

Supplementary Information

The Unusual Effect of AgNO_3 on Growth of Au Nanosstructures and their Catalytic Performance

Xingliang Li, Yun Yang*, Guangju Zhou, Shuhua Han, Wenfang Wang, Lijie Zhang, Wei Chen, Chao Zou, and Shaoming Huang*

Nanomaterials and Chemistry Key Laboratory, Wenzhou University

Wenzhou, Zhejiang 325027, P. R. China. Fax: 0086-57788373124

Email: bachier@163.com; smhuang@wzu.edu.cn

Catalytic reaction of p-nitrophenol to p-aminophenol

2 mL NaBH_4 solution (60 mM) was added into 2 mL p-nitrophenol solution (0.34 mM) and then the formed mixture was stirred for 15 min. 0.5 mL Au colloid (0.02 mM) was introduced to promote the reaction. 3 mL solution was transferred to a quartz cuvette quickly and recorded with UV-vis spectroscopy.

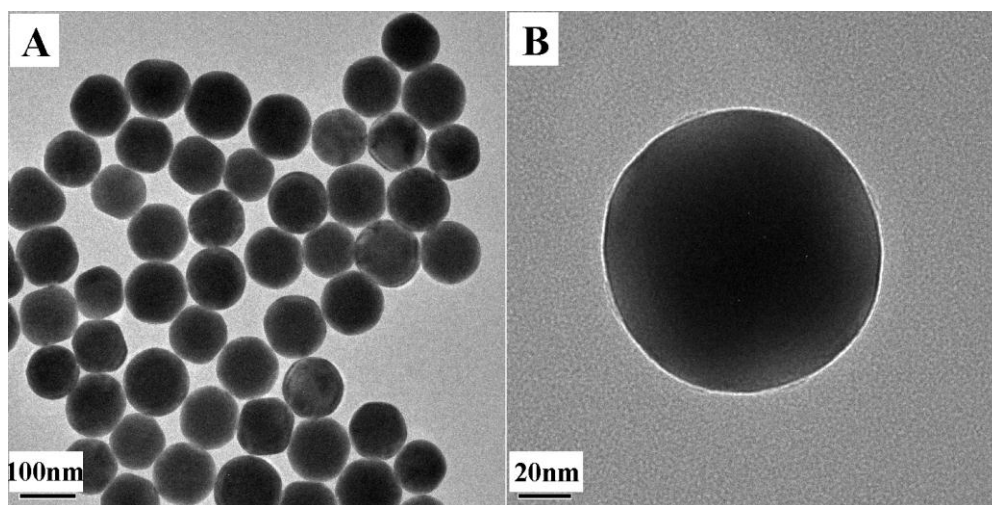


Fig. S1 The typical TEM and HRTEM images of spherical nanoparticles prepared using 50 μL AgNO_3 DEG.

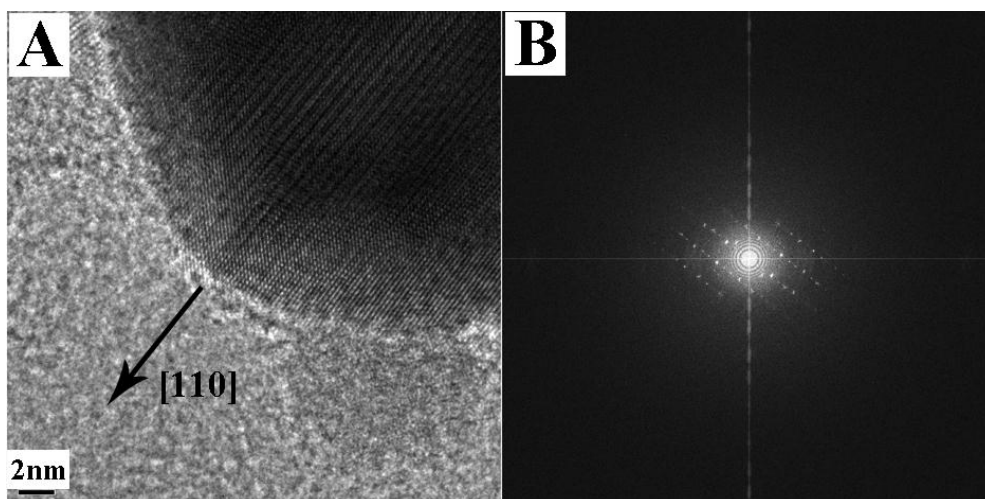


Fig. S2 The typical HRTEM images and corresponding FFT pattern.

