanism of Gold Nanorods

Knowledge of the crystallography of nanorods is crucial for understanding the growth mechanism of such gold nanorods. The result of high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) examination of gold nanorods made by the above seed-mediated method and with aspect ratio ~25 shows that the rods are pentatetradedral twins (Fig. 5). [15]

Murphy etc. [2] postulated that the CTA\(^+\) headgroup binds to the side surface with some preference. The preferential binding is based on steric – the Au atom spacing on the side faces is more comparable to the size of the CTA\(^+\) headgroup than the close-packed \{111\} face of gold. (planar density of \{110\}, \{100\} and \{111\} are 0.555, 0.785 and 0.907, respectively) The \{111\} face is at the two ends of the nanorods. With the binding of CTA\(^+\) headgroups, the side faces that have relatively large surface energy and stress are stabilized. This leads to the growth in the two ends of nanorods along the [110] common axis on \{111\} faces and these faces do not contain CTA\(^+\) headgroups.
Fig. 5 Carton of the crystallography of gold nanorods. The direction of elongation is [110]. The cross-sectional view is a pentagon; each end of the rod is capped with five triangular faces that are Au\{111\}. The sides of the rods are not as well-defined; either Au\{100\} or Au\{110\} faces, or both. (ref. 2)

At this point, it can be preliminarily concluded that the headgroup of the surfactant is the primary director of the nanoparticle shape. However, there still exist some complexions on the headgroup of the surfactant itself. Gao etc. [16] have performed experiments, in which they varied the tail length of the surfactant while keeping the cetyltrimethylammonium headgroup and the bromide counterion the same and ran the synthesis to produce the highest aspect ratio gold nanorods possible with a series of surfactants. If the headgroup were the primary director, it would be expected that the reactions would all produce nanorods with the same aspect ratio. The experiment shows that tail length is also important. [16] (Fig. 6)

Fig. 6 Plot of the aspect ratio of gold nanorods produced versus number of carbon atoms in CnTAB. (ref. 16)
According to the result of FTIR and thermogravimetric analysis, the tails of CTAB interdigitate to make a bilayer on the rods, with the cationic headgroup of the first monolayer facing the gold surface and the second layer’s cationic headgroup facing the aqueous solvent.\[2\]

The dependence of aspect ratio on tail length can be explained by thermodynamic calculation of the tail contribution to the standard free energy of micellization for CnTAB in aqueous solutions: \[2\]

\[
\Delta G^0 = 2.303(2 - \frac{z}{j})RT(0.1128 - 0.3074n)
\]

where \(n\) is the number of carbon atoms in the surfactant tail; \(z\) is the charge on the micelle; \(j\) is the aggregation number of the micelle; \(R\) is the gas constant, and \(T\) is the temperature.

Murphy etc. \[2\] assume that the tail contribution to the free energy formation of a bilayer on gold is similar to that of micellization and the \(z/j\) ratio is small compared to 2. Based on the two assumption, they find that \(\Delta G^0_{n=10} = -29.6\) kJ/mol, \(\Delta G^0_{n=12} = -35.8\) kJ/mol, \(\Delta G^0_{n=14} = -41.9\) kJ/mol, \(\Delta G^0_{n=16} = -48.1\) kJ/mol. As a result, the longer the tail is, the more stabilization can be provided by the surfactant during gold nanorods growth. This process can be illustrated by Fig. 7.

![Fig. 7 “zipping” fashion formation of gold nanorods.](ref 16)
Br⁻ has also been proved to be very important by recent experiments. [2] Monodisperse rods can be obtained only with bromide while all other conditions keeping the same. Silver ion is needed in the case of shapes other than rods. The solubility equilibrium constant (Ksp) for AgBr is 5.0E-13 at room temperature. The metal ion absolute concentrations are 1-100 μM, bromide is 0.1M in the above seed-mediated experiments; Therefore, AgBr is possible to form under the above conditions; furthermore, bromide or silver bromide is possible the initial species that deposit on the gold seed. On the other hand, high concentrations of bromide would be required to drive the ion onto the gold surface since the affinity of bromide or silver bromide for gold is modest. This is also proved since very high concentrations of CTAB (about 0.1M) [17-19] are required to synthesize rods using this seed-mediated method.

