

# Facile synthesis of AgAu alloy and core/shell nanocrystals by using Ag nanocrystals as seeds

Weiwei Xu · Jinzhong Niu · Hangying Shang · Huaibin Shen · Lan Ma · Lin Song Li

Published online: 9 December 2012

© The Author(s) 2012. This article is published with open access at SpringerLink.com

**Abstract** A facile seed-growth method was developed to synthesize AgAu alloy and core/shell nanocrystals (NCs) using different-sized Ag NCs (6.1, 7.4, and 9.6 nm) as seeds and octadecylamine as the reducing agent, surface ligand, and solvent. Pre-synthesized Ag NCs acted as catalysts for the reduction of Au precursors at 130 °C. Transmission electron microscopy, energy-dispersive spectroscopy, and optical absorption spectroscopy were used to characterize as-synthesized NCs. Spherical AgAu alloy NCs were obtained when pre-synthesized 6.1 and 7.4 nm Ag NCs were used as seeds. While, if 9.6 nm Ag NCs were used as seeds, cubic Ag/Au core/shell NCs were finally obtained. The shapes and structures of AgAu NCs are related to the Ag seed sizes and the growth mechanism of alloy and core/shell NCs is discussed in detail. Different reaction temperatures were tested to optimize the synthesis of AgAu alloy NCs, and it was found that the optimum reaction temperature for the growth of AgAu alloy NCs is 130 °C.

**Electronic supplementary material** The online version of this article (doi:10.1007/s13404-012-0077-2) contains supplementary material, which is available to authorized users.

W. Xu · H. Shang · H. Shen (✉) · L. S. Li  
Key Laboratory for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, People's Republic of China  
e-mail: shenhuaibin@henu.edu.cn

W. Xu · L. Ma (✉)  
Life Science Division, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, People's Republic of China  
e-mail: malan@sz.tsinghua.edu.cn

J. Niu  
Department of Mathematical and Physical Sciences, Henan Institute of Engineering, Zhengzhou 451191, People's Republic of China

**Keyword** Metallic composites · Alloys · Core/shell · Nanocrystals · Seeds size

## Introduction

Silver and gold nanocrystals (NCs) have attracted great attention due to their special optical [1], electronic [2], and catalytic [3] properties. In the past two decades, a myriad of chemical methods for generating faceted Ag or Au NCs with a rich variety of shapes, including sphere [4, 5], cube [6], decahedron [7, 8], icosahedrons [8], rods [9, 10], and wires [11], have been developed to tailor their properties and improve their performance in various applications. In addition, people have also developed methods for combining Au and Ag into one single system to tune the optical properties [12–17]. For example, Sun's group reported one-pot synthesis of monodisperse AuAg alloy NCs by the simultaneous reduction of gold and silver salts [13], and AuAg alloy NCs were prepared through interface diffusion of core/shell structured Ag/Au NCs [14]. Tracy and co-workers described a facile controlled synthesis of Au/Ag core/shell and AuAg alloy NCs through digestive ripening, which is a potentially general method for synthesizing alloy NCs [15]. Yang's group reported a general route to control the diameter of noble NCs (Ag, Au, and Pd), the shell thickness of the core/shell NCs (Ag@Pd, Pd@Au, Pd@Ag, Au@Pd, Au@Ag, Pt@Au, and Pt@Pd), and the composition of the alloy (Ag and Au) on the basis of the combining effect of seeding growth and digestive ripening [16]. However, there is still no report about the effect of the seed size on the growth of different shaped NCs.

In this paper, we report the seed size-dependent growth of different-shaped AgAu alloy and core/shell NCs by an organic solvothermal method. The key strategy to produce such different classes of NCs is to precisely control the sizes

of the Ag NCs which are synthesized by thermal reduction of  $\text{AgNO}_3$  in octadecylamine (ODA). Pre-synthesized Ag NCs acted as catalysts for the reduction of Au precursors. When 6.1 and 7.4 nm Ag NCs were used as seeds, spherical AgAu alloy NCs were obtained; while, if 9.6 nm Ag NCs were used as seeds, cubic Ag/Au core/shell NCs were finally obtained.