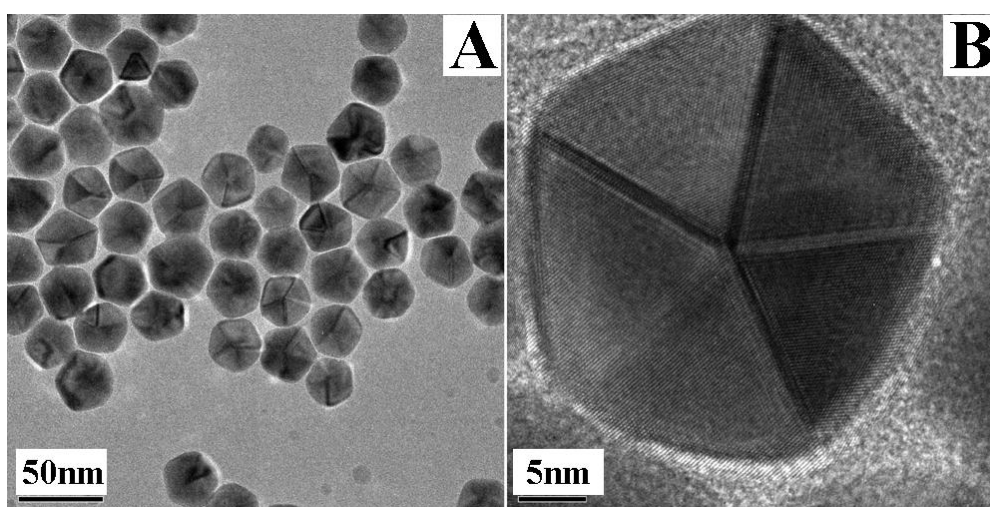


Fig. S3 The typical TEM and HRTEM images of decahedral nanoparticles prepared using 4 mL

AgNO_3 DEG.

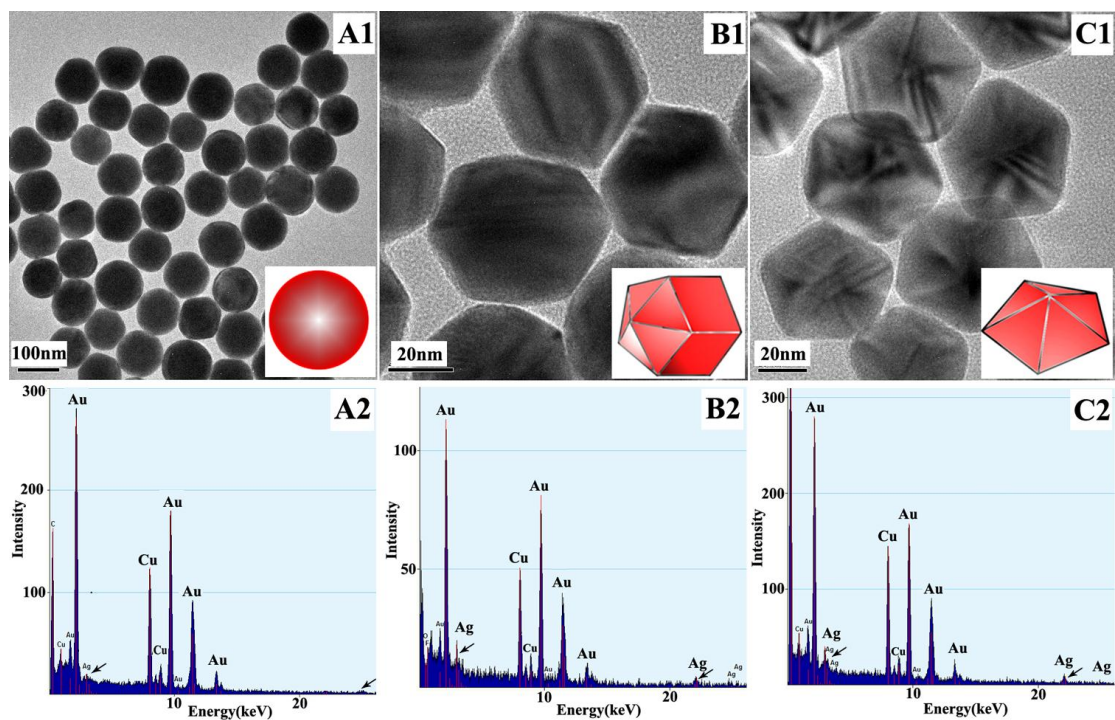


Fig. S4 The typical TEM images and EDS patterns of different nanostructures: (A) spherical nanoparticles (225 °C and 50 uL AgNO₃); (B) short nanorods (225 °C and 500 uL AgNO₃); (C) decahedra (225 °C and 2 mL AgNO₃).