At this point, the general mechanism of nanorods growth becomes clear. [2] This general mechanism is possible only correlative to fcc metals. The mechanism begins with the single crystalline seed particles. Second, surface binding groups (surfactant, metal ions, halides, metal halide) may bind to certain crystal faces of the seed in priority. Third, the addition of more metal ions on certain crystal faces lead to the growth of nanorods. This mechanism is illustrated in Fig. 8.

Fig. 8 Proposed mechanism of surfactant-directed metal nanorods growth. (ref. 2)
5. Method of Synthesis of Gold Nanoparticles of Other Shapes\[14\]

There are several different methods to synthesize nanoparticles of different shapes, such like high temperature solution methods, used by Peng et al. to obtain some interesting shapes for semiconductor systems. \[14\] However, following the seed-mediated method for gold nanorods growth, the seed-mediated method for the growth of gold nanoparticles of different shapes is introduced.

As is mentioned in part 3, slight change the synthesis conditions of nanorods (concentration of different reactants) can result in the formation of gold nanoparticles of other shapes, such as blocks, cubes and tetrapod. The experiment procedure \[14\] involves the preparation of Au seed particles and the subsequent addition of an appropriate quantity of the Au seed solution to the aqueous growth solutions containing desired quantities of CTAB, HAuCl$_4$, ascorbic acid (AA), and in some cases a small quantity of AgNO$_3$. (Almost identical to the method for gold nanorods growth described above)

The morphology and dimension of the gold nanoparticles depend on the concentrations of the seed particles and CTAB, in addition to the reactants (Au$^{3+}$ and AA). All of the above factors are found to be interdependent and can give rise to interesting combinations for various shapes. Details are described below. \[14\]

In typical growth reaction, 0.20mL HAuCl$_4$ solution is added to 4.75 mL CTAB solution (0.1M) followed by the addition of 0.03 mL AgNO$_3$ (0.01M), 0.032 ml L-ascorbic acid (0.1 M), and 0.01 mL Au seed solutions. At 1.6E-2 M CATB and 2.0E-4 M Au$^{3+}$ ions, nanorods and other particles with triangular and square outlines were formed, for an AA concentration 1.6 times the Au$^{3+}$ ion concentration. On increasing the AA concentration, rod length and yield decreased and particles with hexagonal shapes appeared. If AA concentration is further increased, cube-shaped particles are formed. Simultaneous change of all four reactant concentrations can
produce monodisperse Au nanoparticles with hexagonal and cubic profiles in high yield (~90%) at room temperature in aqueous solution. If the seed concentration is raised, keeping other parameters the same as for the cubic shapes, triangular outlines are the major product. (Fig. 9)

Fig. 9 TEM images of Au nanoparticles synthesized under different conditions. [AA] increases from A to C and seed concentration increases from C to D. Scale bar = 100 nm. (ref. 14)

Similarly, if the [AA] concentration is low, such as for a [AA] = 1.6*[Au^{3+}] and with the existence of small quantity of Ag^{+}, the change of concentrations of different reactants can result in different shapes. (Fig. 10)
Fig. 10 TEM images showing cubic to rod-shaped gold particles produced with low AA concentration in the presence of small quantity of silver nitrate. [CTAB] is increased from 1.6E-2 M (A), to 9.5E-2 M (B, C, D). [Au$^{3+}$] decreases from B to C, and seed concentration increased form C to D. Scale bar = 100 nm. (ref. 14)

A lowering of the ratio of concentrations of seed to Au$^{3+}$ ions along with an increase in the concentration of AA can result in the formation of branched Au particles, depending on the concentrations of CTAB and silver nitrate. (Fig. 11)

Fig. 11 TEM images of brached Au nanoparticles, varying in the dimension and number of branches. Tetrapods (A), star-shaped (B), larger tetra-pods (C), and multi-pods (D and E) (ref. 14)
The following table summaries all the conditions described above about the synthesis of different shapes of gold nanoparticles.

