

# Aspect Ratio Fine Control of Gold Nanorods by Photochemical Secondary Growth

DONG Shouan<sup>1</sup>, YANG Fulong<sup>1</sup>, HE Xiaoguang<sup>2</sup>, ZHANG Shiwen<sup>2</sup>, FANG Wei<sup>1</sup>

(1. State Key Lab of Advanced Technologies for Comprehensive Utilization of Platinum Metals,

Kunming Institute of Precious Metals, Kunming 650106, China;

2. Head and Neck Department of the First Affiliated Hospital, Kunming Medical University, Kunming 650031, China)

**Abstract:** The seed-mediated photochemical secondary growth of gold nanorods (Au NRs) and their aspect ratio fine control were studied. In a single-component surfactant growth solution containing CTAB-capped positive charge gold nanoparticles as seed, Au NRs with uniform shape were obtained by the secondary growth which was realized by UV irradiation of 300 nm light in the presence of acetone after reaching the reaction equilibrium of seed-mediated chemical growth. The aspect ratios of Au NRs with an average 10 nm in diameter were finely controlled in the range of 2.3 to 4.2 by changing amount of Ag<sup>+</sup> ions added and corresponding longitudinal plasmon band (LPB) maxima were between 730 and 840 nm. In addition, after reaching LPB maximum, the further UV irradiation made Au NRs shortening. By this approach the aspect ratios of Au NRs could be also controlled in the above same range. The mechanism of shortening Au NRs by UV light is discussed briefly.

**Key words:** metal material; gold nanorod; photochemical secondary growth; aspect ratio; control

**CIF number:** O644.14    **Document Code:** A    **Article ID:** 1004-0676(2013)01-0001-07

## 利用光化学二次生长精细控制金纳米棒的长径比

董守安<sup>1</sup>, 杨辅龙<sup>1</sup>, 何晓光<sup>2</sup>, 张世文<sup>2</sup>, 方卫<sup>1</sup>

(1. 昆明贵金属研究所 稀贵金属综合利用新技术国家重点实验室, 昆明 650106;

2. 昆明医科大学 第一附属医院头颈外科, 昆明 650031)

**摘要:** 研究了晶种媒介的金纳米棒光化学二次生长及其长径比的精细调控。在单一组份的表面活性剂生长溶液中, 以十六烷基三甲基溴化铵(CTAB)封端的带正电荷的金纳米粒子作晶种, 形貌均一的金纳米棒通过二次生长获得, 其二次生长是在晶种媒介的化学生长反应达到平衡后于丙酮存在下用 300 nm 的紫外光照射来实现。通过改变银离子的加入量, 具有约 10 nm 直径金纳米棒的长径比被精细调控在 2.3~4.0 范围内, 相应的纵向等离子体带最大在 730~840 nm 之间。另外, 纵向等离子体带达到最大之后, 进一步的紫外光照射使金纳米棒变短。通过这一途径, 金纳米棒的长径比也能够调控在上述同样范围。简要讨论了紫外光照射使金纳米棒变短的机理。

**关键词:** 金属材料; 金纳米棒; 光化学二次生长; 长径比; 调控

Au NRs have attracted more attention in recent years due to their promising application in the medical imaging of cells and photothermal tumor therapy<sup>[1-9]</sup>. In order to obtain Au NRs, a method of the seed-

mediated chemical reduction of Au(III) ions by ascorbic acid has been proposed by Nikoobakht and El-Sayed<sup>[10]</sup> in an aqueous surfactant cetyltrimethylammonium bromide (CTAB) system. However, in the subsequent study of adopting this method, Murphy et al.<sup>[11]</sup> have noticed that about 15% of the initial gold ions in the growth solution are reduced to form Au NRs. One reason possibly is due to the insufficiency of the amount of ascorbic acid as a weak reducing agent in the growth solution<sup>[12]</sup>, while added more ascorbic acid influences the shape of Au NRs formed<sup>[13]</sup>. Therefore, it is one area of concern how to make Au(I)-CTA<sup>+</sup> complexes in the growth solution completely reducing and forming Au NRs required.

It is known that the photochemical reduction method<sup>[14-17]</sup> is widely used to prepare Au NRs with uniform shape and different size due to relatively simple and easy to control aspect ratios, but a long irradiation time usually is necessary.