## Experimental section

### Chemicals

Hydrogen tetrachloroaurate (III) ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.99 %), silver nitrate ( $\text{AgNO}_3$ , 99.8 %), and triphenylphosphine ( $\text{PPh}_3$ , 99 %) were purchased from Aldrich. Chloroform (analytical grade), ODA (95 %), hexanes (analytical grade), and methanol (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China. All reagents were used as received without further experimental purification.

**Au stock solution** A 0.0309 g  $\text{AuPPh}_3\text{Cl}$  (0.0625 mmol, which was synthesized by reacting  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  with  $\text{PPh}_3$  in ethanol) was dissolved in 0.4 mL chloroform to form the Au stock solution.

**Synthesis of AgAu NCs** Ag NCs (6.1 and 7.4 nm) were made by adding  $\text{AgNO}_3$  (0.25 g, 1.47 mmol) to ODA (10 mL, 8.6 g) at 180 °C and magnetically stirred for 20 and 60 min, respectively [18]. Ag NCs (9.6 and 11 nm) were made by dissolving  $\text{AgNO}_3$  (0.02 g, 0.118 mmol) to ODA (10 mL, 8.6 g) to form a solution, which was slowly heated to 180 °C for 10 min and 1 h, respectively [13]. After cooling to 60 °C, 10 mL methanol and 10 mL chloroform were added into the solution and the NCs were separated by centrifugation (8,000 rpm, 5 min) and then dried at 45 °C. After that, 5 mL ODA was dispersed in a 25 mL flask and degassed at 130 °C for 10 min, and then 10 mg ( $\sim 0.14 \times 10^{-4}$  mmol) Ag NCs (different sizes) which was dissolved in 0.2 mL chloroform was added. Au stock solution (0.1 mL, 0.0156 mmol) was added into the flask and maintained the reaction temperature at 130 °C for 20 min. During this process, the color of the reaction solution changed from yellow to purple-red. After that, Au stock solution was added again and maintained for another 20 min and the absorption peak moved to 508 nm or longer. During this process, the color of the reaction solution has no obvious change. Finally, chloroform and methanol were added to the solution to remove byproducts by centrifugation (8000 rpm, 5 min). UV–vis absorption spectra were recorded using an Ocean Optics spectrophotometer (mode PC2000-ISA). All optical measurements were performed at room temperature under ambient conditions. Transmission electron microscopy (TEM) images were

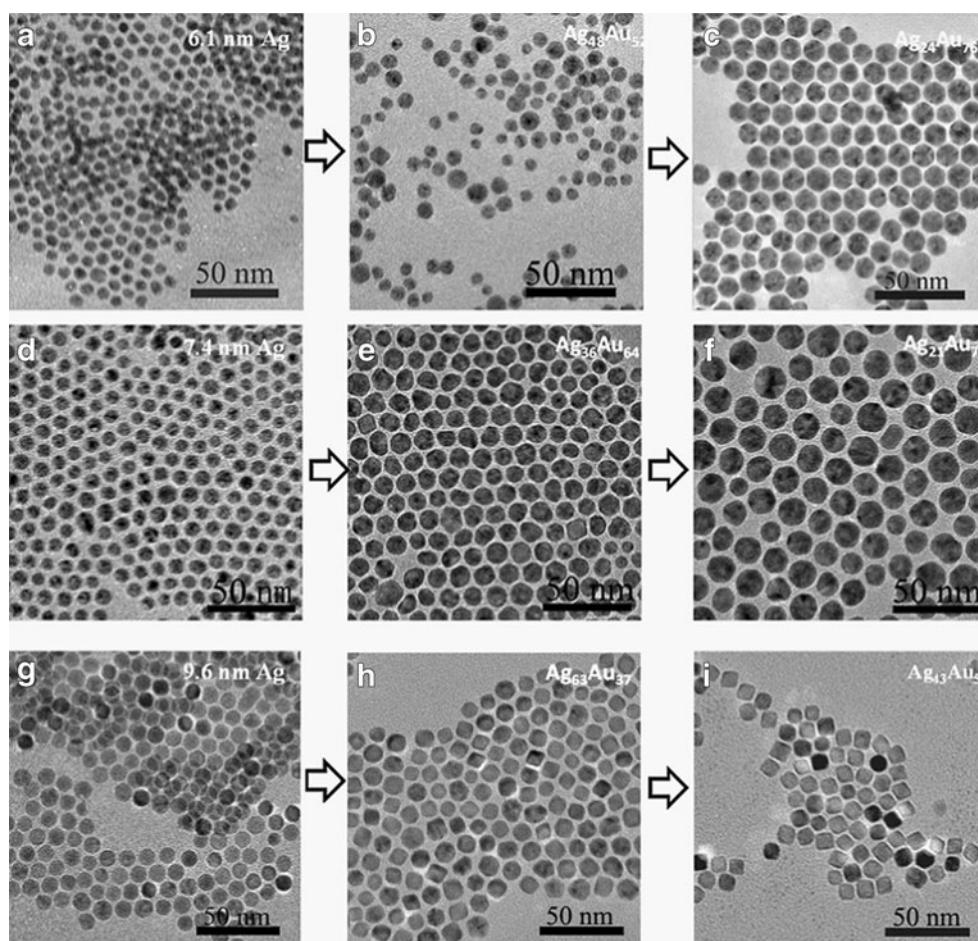
obtained with a JEOL 2010 F microscope operated at accelerating voltage of 200 kV. For each NC sample, the diameter and standard deviation were determined by averaging measurements of 100 NCs.

