

Seed-mediated growth method for high-quality noble metal nanocrystals

NIU WenXin^{1,2}, ZHANG Ling^{1,2} & XU GuoBao^{1*}

¹State Key Laboratory of Electroanalytical Chemistry; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

²Graduate University of the Chinese Academy of Sciences, Beijing 100039, China

Received March 30, 2012; accepted May 11, 2012; published online July 13, 2012

This review highlights work from the authors' laboratory on the recent development of seed-mediated growth method for noble metal nanocrystals. The seed-mediated growth method has become one of the most efficient and versatile methods for synthesizing high-quality noble metal nanocrystals. The seed-mediated growth method can separate the nucleation and growth stages of metal nanocrystals, and thus provide better control over the size, size distribution, and crystallographic evolution of metal nanocrystals. Because of its high controllability, the seed-mediated growth method is especially promising in providing mechanistic insights into the growth mechanisms of noble metal nanocrystals. In this review, the thermodynamic and kinetic parameters for the nucleation and growth of noble metal nanocrystals are systematically summarized. Mechanistic understanding of these parameters is provided. These studies provide useful guidelines for the rational design and synthesis of novel noble metal nanocrystals with high quality.

crystal growth, nanocrystal, noble metal, shape control, seed-mediated growth method

1 Introduction

Noble metal nanocrystals (NCs) have found broad application in spectroscopy [1], plasmonics [2], biosensing [3], biomedicine [4], catalysis [5], and solar energy conversion [6]. All these applications rely on the fascinating physical and chemical properties of noble metal NCs, which are significantly different from those of their bulk counterparts. Tailoring the shapes and sizes of noble metal NCs allows one to control a variety of properties that are relevant to many potential applications. Over the past decade, great progress has been made in developing synthetic methods for noble metal NCs. Among different methods, solution-phase based methods have greater capability and flexibility to

produce metal NCs with well-defined morphologies [7–9]. In solution, many parameters have been shown to greatly affect the growth mode of noble metal NCs; therefore, fundamental understanding of the mechanisms of these parameters is still a challenging task.

Since 2004, our group has applied the seed-mediated growth method to synthesize high-quality noble metal NCs [10–15]. Because of its high controllability, the seed-mediated method is especially promising in providing mechanistic insights into the growth mechanisms of noble metal NCs. This review mainly focuses on the recent development of the seed-mediated growth method for noble metal NCs in our laboratory. We systematically summarize the thermodynamic and kinetic parameters for the nucleation and growth of noble metal NCs. Mechanistic understanding of these parameters is also provided. Finally, perspectives on the future directions of both mechanistic studies and rational synthesis of noble metal NCs are provided.

*Corresponding author (email: guobaouxu@ciac.jl.cn)

2 Nucleation and growth mechanisms of the seed-mediated growth method

2.1 Basics of the seed-mediated growth method

The formation of metal NCs in solution-phase consists of a long chain of reaction steps. Generally, these steps could be divided into two different stages: nucleation and growth. During the nucleation stage, the reduction or decomposition of metal precursors leads to the formation of metal atoms. These metal atoms then self-assemble into small clusters and further grow into relatively stable crystal nuclei. In the growth stage, these crystal nuclei serve as seeds for the subsequent growth of metal NCs. Based on the temporal and spatial differences of the nucleation and growth stages, the synthesis of metal NCs can be divided into two major categories: homogeneous nucleation and heterogeneous nucleation [11]. For the homogeneous nucleation, the seed nanoparticles are generated *in situ*. The nucleation and growth of metal NCs are normally realized through a same chemical reaction. For the heterogeneous nucleation, the seed nanoparticles are pre-synthesized and added into a growth solution to further grow into metal NCs.

For the formation of metal NCs, the temporal separation of the nucleation and growth stages is required for a narrow size and shape distribution [16]. As a representative example of the heterogeneous nucleation, the seed-mediated growth method can nicely meet this requirement. A typical seed-mediated growth process involves the preparation of noble metal seed nanoparticles and their subsequent growth in reaction solutions containing metal precursors, reducing reagents, and shape-directing reagents [17]. The most commonly used shape-directing reagents are cationic surfactants, such as cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) [18]. In the growth stage, the reduction of metal precursors preferentially occurs on the surface of the seeds due to their catalytic properties, leading to the further growth of metal NCs. Compared with other methods, the nucleation and growth stages of the seed-mediated growth of NCs are well separated, and thus a better control over the size, size distribution, and shape evolution of metal NCs is provided. Because of these advantages, the seed-mediated growth method is especially promising in providing mechanistic insights into the growth mechanisms of noble metal NCs.