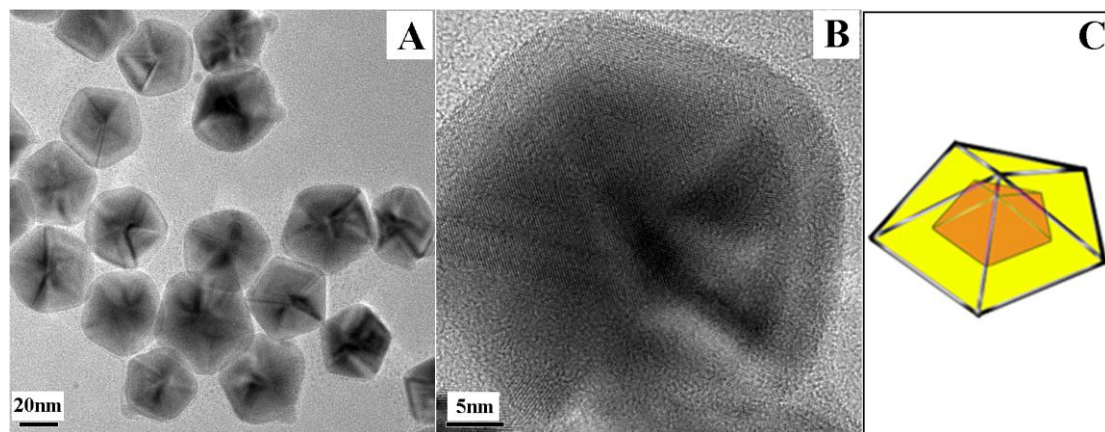


Fig. S5 The typical TEM, HRTEM and schematic images of nanodecahedrons prepared by using 8 mL AgNO₃ DEG at 225 °C.

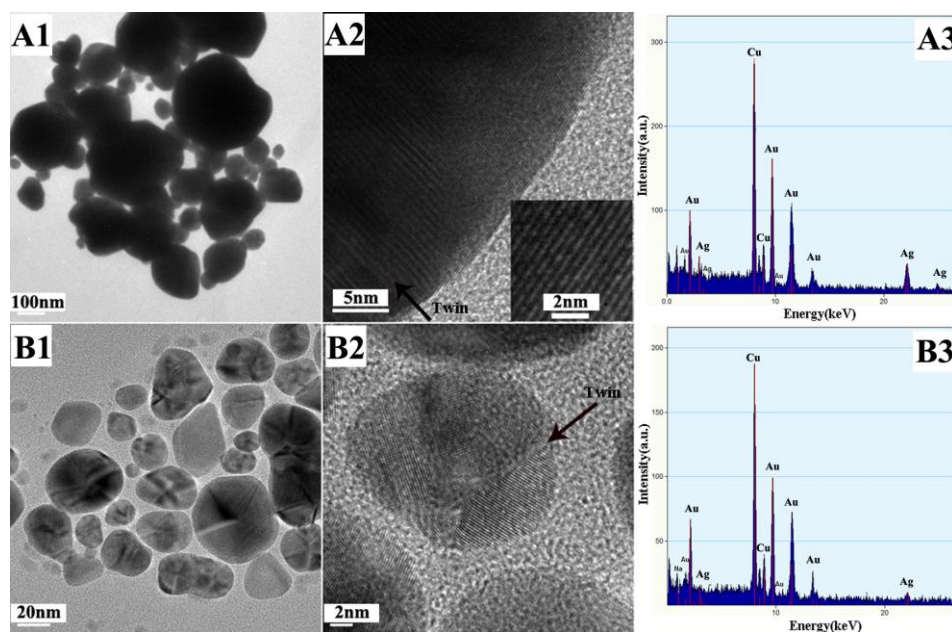


Fig. S6 The typical TEM images, HRTEM images and EDS patterns of nanoparticles prepared with different surfactants: (A) hexadecyl trimethyl ammonium bromide (CTAB); (B) PVP. The reaction conditions are unchanged except for surfactants.