## Results and discussion

In the control experiments, large Au NCs with diameter of 80 nm were obtained after the injection of Au precursors ( $\text{AuPPh}_3\text{Cl}$ ) to ODA solution at 180 °C (see Electronic supplementary material (ESM) Fig. S1). If the Au precursor was injected into ODA at 150 °C, the color of the reaction solution did not change after the injection, which implies that the reduction of Au precursors did not occur at this temperature. If the pre-synthesized Ag NCs were used as seeds, Au was deposited by reduction of  $\text{AuPPh}_3\text{Cl}$  with ODA at 130 °C. At this reaction temperature, the reduction of Au precursors by ODA in the organic phase was not feasible in the absence of the Ag seeds as mentioned above, indicating that Ag NCs acted as catalysts for the reduction of Au precursors. A similar phenomenon was also reported in previous report [19].

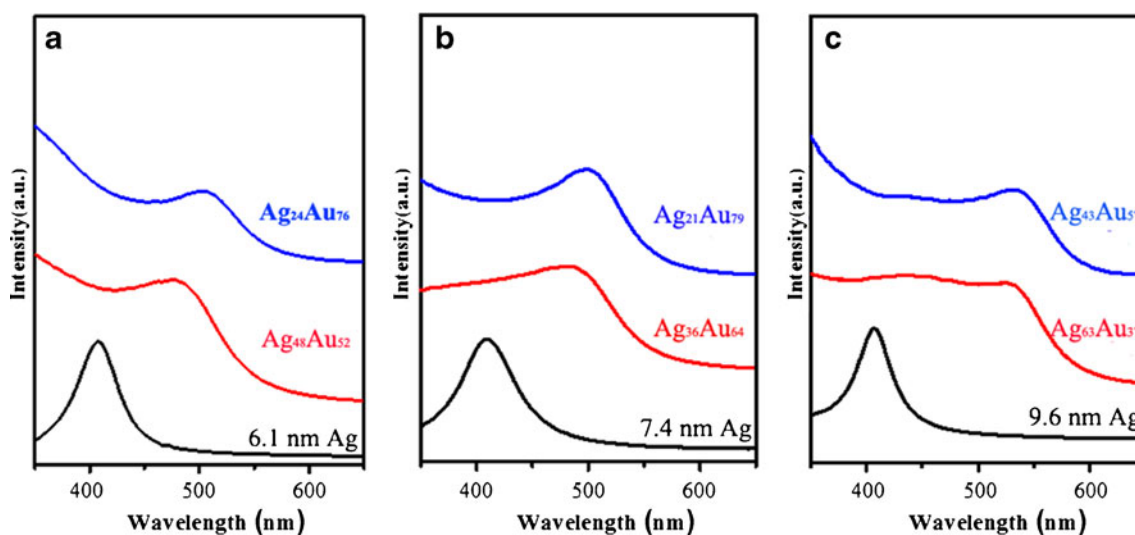
As shown in Fig. 1a–c, the AgAu NCs have typical size distributions of approximately  $\pm 50$  % (Fig. 1b) and  $\pm 10$  % (Fig. 1c) after the first and second round addition of Au precursors when 6.1 nm Ag NCs were used as seed (Fig. 1a). During the reaction process, the color of the reaction solution changed gradually from yellow to purple-red, indicating the composition of AgAu alloy NCs changed from Ag rich to Au rich. The Au/Ag ratio was changed from 0.52/0.48 to 0.76/0.24, which was measured by energy-dispersive X-ray spectroscopy (EDS) attached to a scanning electron microscope (see ESM Fig. S3). When 7.4 nm Ag NCs were used as seed (Fig. 1d), the growth process of AgAu NCs with the addition of Au precursors was similar to that on 6.1 nm Ag seed. The final average size of AuAg NCs was 16 nm (Fig. 1f), which was bigger than that shown in Fig. 1c with an average size of 13 nm. If the average size of Ag seed was increased to 9.6 nm, faceted AgAu NCs (Fig. 1h) were formed after the injection of Au precursors for the first time, and then most of the faceted NCs turned into cubic NCs (Fig. 1i) with the continuous addition of Au precursors for the second time during the growth process. The molar ratio of Ag/Au changed from 63:37 (Fig. 1h) to 43:57 (Fig. 1i) with the addition of Au precursors. After that, the shape of AgAu NCs became uncontrollable if we continued to add excess Au precursors (see ESM Fig. S4). When 11 nm Ag NCs (ESM Fig. S5a) were used as seed, the color of the reaction solution changed gradually from yellow to purple-red to black and formed a precipitate after adding the Au precursors. The AgAu NCs were collected from the bottom of the beaker (see ESM Fig. S5).