For the fast synthesis of shorter Au NRs with aspect ratio controlled, a method of the photochemical secondary growth of Au NRs is proposed. It is mainly based on UV irradiation of a single-component surfactant growth solution containing CTAB-capped gold seed in the presence of acetone after the reaction equilibrium of seed-mediated chemical growth to be reached, so as to make Au NRs formed secondarily growth in a static or disturbed state. This work shows that Au NRs with an average 10 nm in diameter and uniform shape are obtained under the static state, and their aspect ratios are finely controlled in the range of 2.3 to 4.2 by changing amount of Ag<sup>+</sup> ions added, corresponding LPB maxima are between 730 and 840 nm. However, Au NRs with dog-bone liked shape are formed under the disturbed state.

In the secondary growth process under the static state, an interesting phenomenon was found, i.e. Au NRs formed could be shortened by UV irradiation of 300 nm light. After the aspect ratio maximum of Au NRs to be reached through the secondary growth, by the increase of UV irradiation time, the LPB maximum gradually blue-shifts and its intensity decreases. The Au NRs become shorter and shorter. Based on this, the aspect ratios of Au NRs can be also

tuned in the above same range. However, a long irradiation time is necessary. The mechanism of shortening Au NRs by UV light is discussed briefly.

## 1 Experimental section

### 1.1 Materials

HAuCl<sub>4</sub> was prepared from pure gold (Au, 99.99%), the concentration of Au(III) ion in the solution is  $3.05 \times 10^{-3}$  mol/L. CTAB and sodium borohydride were purchased from Fluka AG (Chemische Fabrik CH-9470 Buchs) and Aldrich, respectively. All chemical reagents used were of analytical reagent grade. The concentrations of CTAB, AgNO<sub>3</sub>, ascorbic acid and NaBH<sub>4</sub> solutions were 0.1,  $1.49 \times 10^{-3}$ , 0.01 and 0.01 mol/L, respectively. Double distilled water was used throughout the experiments.

### 1.2 Photochemical secondary growth of Au NRs

CTAB-capped positive charge Au seed with an average size of 3.5 nm was prepared according to the method reported<sup>[10]</sup>.

The procedure of the secondary growth was as follows: first, 1.7 mL of HAuCl<sub>4</sub>, 10 mL of CTAB and 1 mL of AgNO<sub>3</sub> solutions were mixed in a quartz conical flask, 0.55 mL of fresh ascorbic acid solution was added to the solution. After diluting to 25 mL and gently mixing, the color of the solution changed from light-yellow to colorless. This solution was used as a growth solution. Then, 50  $\mu$ L of seed solution was added to the growth solution, the resulting solution was aged for 1 h in dark for reaching growth reaction equilibrium. Finally, two same component solutions prepared by above procedure were irradiated by UV 300 nm light for 1 h in a static and disturbed state, respectively, after 50  $\mu$ L of acetone were added to each solution.

### 1.3 Control of Au NR aspect ratios

#### 1.3.1 Controlled secondary growth with Ag<sup>+</sup> ions

To obtain Au NRs with different aspect ratios, the amount of silver added in the growth solution was changed in the range of 0.25~1.0 mL. The resulting solutions were then irradiated by UV 300 nm light under the static state.

### 1.3.2 Controlling aspect ratios by UV overirradiation

Au NRs solution obtained by the secondary growth was further UV irradiated under the static state for a certain time. Shorter Au NRs with various aspect ratios were obtained because of the shortening of longer Au NRs.