Table 1. Shape of gold particles and corresponding reaction conditions. (ref 14)

<table>
<thead>
<tr>
<th>[CTAB]/M</th>
<th>[Au(NO3)]/M</th>
<th>[AuCl]/M</th>
<th>[AA]/M</th>
<th>Shape PROFILE</th>
<th>Dimension</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6x10^-2</td>
<td>1.25x10^-9</td>
<td>2.0x10^-4</td>
<td>6.0x10^-3</td>
<td>Cube</td>
<td>66 nm</td>
<td>~ 85</td>
</tr>
<tr>
<td>1.6x10^-2</td>
<td>1.25x10^-9</td>
<td>2.0x10^-4</td>
<td>3.0x10^-3</td>
<td>Hexagon</td>
<td>70 nm</td>
<td>~ 80</td>
</tr>
<tr>
<td>1.6x10^-2</td>
<td>1.25x10^-9</td>
<td>2.0x10^-4</td>
<td>6.0x10^-3</td>
<td>Triangle</td>
<td>35 nm</td>
<td>~ 80</td>
</tr>
<tr>
<td>1.6x10^-2</td>
<td>1.25x10^-9</td>
<td>2.0x10^-4</td>
<td>6.0x10^-3</td>
<td>Cube^a</td>
<td>90 nm</td>
<td>~ 70</td>
</tr>
<tr>
<td>9.5x10^-3</td>
<td>1.25x10^-7</td>
<td>4.0x10^-4</td>
<td>6.0x10^-3</td>
<td>Tetrapod^a</td>
<td>30 nm</td>
<td>~ 70</td>
</tr>
<tr>
<td>1.6x10^-2</td>
<td>1.25x10^-9</td>
<td>4.0x10^-4</td>
<td>1.2x10^-2</td>
<td>Star</td>
<td>66 nm</td>
<td>~ 50</td>
</tr>
<tr>
<td>5.0x10^-2</td>
<td>6.25x10^-7</td>
<td>5.0x10^-4</td>
<td>3.0x10^-3</td>
<td>Tetrapod</td>
<td>293 nm</td>
<td>~ 75</td>
</tr>
<tr>
<td>9.5x10^-2</td>
<td>2.5x10^-7</td>
<td>4.0x10^-4</td>
<td>6.4x10^-4</td>
<td>Branched^a</td>
<td>174 nm</td>
<td>~ 95</td>
</tr>
</tbody>
</table>

For triangular profile and cubes, dimension corresponds to edge lengths; for hexagonal profile, dimension corresponds to the distance between opposite sides; and for tetrapods and branched particles, dimensions are averaged over ~120 particles and are reproducible to within 5% of the given value; for the other shapes, the dimensions are averaged over ~120 particles and are within ~%10 of given value.

^a6.0E-5 M AgNO3 is used.

The above is a simple solution-based seed-mediated growth method for various morphology and dimension of gold nanoparticles. It is believed that the formation of various shapes is the outcome of the interplay between the faceting tendency of the stabilizing agent and the growth kinetics, just as nanorods described before.