In the past 10 years, the seed-mediated growth method has become one of the most versatile methods for the crystallographic control of noble metal NCs. The application of the seed-mediated growth method for the shape control of Au NCs was mainly done by the Murphy and El-Sayed groups. The Murphy group designed a three-step seeding protocol that yields long Au nanorods with penta-twinned structures [19]. The El-Sayed group developed a one-step approach that produces single-crystalline Au nanorods with yields near 100% [20]. These studies paved the way for the

application of the seed-mediated growth method for the synthesis of shaped metal NCs with both high quality and reproducibility.

The research in our group focuses on searching for critical parameters and understanding their mechanisms for the seed-mediated growth of noble metal NCs. In the following sections, we will discuss our recent discoveries and understanding of the selection of seeds and the growth kinetics and thermodynamics during NCs growth.

2.2 The nucleation stage of the seed-mediated growth method

Many studies have established that the structure of the original seeds plays a crucial role in the structure and morphology evolution of the final metal NCs [21]. During the early stage of homogenous nucleation, the sizes of seeds typically fall in the range of 100–1000 atoms. These small seed NCs exist for an extremely short time and many parameters could kinetically and thermodynamically influence the structures of these NCs. Therefore, the seed NCs are hard to access with most of the current experimental methods [22]. By using the seed-mediated growth method, we are able to separate the nucleation and growth stages of NC formation and study the correlation between the crystal structures of seeds and the shapes of final NCs. Thus, the effect of seeds on NC growth could be revealed.

Our group has systematically studied the effect of seeds on the seed-mediated growth of single-crystalline Au NCs [13]. Three types of Au seeds were synthesized: ~41.3 nm CPC-capped single-crystalline Au seeds, ~3 nm citrate-capped twinned gold seeds, and ~1.5 nm CTAB-capped single-crystalline Au seeds. After seed-mediated growth in a solution containing CPC, potassium bromide, ascorbic acid, and Au salts, single-crystalline cubic Au NCs were obtained with a high yield (95.2%) when the CPC-capped single-crystalline Au seeds were used (Figure 1(a)). In contrast, single-crystalline cubic NCs were obtained with only a low yield when the ~3 nm twinned nanoparticles and the ~1.5 nm single-crystalline nanoparticles were used as seeds (Figure 1(b) and (c)). These results prove that the crystal structure of seeds fluctuates at very small sizes, whereas their structure will be fixed as their size increases. Because of their relatively large sizes, the CPC-capped single-crystalline seeds can avoid twinning during the growth process, and consequently lead to the formation of exclusively single-crystalline NCs with high-quality. The “large seed” strategy has also been successfully applied to synthesize single-crystalline Pd nanostructures by using 22 nm Pd nanocubes as seeds [10]. Similarly, the utilization of 22 nm Pd nanocube seeds could preserve the single-crystalline nature of the seeds during seed-mediated growth. This “large seed” strategy is based on the intrinsic properties of seeds; therefore, it’s particularly useful for investigating the effect of kinetic and thermodynamic factors on the growth

of single-crystalline noble metal NCs.

2.3 The growth stage of the seed-mediated growth method

The seed-mediated growth method is well known for its effectiveness in size control of metal nanoparticles [7, 17]. For example, Jana and coworkers prepared 20–100 nm spherical gold nanoparticles in diameter with narrow size distributions by using the seed-mediated growth method [23]. Based on the “large seed” strategy, we can simultaneously control the crystal structures and the sizes of metal nanocrystals. For example, monodisperse Pd nanocubes with different sizes were synthesized through the seed-mediated growth method [10]. The final edge length of nanocubes could be easily tuned by adding different volumes of seed solution. This method is able to produce monodisperse Pd nanocubes in high yields with broad size control from 22 to 109 nm (Figure 2).

Another major advantage of the seed-mediated growth method is its versatility in controlling the crystal facets of metal nanocrystals. In principle, the formation of different crystal facets of noble metal NCs is governed by a number of thermodynamic and kinetic factors [8]. If thermodynamic factors dominate the facet growth, the growth of NCs will obey the principle of surface energy minimization [15, 24–26]. Crystal facets with lower surface energy are favored. For example, the absorption of surfactants [8], polymers [16, 27], halide ions [24], and small molecules [28] and underpotential deposition of foreign metals [29] could selectively decrease the surface energy of certain crystal facets and favor the formation of these facets. If growth kinetics dominates, the shapes of NCs are mainly determined by the growth rate of different crystal facets [27, 30–32]. The growth rate of different crystal facets could be manipulated by changing the reaction temperature, the concentration of metal precursor, surfactant, and reductant [8]. The shape evolution of single-crystalline, twinned, or