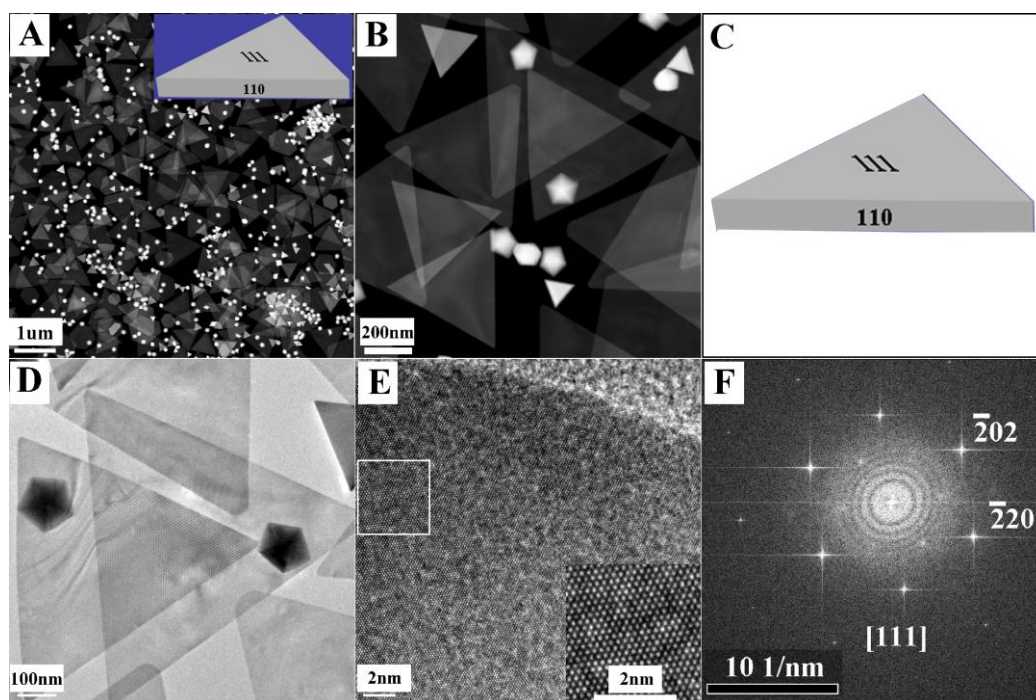


Fig. S7 The typical HAADF, TEM, HRTEM, FFT and schematic images of nanostructures prepared under nitrogen protection. Inset in (E) is the magnified TEM images of selected area. This Fig. shows that the oxygen also plays an important role in the formation of five-fold twin nanoparticles.

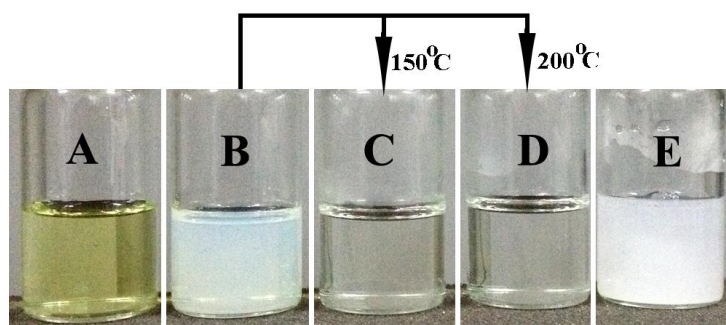


Fig. S8 The optical color of (A) solution containing HAuCl_4 , DEG and PDDA; (B) solution containing HAuCl_4 , DEG, PDDA and AgNO_3 (the molar ratio of Ag/Au is 5); (C) after heating solution b for 3 min at 200 °C; (D) after heating solution b for 20 min at 150 °C; (E) solution containing CTAB+ AgNO_3 + HAuCl_4 (the molar ratio of Ag/Au is 5). The color (C and D) indicate that AgCl is soluble under this conditions.

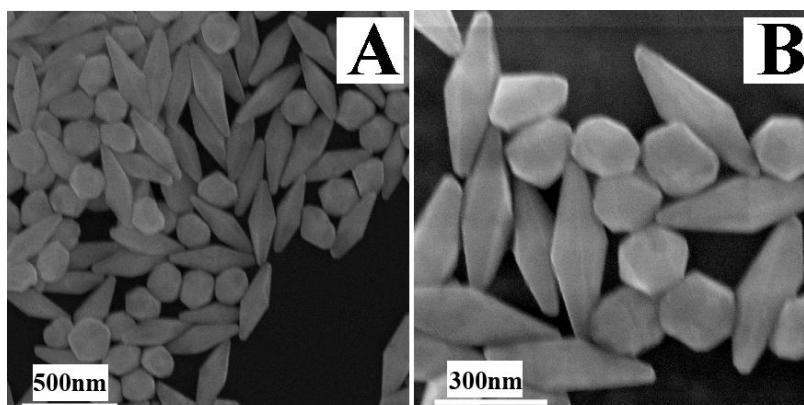


Fig. S9 The typical SEM images of gold nanostructures prepared at 170 °C (300 uL AgNO_3). This indicates that temperature lower than 185 °C can not create monodispersed product.