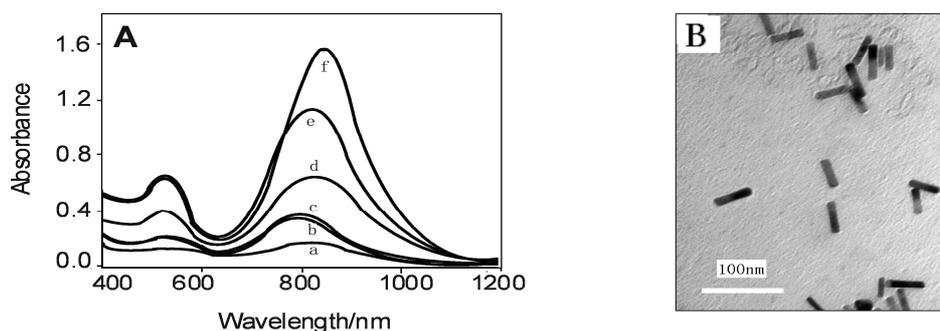
### 1.4 Characterization

Absorption spectra of the solutions were recorded on a Lambda 900 UV/visible/NIR spectrophotometer (Perkin Elmer) during the growth process of Au NRs. TEM images were taken with a JEM-2100, operating at an accelerating voltage of 100 kV. The TEM samples were prepared as follows: Au NR solution was centrifuged for 30 min at a speed of 10000 r/min. The precipitate collected was redispersed in water. 2~3 drops of the Au solution were dropcast on the carbon-coated copper grid and allowed to dry in the open atmosphere.

## 2 Results and discussion

### 2.1 Photochemical secondary growth of Au NRs under the static or disturbed state

Using a CTAB-capped Au seed for preparing Au NRs, it is possible to avoid the formation of noncylindrical NRs,  $\phi$ -shaped particles, and formation of a large fraction of spherical particles in the growth solution system of CTAB-Au(I)-CTA<sup>-</sup>-Ag<sup>+</sup>[10]. Fig.1A shows the absorption spectra of the growth solution containing Au seeds under the static state. It is clear that the absorbance of curve c recorded is low after the seed-mediated chemical growth for 60 min, indicating the reduction of only part gold ions for growing nanorods. This result is in agreement with the case in a single-component surfactant system<sup>[10]</sup>.



**Fig.1 Vis-NIR spectra of the growth solution containing Au seeds under the static state (A) and TEM image (B)**

(A. curve a, b and c : seed-mediated chemical growth for aging 5, 30 and 60 min; curve d, e, and f : secondary growth by UV irradiation for 30, 45 and 60 min after aging for 60 min; B. TEM image of Au NRs in the corresponding solution sample in Fig.1A curve f)

**图 1 含有金晶种的生长溶液在静态情况下的可见-近红外光谱(A)和 TEM 图像(B)**

(A. 紫外可见光谱：曲线 a、b 和 c 为静置 5、30 和 60 min 时晶种媒介的化学生长；曲线 d、e 和 f 为静置陈化 60 min 后紫外光照射 30、45 和 60 min 时的二次生长； B. 图 1A 曲线 f 对应溶液样品中金纳米棒的 TEM 图像)

For the purpose of increasing the yield of Au NRs, after the seed-mediated chemical growth for 60 min, the photochemical secondary growth was carried out in the presence of small amount of acetone. It can be seen from curves d, e and f in Fig.1A that by increasing UV irradiation time, the LPB maxima of Au NRs red-shift and their intensity increases. After 60 min irradiation, the LPB maximum appears at 840 nm and do not change with the increase of irradiation

time. By comparison to the chemical growth (Fig.1A, curve c), the LPB red-shifts about 47 nm and its intensity is 4.2 times larger than that of the former. Obviously, the secondary growth of Au NRs happened. The Au(I)-CTAB complexes remained in growth solution are further photochemically reduced, produced Au(0) atoms diffuses to the end of NRs formed, growing into Au NRs with high aspect ratio. The increase of absorbance implies the high yield of Au

NRs formed.

Fig.1B is the TEM image of Au NRs in the corresponding solution sample in Fig.1A curve f. The average diameter and aspect ratio of Au NRs with high dispersibility are 10.1 nm and 4.2, respectively.

Fig.2A shows the evolution of absorption spectra of the photochemical secondary growth of Au NRs under the disturbed state. The LPB maxima distinct blue-shift as compared to Fig.1A curves d, e and f, implying the decrease of aspect ratio of Au NRs. After 70 min irradiation, the LPB maximum appears at 758

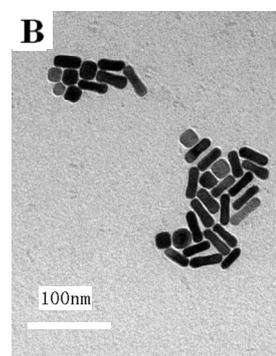
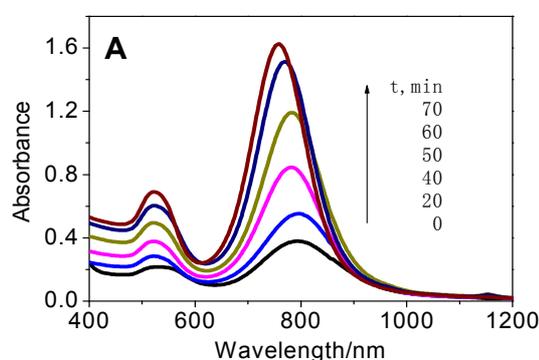