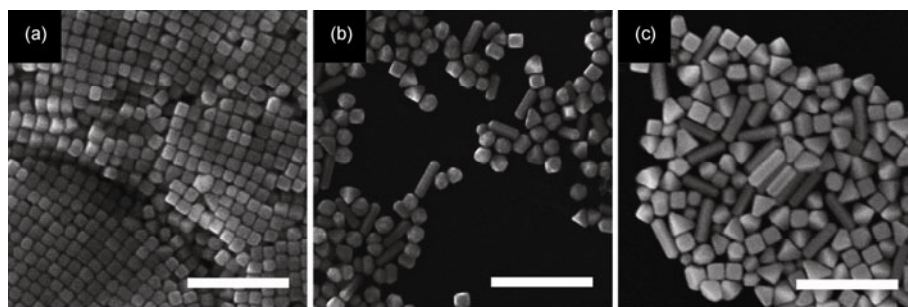


Figure 1 The effect of seed crystal structures. SEM images of Au NCs synthesized with different types of seeds. (a) ~41.3 nm CPC-capped single-crystalline Au seeds, (b) ~3 nm citrate-capped twinned Au seeds, and (c) ~1.5 nm CTAB-capped single-crystalline Au seeds (scale bars: 500 nm). Reproduced with permission from ref. [13].

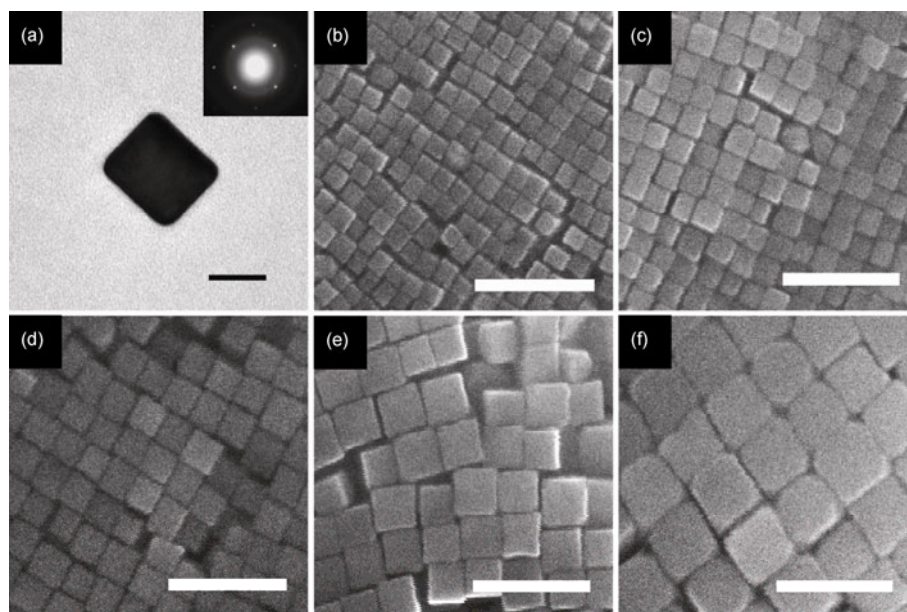


Figure 2 (a) TEM image of a single seed Pd nanocube. The inset shows its corresponding selected area electron diffraction (SAED) pattern (scale bar: 20 nm). (b–f) SEM images of 37, 44, 56, 76 and 109 nm Pd nanocubes (scale bars: 200 nm). Reproduced with permission from ref. [10].

multiple-twinned seeds is dramatically different [32, 33]; therefore, it is difficult to strictly identify the influence of thermodynamic and kinetic parameters on the growth of NC facets. Fortunately, the structures of noble metal NCs can be fixed as single-crystalline by using the “large seed” strategy, thus the final shapes are mainly determined by the crystal facets formed during the growth stage, which will enable us to study the correlation between the growth conditions and the crystal facets of NCs.

The kinetics and thermodynamics in the synthesis of single-crystalline Pd NCs in the presence of potassium iodide (KI) have been systemically investigated [12]. An orthogonal experimental design was applied to understand the correlation between the shape and the reaction conditions of Pd NCs (Figure 3). In the absence of KI or in the presence of

extremely low concentrations of KI, Pd nanocubes enclosed by six {100} facets were favored. The bromide anions from CTAB surfactant preferentially stabilize the Pd {100} facets [34]. RD NCs enclosed by twelve {110} facets were favored at relatively high temperatures and relatively high KI concentrations. Thermodynamically, the introduction of KI could increase the stability of the Pd {110} facets. Kinetically, high temperature could promote the preferential reduction of Pd salts on the Pd {111} and {100} facets, leading to the disappearance of these two crystal facets. These two factors promote the formation of RD NCs. Octahedral NCs enclosed by eight {111} facets were favored at relatively low temperatures and relatively high concentrations. In this case, the reduction of Pd salts on {100} and {110} facets is faster than that on {111} facets. Therefore, octahe-