**Fig. 1** TEM images of as-prepared NCs. (a) 6.1 nm Ag NCs; (b) and (c) AgAu alloy NCs synthesized in use of 6.1 nm Ag NCs; (d) 7.4 nm Ag NCs; (e) and (f) AgAu alloy NCs synthesized in use of 7.4 nm Ag NCs; (g) 9.6 nm Ag seed; (h) and (i) Ag/Au core/shell NCs synthesized in use of 9.6 nm Ag NCs. The compositions of each sample measured by EDS are indicated

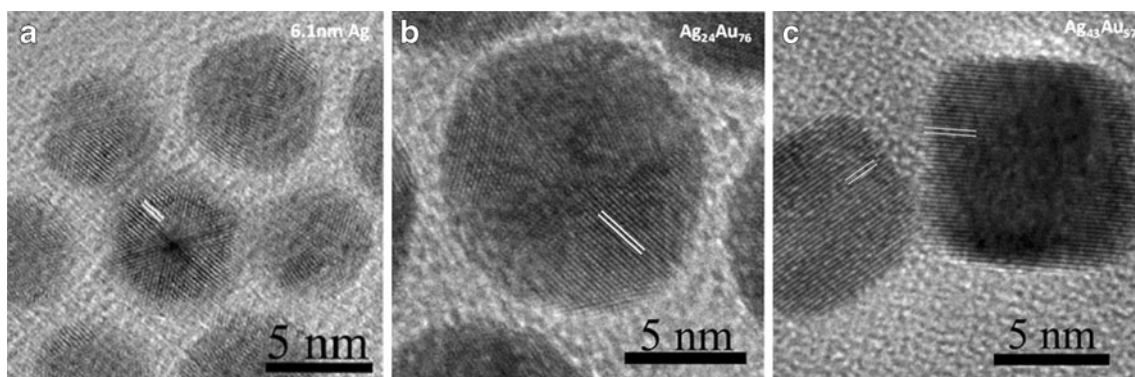


The formation of the AgAu alloy and core/shell structures can be demonstrated by the absorption peaks in the UV–Vis spectra. Figure 2a and b show the absorption peaks of 6.1 nm and 7.4 nm sized spherical Ag NCs, which are both located at 405 nm. After the addition of Au precursors, the absorption peaks red shifted to 494 nm, and then to 508 nm, respectively.