Fig.2 Evolution of Vis-NIR spectra of the growth solution containing Au seeds under the disturbed state (A) and TEM image of the solution sample obtained after 70 min irradiation (B)

图 2 含有金晶种的生长溶液在扰动条件下的可见-近红外光谱的演化(A)和照射 70 min 后所得溶液样品的 TEM 图像(B)

## 2.2 Effect of the concentration of $\text{Ag}^+$ ions

It is known that the growth of Au NRs is influenced by a lot of factors in the corresponding component surfactant solution system, such as the concentrations of CTAB,  $\text{HAuCl}_4$  and  $\text{AgNO}_3$  and so on. It is available for obtaining Au NRs desired to change the amount of  $\text{AgNO}_3$  added<sup>[10-11, 14]</sup>. Therefore, the effect of the concentration of  $\text{Ag}^+$  ions on the secondary growth of Au NRs was studied.

Fig.3A shows the absorption spectra of the growth solution containing Au seeds in the different concentration of  $\text{Ag}^+$  ions. It can be seen that by increasing the  $\text{AgNO}_3$  solution in the range of 0.25~1.0 mL (Fig.3A curve a~d), the LPB maximum of Au NRs red-shifts from 730 to 840 nm. The intensity of the LPB reaches the maximum in the cases of adding 0.75~1.0 mL of the  $\text{AgNO}_3$  solution. However, by increasing the  $\text{AgNO}_3$  solution to more than 1.0 mL,

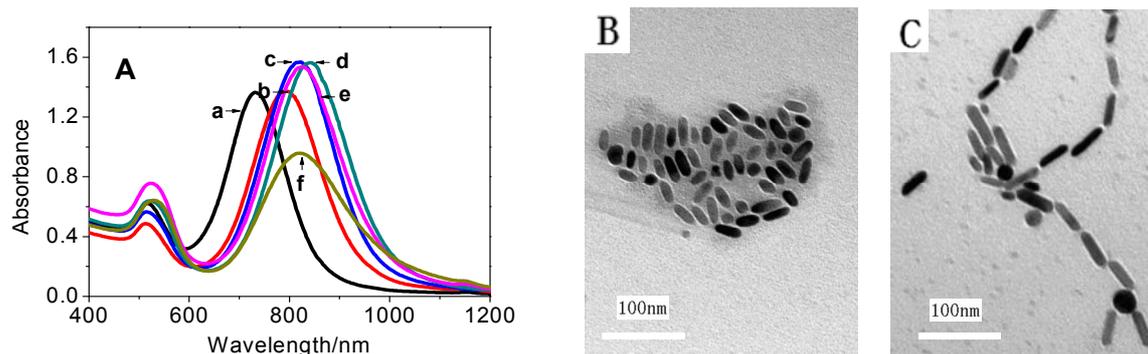
Fig.2B is the TEM image of Au NRs in the corresponding case. It seems that the Au NRs with dog bone-like shapes are formed and there are some the nanoparticles with cube shapes.

Comparing Fig.1 with Fig.2 it can be seen that the photochemical secondary growth under the static state is optimum for the preparation of shorter Au NRs. This approach does not need for long irradiation time and Au NRs can be prepared in a larger solution volume.

the LPB starts blue-shift and its intensity decreases (curve e and f). It is obvious that by means of adding the  $\text{AgNO}_3$  solution, the LPB maximum of Au NRs can be finely controlled in the range of 730~840 nm in the photochemical secondary growth.

Fig.3B and 3C are the TEM images of Au NRs obtained in the case of adding 0.25 and 0.5 mL of  $\text{AgNO}_3$  solution, respectively. The TEM image in the case of adding 1.0 mL of the  $\text{AgNO}_3$  solution has been given in Fig.1B. On the basis of the measure for these images, Au NRs with aspect ratios of 2.3~4.2 and  $\approx 10$  nm in diameter were obtained.