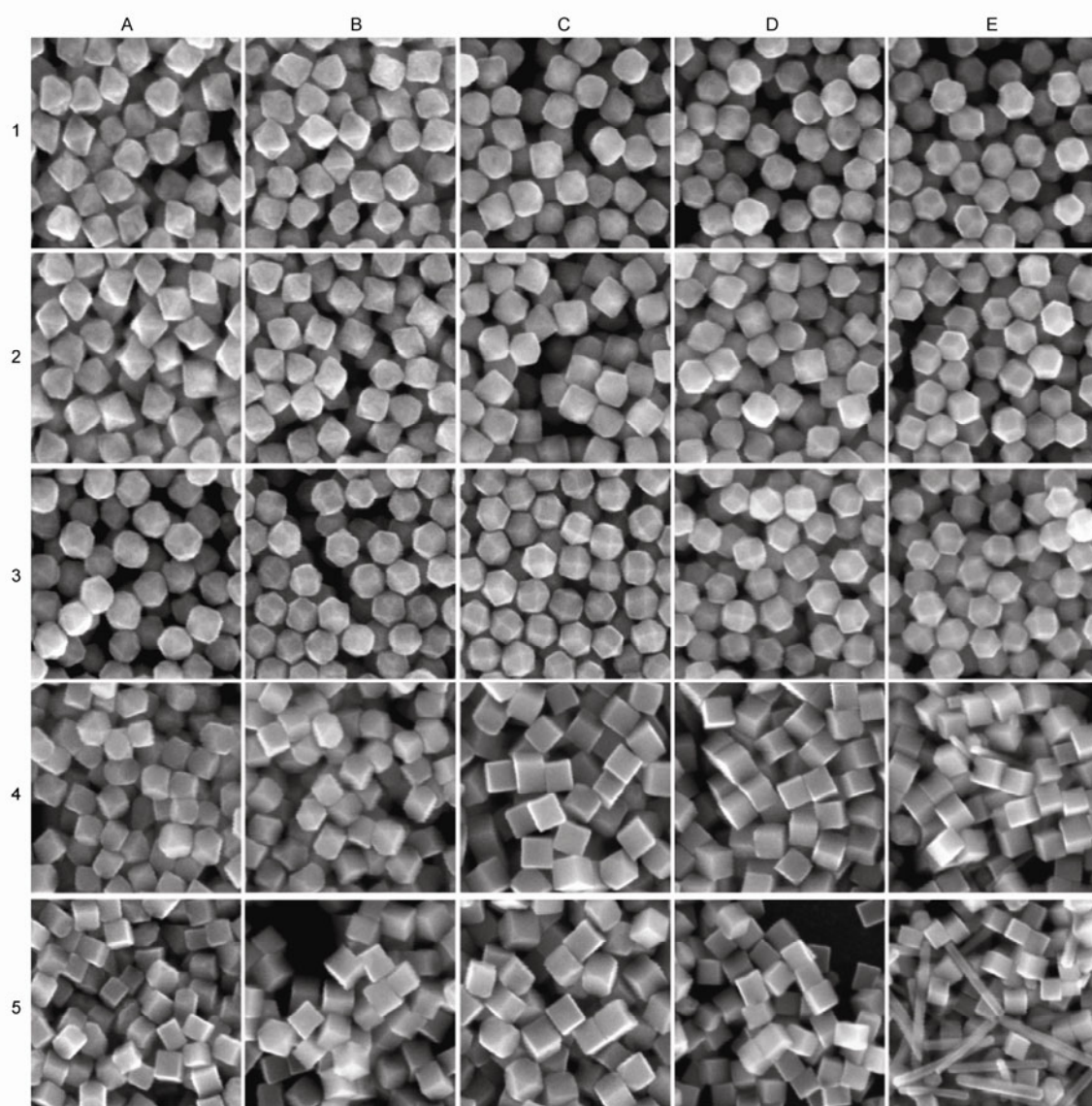


Figure 3 SEM images of polyhedral Pd nanocrystal samples synthesized under different conditions (scale bar: 200 nm). In columns (A–E), the reaction temperatures are 30, 40, 50, 60, and 80 °C, respectively. In rows 1–4, 5 μL of 10 mM, 25 μL of 1 mM, 5 μL of 1 mM, and 5 μL of 0.1 mM KI solutions were added, respectively. In row 5, no KI was added. Reproduced with permission from ref. [12].

dral NCs exclusively enclosed by $\{111\}$ facets were obtained.