The red shift of absorption peaks indicates that the composition of spherical AgAu NCs changed from Ag rich to Au rich, which is in accordance with the EDS results of AgAu NCs, and confirms the AgAu NCs are the alloy structure. When metal NCs are enlarged, their optical properties change only slightly as observed. However, when anisotropy is added to the



**Fig. 2** UV–vis absorption spectra of as-prepared AgAu NCs by using (a) 6.1 nm, (b) 7.4 nm, and (c) 9.6 nm Ag NCs



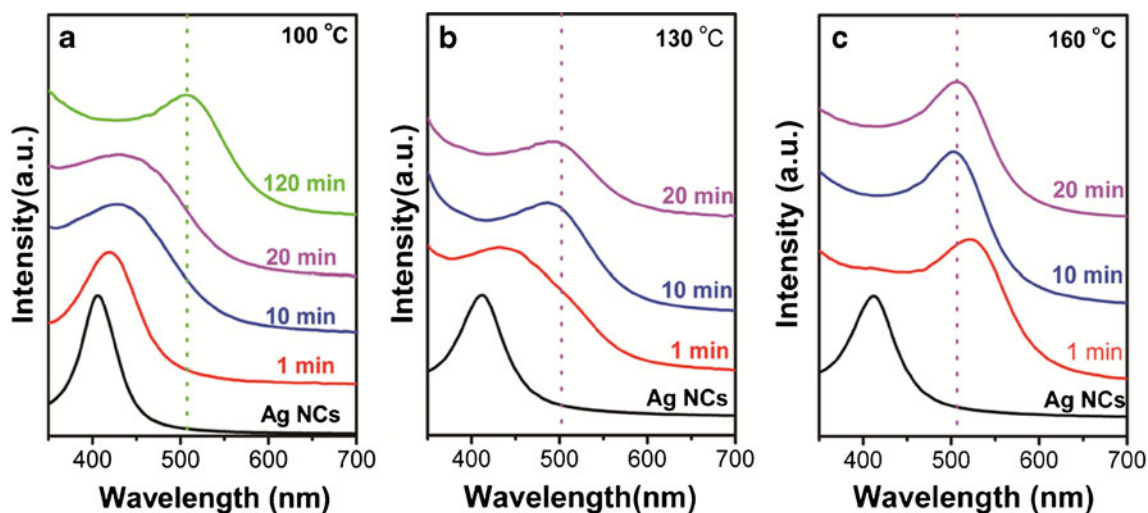
**Fig. 3** High resolution TEM images of as-prepared (a) 6.1 nm Ag NCs, (b)  $\text{Ag}_{24}\text{Au}_{76}$  alloy NCs, and (c)  $\text{Ag}_{43}/\text{Au}_{57}$  core/shell NCs

NCs, the optical properties of the NCs change dramatically. For example, spherical Ag/Au core/shell nanocrystals (shell thickness around 2 nm and size around 15 nm) have an absorption peak at 524 nm [14], and hollow Au octahedra NCs (shell thickness around 3 nm and size around 15 nm), which were synthesized by a replacement reaction performed on spherical Ag NCs, have absorption peaks at 430 and 720 nm [20]. Cubic Au/Ag core/shell NCs (thickness around 1 nm and size around 15 nm) have absorption peak at 410 and 510 nm [17]. In our result, Fig. 2c shows the absorption peak of 9.6 nm Ag NCs located at 408 nm. After the first round addition of Au precursors, the absorption peak red shifted and broadened. There are two absorption peaks (Fig. 1h): the one at 433 nm is the absorption peak for AgAu alloy NCs, and the other one is at 529 nm which is close to the absorption peak for Au NCs (520 nm) at this size. With the second round addition of Au precursors (Fig. 1i), the absorption signal at 433 nm became weaker and the absorption signal at 529 nm became stronger than before.