In addition, after centrifuging the Au NR solution obtained by the photochemical secondary growth, the supernatant is the colorless, and its color is not changed by adding  $\text{NaBH}_4$  solution, indicating complete reduction of  $\text{Au(I)-CTA}^+$  complex in the growth solution for growing Au NRs.



**Fig.3 Vis-NIR spectra of the growth solution containing Au seeds in the presence of different  $\text{AgNO}_3$  amount (A) and corresponding TEM images (B, C)**

(A. Spectrum curves in the presence of  $\text{AgNO}_3$  solution: a. 0.25, b. 0.50, c. 0.75, d. 1.0, e. 1.25, f. 2.0 mL

B and C. TEM images obtained in the case of adding 0.25 and 0.5 mL of  $\text{AgNO}_3$  solution)

**图 3 含有金晶种的生长溶液在不同硝酸银量存在下的可见-近红外光谱(A)和相应的 TEM 图像(B、C)**

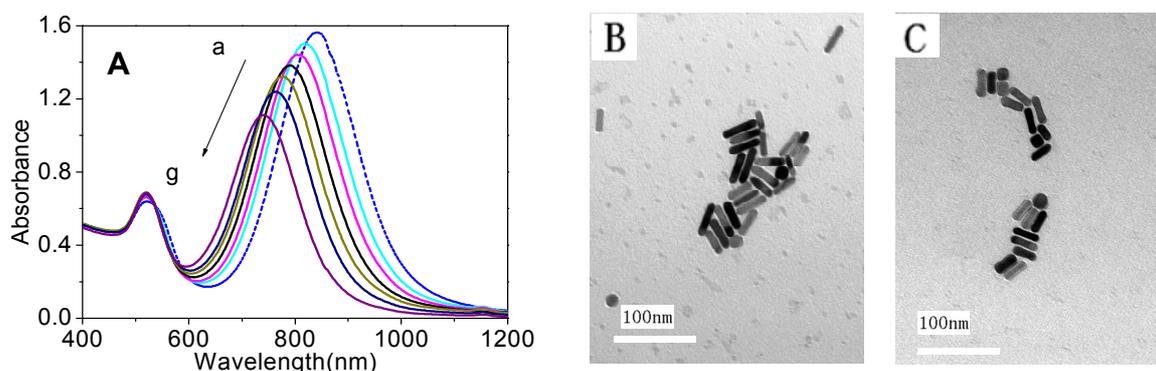
(A.  $\text{AgNO}_3$  溶液量不同时 的光谱曲线: a. 0.25, b. 0.50, c. 0.75, d. 1.0, e. 1.25, f. 2.0 mL;

B、C.  $\text{AgNO}_3$  溶液加入量为 0.25 和 0.5 mL 时对应的金纳米棒 TEM 图像)

### 2.3 Shortening Au NRs by UV overirradiation

In the secondary growth under the static state, an interesting phenomenon of shortening Au NRs by UV light overirradiation was found. Fig.4A shows the evolution of absorption spectra of the growth solution containing Au seeds with increase of UV irradiation time after the aspect ratio maximum of Au NRs to be

reached. Obviously, the LPB maximum as a function of irradiation time gradually blue-shifts and its intensity decreases, but the TPB retains almost constant. Up to 35 h, no further spectrum change are observed. These implicate that the Au NRs become shorter and shorter, and their diameter is not changed.



**Fig.4 Evolution of Vis-NIR spectra of Au NRs with UV irradiation after the secondary growth (A) and TEM images (B, C)**

(A. Vis-NIR Spectrum curves vs. irradiation time: a. 1, b. 3, c. 5, d. 9, e. 13, f. 23, g. 35 h; B and C. TEM images of Au NRs corresponding to 13 and 35 h)

**图 4 二次生长后金纳米棒的 Vis-NIR 光谱随紫外照射演化(A)和对应的 TEM 图像(B、C)**

(A. Vis-NIR 光谱曲线对应的紫外照射时间: a. 1, b. 3, c. 5, d. 9, e. 13, f. 23, g. 35 h; B、C. 辐射 13 和 35 h 后对应的金纳米棒 TEM 图像)

In order to confirm these results, the solution samples obtained by 13 and 35 h UV irradiation were characterized by TEM, respectively. On the basis of the TEM images shown in Fig.1B and Fig.4B and 4C, the average aspect ratios of Au NRs decrease from

starting 4.2 to 3.5 and 2.5, respectively, while their diameter retains almost constant ( $\approx 9.8$  nm). It will be seen from this that Au NRs can be shortened by increasing the time of UV irradiation. As a result, the aspect ratios of Au NRs were finely controlled ranging

from 2.5 to 4.2. However, when this procedure is adopted, the long reaction time is required.