The “large seed” strategy was also used to selectively synthesize single-crystalline rhombic dodecahedral, octahedral, and cubic Au NCs (Figure 4) [13]. The CPC-capped 41.3 nm single-crystalline Au NCs and CPC were used as seeds and surfactant for the seed-mediated growth, respectively. The competition between the AuCl_4^- reduction and the stabilizing effect of CPC on the $\{111\}$ and $\{110\}$ facets of Au NCs determined the formation of the rhombic dodecahedral (RD) and octahedral Au NCs. CPC surfactants can alter the surface energies of Au facets in the order $\{100\} > \{110\} > \{111\}$. Therefore, octahedral NCs were obtained when the stabilizing effect of CPC on $\{111\}$ facet dominated. When the reduction of AuCl_4^- on $\{111\}$ facets dominated, thermodynamically less-favored RD shapes were produced. Cubic Au NCs were obtained when bromide ions were introduced to selectively stabilize the $\{100\}$ facets of Au NCs.

2.4 Seed-mediated epitaxial growth

Another advantage of the seed-mediated growth method is the synthesis of metal heterostructures [35–39]. In this case, seeds of metal A could serve as nucleation centers for the growth of metal B. This seed-mediated epitaxial growth is especially efficient in synthesizing noble metal core-shell NCs. By using this method, the synthesis of concave trisoctahedral (TOH) Pd@Au core-shell NCs bound by $\{331\}$ high-index facets was achieved. Pd nanocubes with an average size of 22 nm were synthesized as the seeds. Then the Pd seeds were added to an aqueous solution of HAuCl_4 ,

ascorbic acid, and CTAC at 30 °C. The rapid reduction of HAuCl_4 by ascorbic acid leads to the formation of Au shells on the Pd nanocube seeds. SEM and TEM images show that the TOH nanocrystal comprises eight trigonal pyramids, which can be generated from an octahedron by “pulling out” the centers of each of its triangular face (Figure 5(a–c)). The high-angle annular dark-field scanning TEM (HAADF-STEM) image with enhanced elemental contrast clearly reveals a Pd nanocube residing at the center of each TOH Pd@Au core-shell nanocrystal (Figure 5(d–f)).

3 Conclusion and perspectives

In conclusion, we have shown that the “large seed” strategy is a robust approach to the synthesis of single-crystalline metal NCs. Because of their high monodispersity, the high-quality metal NCs we obtained can spontaneously assemble into ordered arrays in large scale. These metal NCs have been successfully applied in electrochemiluminescence [14], surface enhanced Raman spectroscopy [40], DNA-directed three-dimensional assembly [41], and electrocatalysis [42, 43]. In terms of growth mechanisms of NCs with different shapes, the kinetics and thermodynamics of the NC growth were investigated and qualitatively analyzed. Identification of these critical factors and understanding their mechanisms provide useful guidelines for the design of novel noble metal NCs with high-quality.

There are still many opportunities and challenges before the seed-mediated growth method reaches its full potential. First, a theoretical framework should be built to guide the rational design of noble metal NCs, which requires the ac-

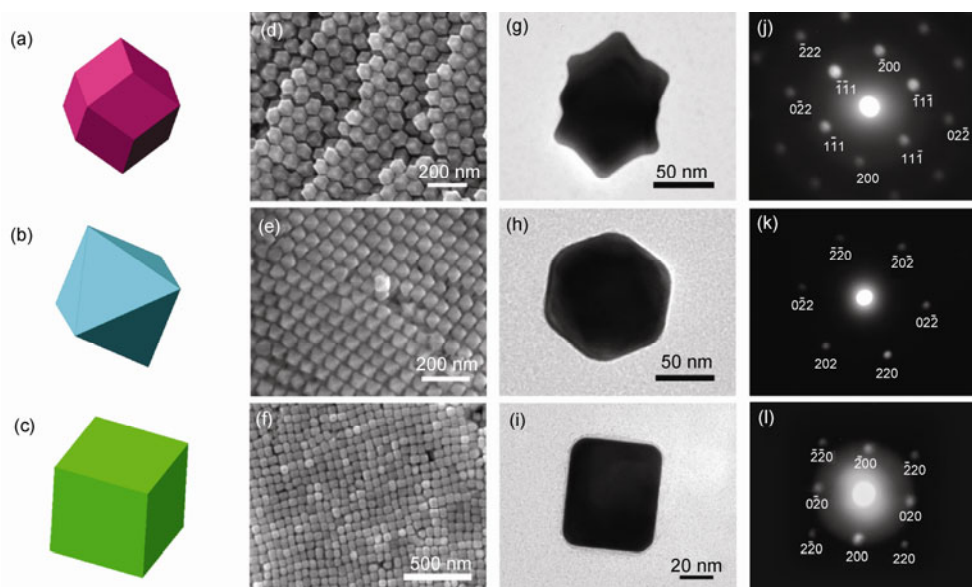


Figure 4 Geometrical models (a–c), SEM images (d–f), TEM images (g–i), and corresponding SAED patterns (j–l) of rhombic dodecahedral Au NCs bound by $\{110\}$ facets, octahedral Au NCs bound by $\{111\}$ facets, and cubic Au NCs bound by $\{100\}$ facets, respectively. Reproduced with permission from ref. [13].