Electrons in the conduction band of nanoscale metals are free to oscillate upon excitation with incident radiation, which is called localized surface plasmon resonance (LSPR). However, since the oscillation distance is restricted by the nanoparticle size for metals on the nanoscale, nanoparticles have some important optical properties. These characteristics include strong plasmon absorption, enhanced Rayleigh scattering, and localized electromagnetic field at the nanoparticle surface.
Plasmon absorption in metal nanoparticles is highly dependent on nanoparticle shape, size and dielectric constant of the surrounding medium \[^{[1]}\]. Fig. 12 shows absorption spectra for gold nanorods of various aspect ratios. Spherical gold particles only have single plasmon absorption peak and the peak is relatively independent of size. Anisotropic gold nanorods have two principle plasmon absorption peaks; one at shorter wavelength corresponding to absorption and scattering of light along the short axis of the nanorods (also called transverse plasmon band), and the other band at longer wavelength corresponding to absorption and scattering of light along the long axis of the nanorods (also called longitudinal plasmon band). The second peak, longitudinal band is tunable with nanorods aspect ratio from the visible to the near-IR. Strong plasmon absorption and sensitivity to local environment make metal nanoparticle attractive candidates as colorimetric sensors for analytes including DNA, metal ions, and antibodies. Haes et al. \[^{[7]}\] have already used the surface plasmon resonance from an array of silver nanoparticles created by nanosphere lithography to detect the interaction of amyloid \(\beta\)-derived diffusible ligands (ADDL) and anti-ADDL antibody, since the surface plasmon resonance absorption will shift (change of color) when environment changes.

![Gold Nanoparticles](image)

Fig. 12 Gold nanoparticles – absorption of various sizes and shapes. (ref.5)
Enhanced Rayleigh scattering cross section due to surface field effects can be used as a powerful technique to image biological systems. El-Sayed et al. [21] are able to distinguish between cancer and non-cancer cells from the strong scattering images of the gold nanoparticles conjugated to antibodies that bind only to the cancer, but not to the non-cancer cells. This scattering is observed from a simple optical microscope. The gold nanoparticles conjugated to antibodies obtain a 600% greater binding ratio to the cancerous cells that to non-cancerous cells. This enables detection of cancerous cells by observing the scattered light. (Fig. 13)

Inelastic visible light scattering from metal nanoparticles is also a useful means to gain chemical information about the nanoparticle’s environment. Surface enhanced Raman scattering (SERS) is a powerful analytical tool for determining chemical information for molecules on metallic substrates on the 10-150 nm size scale. [22] Usually, Raman vibrations of molecules are very weak; but in the presence of metals (copper, silver, gold) with nanoscale roughness, the molecular Raman vibrations excited by visible light are enhanced by orders of magnitude. [22] There are two operational mechanisms to describe the overall SERS enhancement: The electromagnetic (EM) and chemical (CHEM) enhancement mechanisms. EM enhancement is due to the increased local electric field incident on an absorbed molecule at a metallic surface, due to visible light absorption by the metal. CHEM enhancement results from electronic resonance/charge transfer between a molecule and a metal surface, which leads to an increase of the polarizability of the molecule. [22] Anisotropic metallic nanoparticles (such as gold nanorods) is excellent candidates as SERF substrates, since their plasmon absorption bands can be tuned with aspect ratio to be in resonance with common visible laser sources and thus optimizing the EM enhancement.
Fig. 13 Light scattering of cell labeled with (a-c) gold nanoparticles and (d-f) anti-EGFR coated gold nanoparticles. The anti-EGFR coated gold nanoparticles bind specifically to the cancerous cells, while all other gold nanoparticles are non-specifically bound. (a&d) nonmalignant epithelial cell like HaCaT (human deratinocytes), (b&d) malignant epithelial cell likes HOC 313 clone 8 (human oral squamous cell carcinoma) (c&f) malignant epithelial cell lines HSC 3 (human oral squamous cell carcinoma). (ref. 21)

7. Summary

Metal nanoparticles have promising applications in the fields of electronics, photonics, biochemical sensing and imaging, etc., due to their unusual properties, especially optical properties, such as strong plasmon absorption, enhanced Rayleigh scattering and surface enhanced Raman Scattering. There are many different ways to synthesize metal nanoparticles and can be divided into two categories: top down method and bottom up method. As for gold nanoparticles in shapes other than sphere, seed-mediated growth method is a very simple and efficient way at high yield. The growth mechanism of gold nanorods can be explained as the outcome of the interplay between the faceting tendency of the stabilizing agent and the growth kinetics, in a “zipping” fashion. The growth mechanism of gold nanoparticles of other shapes (cubes, hexagon, triangular, tetrapods, etc.) using seed-mediated growth method is
similar to that of gold nanorods.

References