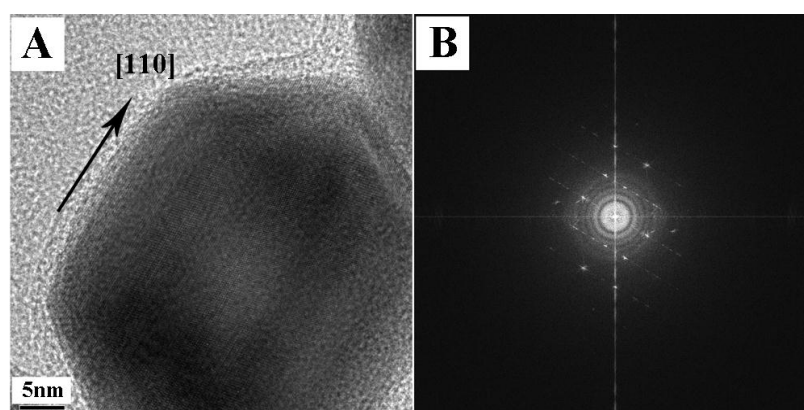


Fig. S10 The typical HRTEM images (A) of gold nanorod prepared using 500 uL AgNO_3 at 225 °C and corresponding FFT pattern (B). FFT image demonstrates the five-fold twin crystalline feature.

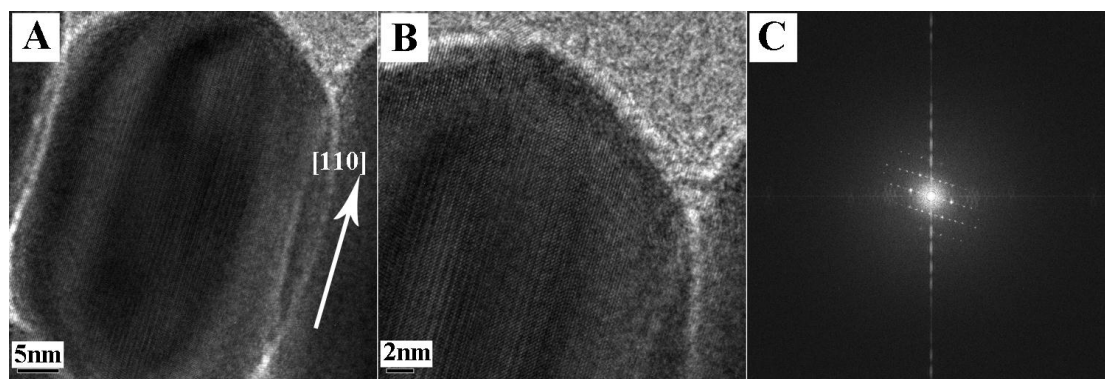


Fig. S11 The typical HRTEM images (A and B) of gold nanorod prepared using 200 μL AgNO_3 at 225 $^\circ\text{C}$ and corresponding FFT pattern (C). FFT image demonstrates the five-fold twin crystalline feature.