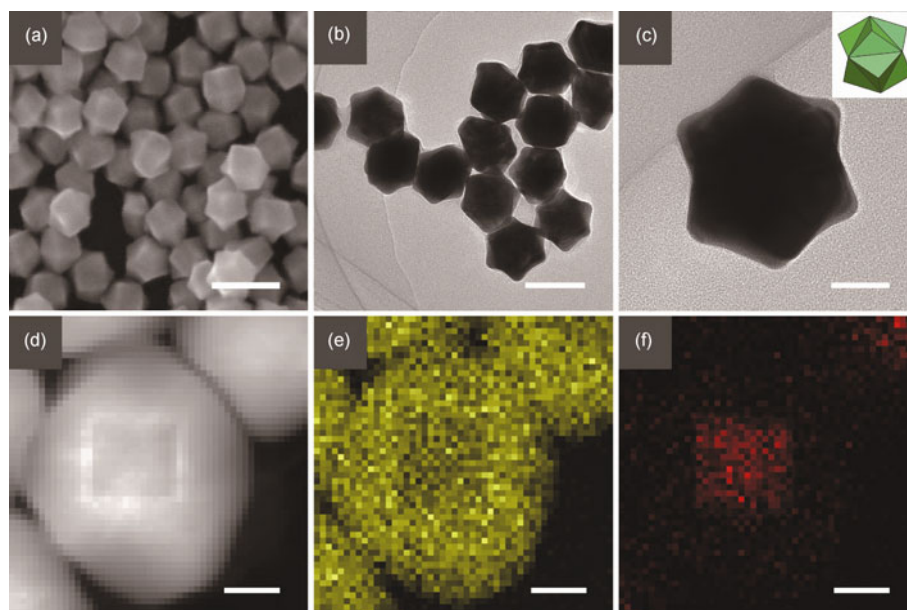


Figure 5 Electron microscopic images of concave trisoctahedral Pd@Au core-shell NCs. (a) SEM image (scale bar: 200 nm), (b) TEM image (scale bar: 100 nm), (c) TEM image and geometrical model of a single nanocrystal (scale bar: 50 nm), (d–f) Overall HAADF-STEM and Au, Pd elemental mapping images of an individual nanocrystal, respectively (scale bars: 20 nm) [14]. Reproduced by permission of The Royal Society of Chemistry.

cumulation of deeper fundamental understanding of the NCs growth. For example, the dynamics of the interaction between the surfactant and NC surface must be further explored and better understood at the molecular level. The kinetics and thermodynamics of the growth NCs should be quantitatively described. Theoretical calculations should also be employed to assist the interpretation of experimental data. Second, there are still a lot of opportunities in the fields of NC synthesis and design. For instance, the methodology described here could be readily applied to other noble metals such as Ag, Cu, Rh, Ir, and Ru. The seeds used in the seed-mediated growth method could be extended to singly twinned, multiply planar-twinned, and cyclic pentawinned structures. Moreover, the seed-mediated growth method could adopt the growth conditions from other methods, such as polyol process [44], electrochemical [45], and photochemical methods [46]. It is expected that such studies will contribute to the rational design and synthesis of noble metal NCs with high quality and pave their way for future application.

This project was supported by the National Natural Science Foundation of China (21175126).

- Anema JR, Li J-F, Yang Z-L, Ren B, Tian Z-Q. Shell-isolated nanoparticle-enhanced Raman spectroscopy: Expanding the versatility of surface-enhanced Raman scattering. *Annu Rev Anal Chem*, 2011, 4: 129–150
- Halas NJ. Plasmonics: An emerging field fostered by *Nano Letters*. *Nano Lett*, 2010, 10: 3816–3822
- Anker JN, Hall WP, Lyandres O, Shah NC, Zhao J, Van Duyne RP. Biosensing with plasmonic nanosensors. *Nat Mater*, 2008, 7: 442–453