Due to the two absorption peaks, we think that the core within the Au shells is AgAu alloy rather than pure Ag cores in the cubic structure, and this is confirmed by a simple calculation of

the atomic ratio for Au to Ag. We assume that the cubic AgAu core/shell NCs (Fig. 1i) are formed by a 9.6 nm Ag core and Au shells which surrounding the Ag core. Based on this model, the Au/Ag atomic ratio should be 0.911. This value is much smaller than the result of 1.325 by EDS measurement (see ESM Fig. S3f). It indicates that Au is actually richer than in the simple model with spherical Ag core/Au shell structure. So the initial pure spherical Ag cores must have been partly replaced by Au atoms to form the AgAu alloy cores, which is in accordance with the absorption peak of AgAu alloy NCs at 433 nm (Fig. 2c). Similar calculation of the atomic ratio for Ag/Au core/shell structure has been reported in previous literature [14].

We speculate the growth mechanism of different structured NCs is as follows. When 6.1 nm Ag NCs were used as seed, the HRTEM images show that the finally formed AgAu NCs (13 nm) have high crystallinity with continuous lattice fringes ( $d$  spacing of 0.203 nm) throughout the whole particles, and the shape does not change between Fig. 3a and b. During this process, the reduction of Au precursors, the atom diffusion and NCs growth happened at the same time. When Au precursor is catalyzed by Ag seed, the motion of Ag



**Fig. 4** UV-vis absorption spectra of spherical AgAu alloy NCs prepared at (a) 100 °C, (b) 130 °C, and (c) 160 °C

atoms facilitates the diffusion of Au atoms into the Ag seed in the growth process. A fast diffusion competes with the Au deposition process which leads to the growth of alloy AgAu NCs (as shown in Fig. 1b), and then AgAu NCs reached 13 nm with the continuous increase of Au precursors. If 9.6 nm Ag NCs were used as seed, the spherical Ag NCs were turned to cubic Ag/Au core/shell NCs (Figs. 1i and 3c). During this process, the diffusion rate of Au atoms into Ag seeds is slower than the Au deposition process because of the decrease of surface energy with the increase of Ag size, and thus a layer of Au shell was formed on the AgAu alloy cores.

Meanwhile, different reaction temperatures were tested to investigate their influence on the formation of AgAu alloy NCs (Fig. 4). When the injection temperature was set at 100 °C, the color of the reaction solution changed slowly and the absorption peak red shifted to 501 nm after the reaction proceeded 2 h (Fig. 4a). If the injection temperature was set at 130 °C, the color of the reaction solution quickly changed and the absorption peak red shifted with the increase of reaction time, and was steady at 501 nm after the reaction proceeded 20 min (Fig. 4b). When the injection temperature was set at 160 °C, the AgAu NCs had broad size distributions after the addition of Au precursors at 1 min (Fig. S7a) and the absorbance band was located at 522 nm (Fig. 4c). The reason for this phenomenon is that reduction of the Au precursor occurred rapidly, and formed Ag<sub>core</sub>/Au<sub>shell</sub> structure. After reaction for 10 min, the absorption peak blue shifted slightly to 509 nm, indicating the end of the diffusion process. The size distribution of AgAu alloy NCs synthesized at 130 °C is better than the results at 160 °C (Fig. 1c). So, 130 °C is the proper reaction temperature to synthesize AuAg alloy NCs.

## Conclusion

In conclusion, a facile seed-growth method was developed to synthesize AgAu alloy and core/shell NCs by using ODA as the reducing agent, surface ligand, and solvent. Pre-synthesized Ag NCs acted as catalysts for the reduction of Au precursors. Through controlling the size of the Ag seed, size and shape control for AgAu NCs with alloy or core/shell structures was obtained. Different reaction temperatures were tested to optimize the synthesis of AgAu alloy NCs, and it was found that a proper reaction temperature for the growth of AgAu alloy NCs is 130 °C.