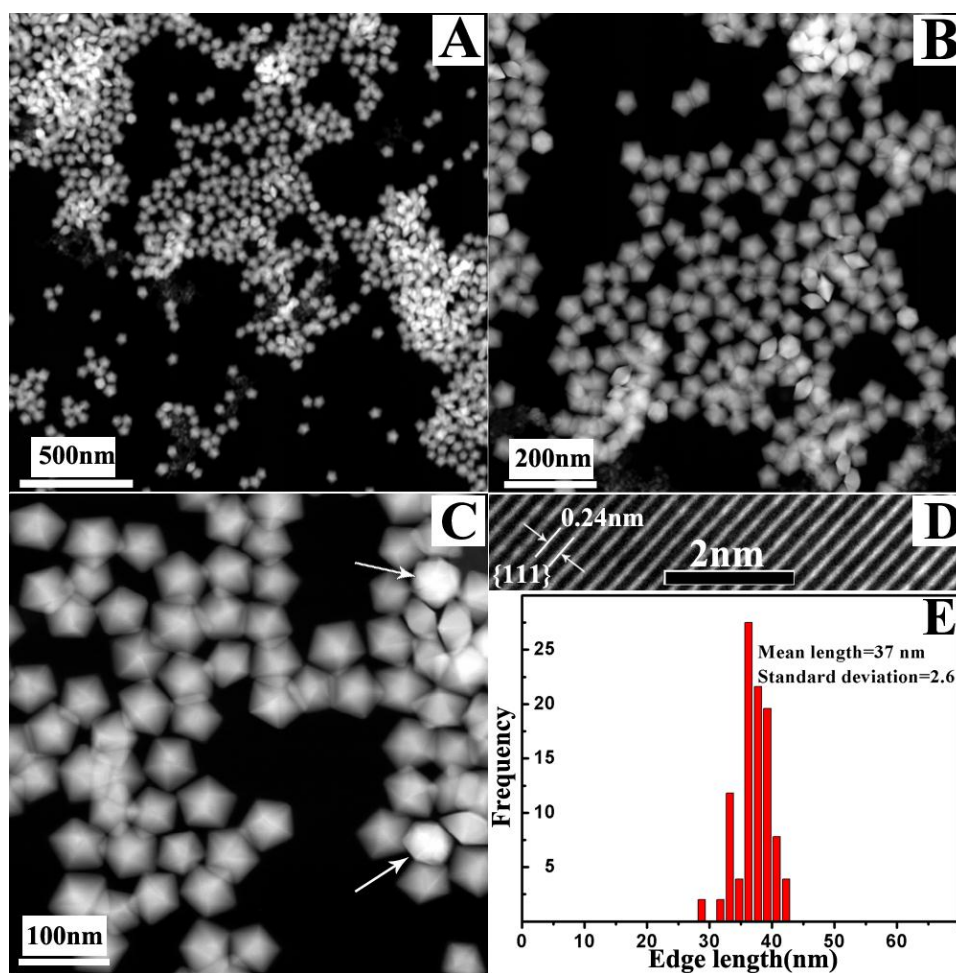


Fig. S12 The typical HAADF (A, B and C), HRTEM (D) images and size distribution histogram (E) of Au decahedral nanoparticles (217 $^\circ\text{C}$ and 5 mL AgNO_3). The nanoparticles designated by the arrows are other shaped.

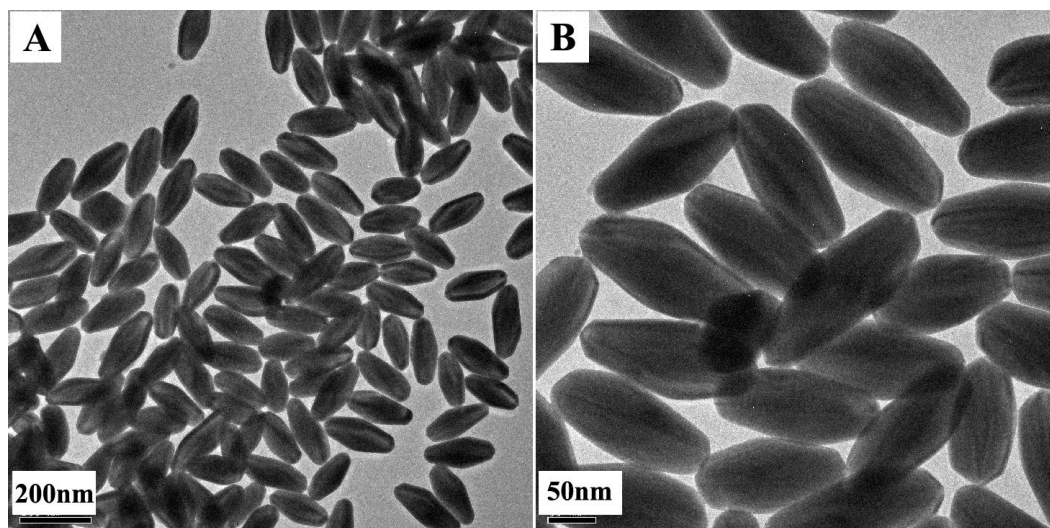


Fig. S13 The typical TEM images of gold nanobipyramids prepared using 500 μL AgNO_3 at 190 $^\circ\text{C}$ (reaction time is 2h). The Figure demonstrates that high yield.