- Dreaden EC, Alkilany AM, Huang X, Murphy CJ, El-Sayed MA. The golden age: Gold nanoparticles for biomedicine. *Chem Soc Rev*, 2012, 41: 2740–2779
- Zhou K, Li Y. Catalysis based on nanocrystals with well-defined facets. *Angew Chem Int Edit*, 2012, 51: 602–613
- Linic S, Christopher P, Ingram DB. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. *Nat Mater*, 2011, 10: 911–921
- Murphy CJ, San TK, Gole AM, Orendorff CJ, Gao JX, Gou L, Hunyadi SE, Li T. Anisotropic metal nanoparticles: Synthesis, assembly, and optical applications. *J Phys Chem B*, 2005, 109: 13857–13870
- Tao AR, Habas S, Yang PD. Shape control of colloidal metal nanocrystals. *Small*, 2008, 4: 310–325
- Xia YN, Xiong YJ, Lim B, Skrabalak SE. Shape-controlled synthesis of metal nanocrystals: Simple chemistry meets complex physics? *Angew Chem Int Ed*, 2009, 48: 60–103
- Niu W, Li Z-Y, Shi L, Liu X, Li H, Han S, Chen J, Xu G. Seed-mediated growth of nearly monodisperse palladium nanocubes with controllable sizes. *Cryst Growth Des*, 2008, 8: 4440–4444
- Niu W, Xu G. Crystallographic control of noble metal nanocrystals. *Nano Today*, 2011, 6: 265–285
- Niu W, Zhang L, Xu G. Shape-controlled synthesis of single-crystalline palladium nanocrystals. *ACS Nano*, 2010, 4: 1987–1996
- Niu W, Zheng S, Wang D, Liu X, Li H, Han S, Chen J, Tang Z, Xu G. Selective synthesis of single-crystalline rhombic dodecahedral, octahedral, and cubic gold nanocrystals. *J Am Chem Soc*, 2008, 131: 697–703
- Zhang L, Niu W, Li Z, Xu G. Facile synthesis and electrochemiluminescence application of concave trisoctahedral Pd@Au core-shell nanocrystals bound by {331} high-index facets. *Chem Commun*, 2011, (47): 10353–10355
- Zhang L, Niu W, Xu G. Seed-mediated growth of palladium nanocrystals: The effect of pseudo-halide thiocyanate ions. *Nanoscale*, 2011, 3: 678–682
- Tao A, Sinsermsuksakul P, Yang P. Polyhedral silver nanocrystals with distinct scattering signatures. *Angew Chem Int Ed*, 2006, 45: 4597–4601
- Murphy CJ, Gole AM, Hunyadi SE, Orendorff CJ. One-dimensional