For the mechanism of shortening Au NRs, perhaps it can be attributable to the ablation of nanorods by UV overirradiation. The ablation of Au NRs is relevant to two main factors: the photon energy and chemical dissolution. When the growth solution is irradiated for an excess time, on the one hand, the solution temperature increases ( $\approx 40^\circ\text{C}$ ), resulting in the relative instability of the micelles capping the longer gold nanorods<sup>[18]</sup>. On the other hand, Au NRs absorb certain heat energy. The deposited heat energy makes the atomic diffusion motion at Au NR ends fast. One-by-one breaking away of Au atoms from rod ends leads to the size reduction. Perhaps, it is reasonable to explain this phenomenon by the difference of the energies between UV 300 nm light (4.13 eV) and the cohesive energy (3.99 eV) of gold<sup>[15]</sup>.

In addition, there are some amounts of  $\text{Cl}^-$  and  $\text{H}^+$  ions in the growth solution containing Au seeds due to the chemical reduction of  $\text{HAuCl}_4$  by ascorbic acid, which provides an environmental condition of oxidizing Au atoms at rod ends by oxygen dissolved in the solution<sup>[19]</sup>. In order to verify chemical oxidation of Au NRs in the ablation, the mixture growth solution obtained by 35 h irradiation was centrifuged after adding a certain amount of ethanol, so as to deposit all Au particles. Then, a portion of fresh prepared  $\text{NaBH}_4$  solution was added to this colorless supernatant, resulting in the solution to become red again. This indicates the formation of some Au particles due to the reduction of Au(I)-CTAB complex ions which are released by the chemical oxidation of oxygen dissolved in the solution. This experiment shows that the chemical oxidation of Au NRs indeed occurs and starts from ends of NRs.

### 3 Conclusions

Au NRs were prepared by the photochemical secondary growth after aging the growth solution containing a CTAB-capped positive charge gold seed. For the fine control of the aspect ratio of nanorods, the different growth ways were adopted. Au NRs with the aspect ratios of 2.3~4.0 and  $\approx 10$  nm in diameter were

obtained by changing  $\text{AgNO}_3$  amount added under the static state of keeping growth solution. However, Au NRs with dog-bone like shape were formed under the disturbed state. After reaching an aspect ratio maximum of Au NRs by the photochemical secondary growth, UV 300 nm irradiation for an excess time made Au NRs selectively shorten. By means of this approach, the aspect ratios of Au NRs were also finely controlled in the above range.

For the mechanism of shortening Au NRs by UV light, the factors of both heat energy and chemical oxidation dissolution are responsible.