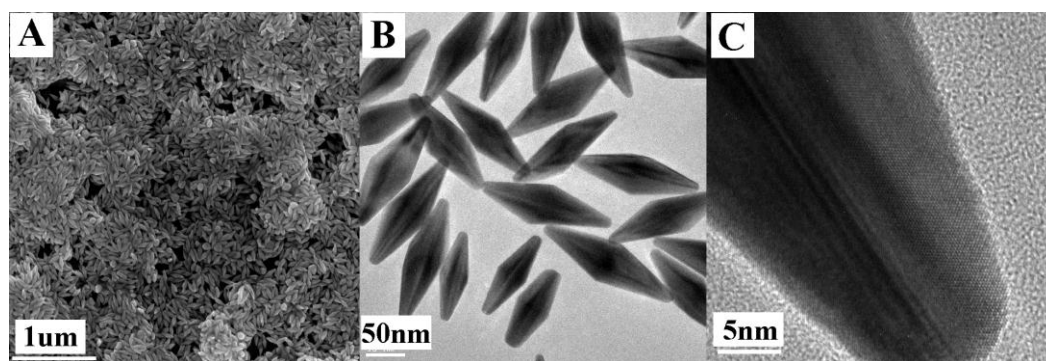


Fig. S14 The typical SEM, TEM and HRTEM images of gold nanobipyramids prepared using 300 μL AgNO_3 at 200 $^\circ\text{C}$ (reaction time is 25 min). The Figure demonstrates that high yield.

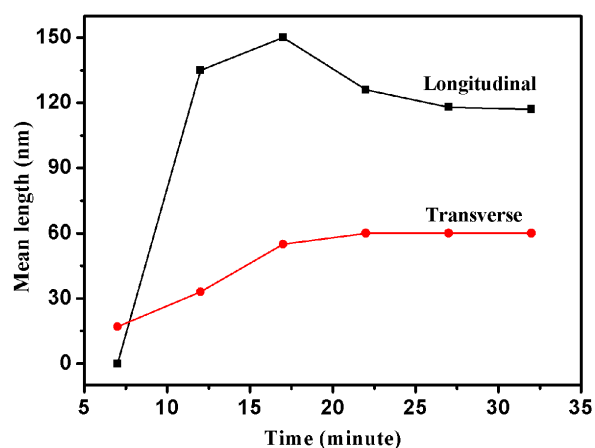


Fig. S15 The longitudinal and transverse length change as a function of reaction time (215 $^\circ\text{C}$; 170 μL AgNO_3). This result is calculated based on Fig. 7. The result shows that transverse length has no more change after about 20 min.

The discussion about total surface area and edge atom number

The catalytic performance of NPs always is surface-area-dependent and large area provides more surface atoms which play important roles in catalysis. Compared with large-sized NPs, small-sized ones have large surface area and therefore exhibit better catalytic performance. For decahedra, given that all decahedra have the same size, the total surface area (S) can be calculated using equation (1).

$$S = nS_d \quad (1)$$

S_d is the surface area of one decahedron NP and n is the total number of decahedron NPs.

In fact, one decahedron is composed of 5 tetrahedra with the same edge length (Y. Zhang, Y.-H. Wen, Z.-Z. Zhu and S.-G. Sun, *J. Phys. Chem. C*, 2010, **114**, 18841–18846; Y. Yang, W. Wang, X. Li, W. Chen, N. Fan, C. Zou, X. Chen, X. Xu, L. Zhang and S. Huang, *Chem. Mater.*, 2013, **25**, 34). The surface area of one tetrahedron (S_t) can be calculated with equation 2.

$$S_t = a^2\sqrt{3} \quad (2)$$

Where, a is the edge length. Therefore the surface area of one {111} facet ($S_{\{111\}}$) is known according to equation 3.

$$S_{\{111\}} = \frac{1}{4}S_t \quad (3)$$

One decahedron NP has 10 {111} and the surface area of one decahedron can be obtained according to equation 4. In order to calculate S , we also need to know n which can be obtained based on the equation (5).

$$S_d = 10S_{\{111\}} = 2.5a^2\sqrt{3} \quad (4)$$

$$n = \frac{M}{M_d} \quad (5)$$

Here, M and M_d are the total mass of introduced Au and the mass of one decahedron respectively. In all cases, M is unchanged and can be considered as constant. Based on the discussion above, the total volume or mass of 5 tetrahedra are equal to that of one decahedron (equation 6).

$$M_t = V\rho = \frac{\rho a^3}{12}\sqrt{2} \quad (6)$$

Where, M_t and V are the mass and volume of one tetrahedron respectively. ρ is the Au density. Thus, the mass of one decahedron (M_d) can be calculated with the equation 7.