- colloidal gold and silver nanostructures. *Inorg Chem*, 2006, 45: 7544–7554
- 18 Gao JX, Bender CM, Murphy CJ. Dependence of the gold nanorod aspect ratio on the nature of the directing surfactant in aqueous solution. *Langmuir*, 2003, 19: 9065–9070
- 19 Jana NR, Gearheart L, Murphy CJ. Wet chemical synthesis of high aspect ratio cylindrical gold nanorods. *J Phys Chem B*, 2001, 105: 4065–4067
- 20 Nikoobakht B, El-Sayed MA. Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method. *Chem Mater*, 2003, 15: 1957–1962
- 21 Elechiguerra JL, Reyes-Gasca J, Yacaman MJ. The role of twinning in shape evolution of anisotropic noble metal nanostructures. *J Mater Chem*, 2006, 16: 3906–3919
- 22 Erdemir D, Lee AY, Myerson AS. Nucleation of crystals from solution: Classical and two-step models. *Acc Chem Res*, 2009, 42: 621–629
- 23 Jana NR, Gearheart L, Murphy CJ. Evidence for seed-mediated nucleation in the chemical reduction of gold salts to gold nanoparticles. *Chem Mater*, 2001, 13: 2313–2322
- 24 Ha TH, Koo HJ, Chung BH. Shape-controlled syntheses of gold nanoprisms and nanorods influenced by specific adsorption of halide ions. *J Phys Chem C*, 2007, 111: 1123–1130
- 25 Huang X, Zheng N. One-Pot, High-yield synthesis of 5-fold twinned Pd nanowires and nanorods. *J Am Chem Soc*, 2009, 131: 4602–4603
- 26 Huang X, Zhang H, Guo C, Zhou Z, Zheng N. Simplifying the creation of hollow metallic nanostructures: One-pot synthesis of hollow palladium/platinum single-crystalline nanocubes. *Angew Chem Int Ed*, 2009, 48: 4808–4812
- 27 Chen Y, Gu X, Nie CG, Jiang ZY, Xie ZX, Lin CJ. Shape controlled growth of gold nanoparticles by a solution synthesis. *Chem Commun*, 2005: 4181–4183
- 28 Chen M, Wu B, Yang J, Zheng N. Small adsorbate-assisted shape control of Pd and Pt nanocrystals. *Adv Mater*, 2012, 24: 862–879
- 29 Personick ML, Langille MR, Zhang J, Mirkin CA. Shape control of gold nanoparticles by silver underpotential deposition. *Nano Lett*, 2011, 11: 3394–3398
- 30 Xiong Y, Cai H, Yin Y, Xia Y. Synthesis and characterization of fivefold twinned nanorods and right bipyramids of palladium. *Chem Phys Lett*, 2007, 440: 273–278
- 31 Xiong YJ, Cai HG, Wiley BJ, Wang JG, Kim MJ, Xia YN. Synthesis and mechanistic study of palladium nanobars and nanorods. *J Am Chem Soc*, 2007, 129: 3665–3675
- 32 Wu H-Y, Huang W-L, Huang MH. Direct high-yield synthesis of high aspect ratio gold nanorods. *Cryst Growth Des*, 2007, 7: 831–835
- 33 Niu ZQ, Peng Q, Gong M, Rong HP, Li YD. Oleylamine-mediated shape evolution of palladium nanocrystals. *Angew Chem Int Edit*, 2011, 50: 6315–6319
- 34 Zhang YW, Grass ME, Kuhn JN, Tao F, Habas SE, Huang WY, Yang PD, Somorjai GA. Highly selective synthesis of catalytically active monodisperse rhodium nanocubes. *J Am Chem Soc*, 2008, 130: 5868–5869
- 35 Carbo-Argibay E, Rodriguez-Gonzalez B, Pacifico J, Pastoriza-Santos I, Perez-Juste J, Liz-Marzan LM. Chemical sharpening of gold nanorods: The rod-to-octahedron transition. *Angew Chem Int Edit*, 2007, 46: 8983–8987
- 36 Carbo-Argibay E, Rodriguez-Gonzalez B, Pastoriza-Santos I, Perez-Juste J, Liz-Marzan LM. Growth of pentatwinned gold nanorods into truncated decahedra. *Nanoscale*, 2010, 2: 2377–2383
- 37 Xiang YJ, Wu XC, Liu DF, Jiang XY, Chu WG, Li ZY, Ma Y, Zhou WY, Xie SS. Formation of rectangularly shaped Pd/Au bimetallic nanorods: Evidence for competing growth of the Pd shell between the {110} and {100} side facets of Au nanorods. *Nano Lett*, 2006, 6: 2290–2294
- 38 Xiang YU, Wu XC, Liu DF, Li ZY, Chu WG, Feng LL, Zhang K, Zhou WY, Xie SS. Gold nanorod-seeded growth of silver nanostructures: From homogeneous coating to anisotropic coating. *Langmuir*, 2008, 24: 3465–3470
- 39 Fan F-R, Liu D-Y, Wu Y-F, Duan S, Xie Z-X, Jiang Z-Y, Tian Z-Q. Epitaxial growth of heterogeneous metal nanocrystals: From gold nano-octahedra to palladium and silver nanocubes. *J Am Chem Soc*, 2008, 130: 6949–6950
- 40 Zhu Z, Meng H, Liu W, Liu X, Gong J, Qiu X, Jiang L, Wang D, Tang Z. Superstructures and SERS properties of gold nanocrystals with different shapes. *Angew Chem Int Ed*, 2011, 50: 1593–1596
- 41 Jones MR, Macfarlane RJ, Lee B, Zhang J, Young KL, Senesi AJ, Mirkin CA. DNA-nanoparticle superlattices formed from anisotropic building blocks. *Nat Mater*, 2010, 9: 913–917
- 42 Erikson H, Sarapuu A, Alexeyeva N, Tammeveski K, Solla-Gullon J, Feliu JM. Electrochemical reduction of oxygen on palladium nanocubes in acid and alkaline solutions. *Electrochim Acta*, 2012, 59: 329–335
- 43 Erikson H, Sarapuu A, Tammeveski K, Solla-Gullon J, Feliu JM. Enhanced electrocatalytic activity of cubic Pd nanoparticles towards the oxygen reduction reaction in acid media. *Electrochem Commun*, 2011, 13: 734–737
- 44 Wiley B, Sun Y, Xia Y. Synthesis of silver nanostructures with controlled shapes and properties. *Acc Chem Res*, 2007, 40: 1067–1076
- 45 Tian N, Zhou Z-Y, Sun S-G. Platinum metal catalysts of high-index surfaces: From single-crystal planes to electrochemically shape-controlled nanoparticles. *J Phys Chem C*, 112: 19801–19817
- 46 Millstone JE, Hurst SJ, Metraux GS, Cutler JI, Mirkin CA. Colloidal gold and silver triangular nanoprisms. *Small*, 2009, 5: 646–664