### References:

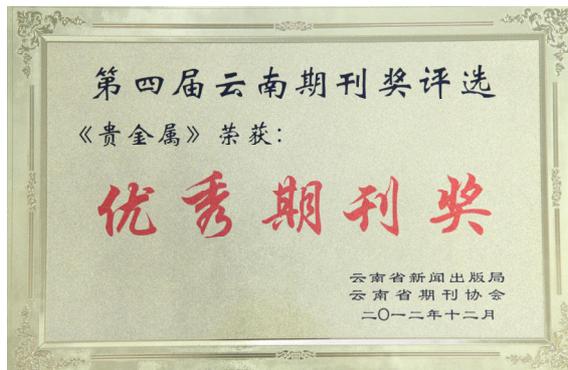
- [1] Huang X H, Neretina S, El-Sayed, M A. Gold nanorods: from synthesis and properties to biological and biomedical applications[J]. *Adv Mater*, 2009, 21: 4880-4910.
- [2] Tong L, Wei Q, Wei A, et al. Gold nanorods as contrast agents for biological imaging: optical properties, surface conjugation and photothermal effects[J]. *Photochem Photobiol*, 2009, 85: 21-32.
- [3] Murphy C J, Gole A M, Stone J W, et al. Gold nanoparticles in biology: beyond toxicity to cellular imaging[J]. *Acc Chem Res*, 2008, 41: 1721-1730.
- [4] Maltzahn G von, Centrone A, Park J H, et al. SERS-coded gold nanorods as a multifunctional platform for densely multiplexed near-infrared imaging and photothermal heating[J]. *Adv Mater*, 2009, 21: 3175-3180.
- [5] El-Sayed I H, Huang X H, El-Sayed M A. Selective laser photo-thermal therapy of epithelial carcinoma using anti-EGFR antibody conjugated gold nanoparticles[J]. *Cancer Lett*, 2006, 239: 129-135.
- [6] Kim K, Huang S W, Ashkenazi S, et al. Photoacoustic imaging of early inflammatory response using gold nanorods[J]. *Appl Phys Lett*, 2007, 90: 223901-223903.
- [7] Durr N J, Larson T, Smith D K, et al. Two-photon luminescence imaging of cancer cells using molecularly targeted gold nanorods[J]. *Nano Lett*, 2007, 7(4): 941-945.
- [8] Dickerson E B, Dreaden, E C, Huang, X H, et al. Gold nanorod assisted near-infrared plasmonic photothermal therapy (PPTT) of squamous cell carcinoma in mice[J]. *Cancer Letters*, 2008, 269: 57-66.
- [9] Tong L, Zhao Y, Huff T B, et al. Gold nanorods mediate tumor cell death by compromising membrane integrity[J]. *Adv Mater*, 2007, 19: 3136-3141.

- [10] Nikoobakht B, El-Sayed M A. Preparation and growth mechanism of gold Nanorods NRs using seed-mediated growth method[J]. Chem Mater, 2003, 15: 1957-1962.
- [11] Orendorff C J, Murphy C J. Quantitation of metal content in the silver-assisted growth of gold nanorods[J]. J Phys Chem B, 2006, 110: 3990-3994.
- [12] Ratto F, Matteini P, Rossi F, et al. Size and shape control in the overgrowth of gold nanorods[J]. J Nanopart Res, 2010, 12: 2029-2036.
- [13] Kang S K, Choi I, Lee J, et al. Investigation on shape variation of Au nanocrystals[J]. Current Appl Physics, 2008, 8: 810-813.
- [14] Kim F, Song J H, Yang P. Photochemical synthesis of gold nanorods[J]. J Am Chem Soc, 2002, 124: 14316-14317.
- [15] Miranda O R, Ahmadi T S. Effects of intensity and energy of CW UV light on the growth of gold nanorods[J]. J Phys Chem B, 2005, 109: 15724-15734.
- [16] Nishioka K, Niidome Y, Yamada S. Photochemical reactions of ketones to synthesize gold nanorods[J]. Langmuir, 2007, 23: 10353-10356.
- [17] Ahmed M, Narain R. Rapid synthesis of gold nanorods using a one-step photochemical strategy[J]. Langmuir, 2010, 26: 18392-18399.
- [18] Becker R, Liedberg B, Käll P O. CTAB promoted synthesis of Au nanorods - temperature effects and stability considerations[J]. J Colloid and Inter Science, 2010, 343: 25-30.
- [19] Tsung C K, Kou X S, Shi Q, et al. Selective shortening of single-crystalline gold nanorods by mild oxidation[J]. J Am Chem Soc, 2006, 128: 5352-5353.

### 《贵金属》季刊获奖信息

- 由云南省新闻出版局和云南省期刊协会每三年组织一次的**第四届云南省优秀期刊奖**评选中，2012 年全省共评选出优秀期刊 28 种，优秀主编（社长）28 名，优秀栏目 73 个，优秀编辑 83 人。《贵金属》期刊获得了全部奖项的表彰，分别为：

- 1 《贵金属》期刊获**优秀期刊奖**。
- 2 钱琳获**优秀主编（社长）奖**。
- 3 “研究与应用”栏目获**优秀栏目奖**。
- 4 姜东慧获**优秀编辑奖**。



- 在中国有色金属学会组织的 2012 年**中国有色金属出版物奖**评选中，《贵金属》期刊获得**期刊奖二等奖**，发表在《贵金属》期刊上的论文 1 篇获评**学术论文奖一等奖**，2 篇获评**学术论文奖二等奖**。