**Acknowledgments** This work was financially supported by the research project of the National Natural Science Foundation of China (21071041) and Program for New Century Excellent Talents in University of Chinese Ministry of Education.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

## References

- Sanders AW, Routenberg DA, Wiley BJ, Xia Y, Dufresne ER, Reed MA (2006) Observation of plasmon propagation, redirection, and fan-out in silver nanowires. *Nano Lett* 6:1822–1826
- Bishop PT, Ashfield LJ, Berzins A, Boardman A, Buche V, Cookson J, Gordon RJ, Salcianu C, Sutton PA (2010) Printed gold for electronic applications. *Gold Bull* 43:181–188
- Juliusa M, Roberts S, Fletcher JCQ (2010) A review of the use of gold catalysts in selective hydrogenation reactions Lynsey McEwana. *Gold Bull* 43:298–306
- Zheng N, Fan J, Stucky GD (2006) One-step one-phase synthesis of monodisperse noble-metallic nanoparticles and their colloidal crystals. *J Am Chem Soc* 128:6550–6551
- Chen M, Feng YG, Wang X, Li TC, Zhang JY, Qian DJ (2007) Silver nanoparticles capped by oleylamine: formation, growth, and self-organization. *Langmuir* 23:5296–5304
- Skrabalak SE, Chen J, Sun Y, Lu X, Au L, Cobley CM, Xia Y (2008) Gold nanocages: synthesis, properties, and applications. *Acc Chem Res* 41:1587–1595
- Zhang Q, Xie J, Yu Y, Yang J, Lee JY (2010) Tuning the crystallinity of Au nanoparticle. *Small* 6:523–527
- Seo D, Yoo CI, Chung IS, Park SM, Ryu S, Song H (2008) Shape adjustment between multiply twinned and single-crystalline polyhedral gold nanocrystals: decahedra, icosahedra, and truncated tetrahedra. *J Phys Chem C* 112:2469–2475
- Ming T, Feng W, Tang Q, Wang F, Sun L, Wang J, Yan C (2009) Growth of tetrahedral gold nanocrystals with high-index facets. *J Am Chem Soc* 131:16350–16351
- Khanal BP, Zubarev ER (2008) Purification of high aspect ratio gold nanorods: complete removal of platelets. *J Am Chem Soc* 130:12634–12635
- Wang C, Hu Y, Lieber CM, Sun S (2008) Ultrathin Au nanowires and their transport properties. *J Am Chem Soc* 130:8902–8903
- Xing S, Feng Y, Tay YY, Chen T, Xu J, Pan M, He J, Hng HH, Yan Q, Chen H (2010) Reducing the symmetry of bimetallic Au@Ag nanoparticles by exploiting eccentric polymer shells. *J Am Chem Soc* 132:9537–9539
- Wang C, Yin H, Chan R, Peng S, Dai S, Sun S (2009) One-pot synthesis of oleylamine coated AuAg Alloy NPs and their catalysis for CO oxidation. *Chem Mater* 21:433–435
- Wang C, Peng S, Chan R, Sun S (2009) Synthesis of AuAg alloy nanoparticles from core/shell-structured Ag/Au. *Small* 5:567–570
- Shore MS, Wang J, Johnston-Peck AC, Oldenburg AL, Tracy JB (2011) Synthesis of Au(core)/Ag(shell) nanoparticles and their conversion to AuAg alloy nanoparticles. *Small* 7:230–234
- Yang Y, Gong X, Zeng H, Zhang L, Zhang X, Zou C, Huang S (2010) Combination of digestive ripening and seeding growth as a generalized route for precisely controlling size of monodispersed noble monometallic, shell thickness of core-shell and composition of alloy nanoparticles. *J Phys Chem C* 114:256–264
- Ma Y, Li W, Cho EC, Li Z, Yu T, Zeng J, Xie Z, Xia Y (2010) Au@Ag core-shell nanocubes with finely tuned and well-controlled sizes, shell thicknesses, and optical properties. *ACS NANO* 4:6725–6734
- Wang D, Xie T, Peng Q, Li Y (2008) Ag, Ag<sub>2</sub>S, and Ag<sub>2</sub>Se nanocrystals: synthesis, assembly, and construction of mesoporous structures. *J Am Chem Soc* 130:4016–4022
- Yang J, Ying JY (2009) Room-temperature synthesis of nanocrystalline Ag<sub>2</sub>S and its nanocomposites with gold. *Chem Commun* 22:3187–3189
- Yin Y, Erdonmez C, Aloni S, Alivisatos AP (2006) Faceting of nanocrystals during chemical transformation: from solid silver spheres to hollow gold octahedra. *J Am Chem Soc* 128:12671–12673