$$M_d = 5M_t = \frac{5\rho a^3}{12}\sqrt{2} \quad (7)$$

According to equation 1, 4, 5 and 7, S can be figured out according to the equation 8 which means that S is inversely proportional to edge length.

$$S = n\mathcal{S} = \frac{9M}{\rho a} \quad (8)$$

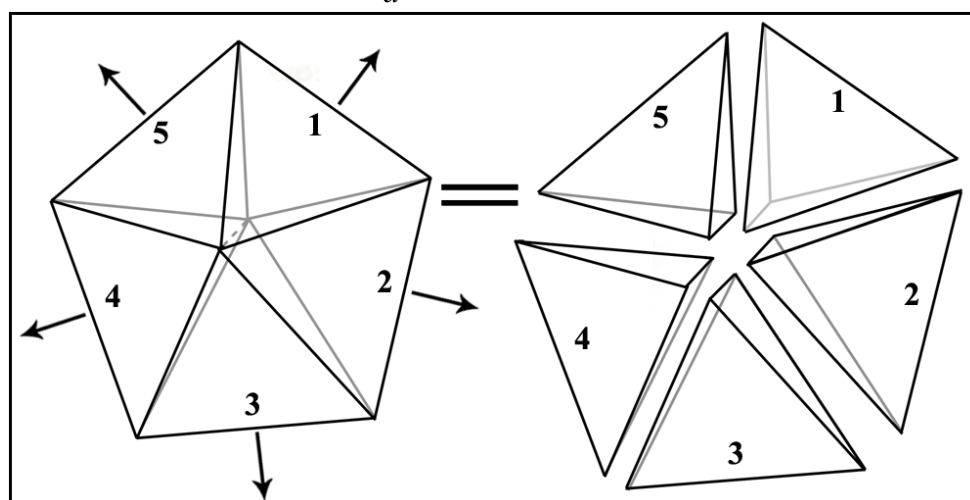
For the total number of edge atoms, it can be calculated according to equation 9 (one decahedron has 15 edges),

$$A_e = 15amn = \frac{18m\sqrt{3}M}{\rho a^2} \quad (9)$$

Where, m is the edge atom number of per unit length. Here, for m , M and ρ are unchanged, a constant K is used and the equation 9 can be simplified to equation 11,

$$K = \frac{18m\sqrt{3}M}{\rho} \quad (10)$$

$$A_e = \frac{K}{a^2} \quad (11)$$



Scheme S16. The schematic relation between decahedron and tetrahedron.

The size- and shape-dependent catalytic performance

Parameter control (shape and size) is critical to material properties modulation, such as catalytic performance and optical property. Previously, several groups demonstrated metal NPs could catalyze the reduction of p-nitrophenol to p-aminophenol by sodium borohydride.¹⁻⁴ We chose this reaction to investigate the effect of shape and size on catalytic performance of the NPs prepared in our experiment. The solution containing p-nitrophenol and sodium borohydride has a characteristic absorption peak at about 420 nm, which facilitates monitoring the reaction progress with UV-vis spectrum. When decahedral Au NPs were added to the solution, the absorption of p-nitrophenol decreased with reaction time gradually (Fig. S17 A). Through measuring and comparing the peak value of different stages, the conversion rate can be calculated and used to evaluate the catalytic performance of materials. Here, decahedra with 21 nm, 33 nm and 51 nm edge were selected to catalyze the reduction. In a comparative experiment, the reaction without NPs was also carried out. Clearly, the absence of NPs caused very slow reduction (Fig. S17 B). When 51 nm decahedra were added, the reduction rate was accelerated and about 42% p-nitrophenol was changed to p-aminophenol within 30 min. If the 33 nm edged decahedra acted as catalyst, 85% p-nitrophenol was converted after 30 min. In case of 21 nm decahedra, 17 min reaction time almost caused the complete conversion. Above observation indicates that small sized NPs are more active than large ones. The total active surface area (S) and the total number of edge atoms (A_e) are believed to be the key factors. The decahedral NP actually is made of 5 tetrahedrons and therefore the surface area can be calculated according to the following equation 2,

$$S = \frac{9M}{\rho a} \quad (8)$$

Where, M , ρ and a are designated as the total mass of Au, the density of Au and the edge length of decahedron respectively. The equation 2 shows that the total surface area is inversely proportional to edge size when the total mass of NPs is unchanged. Accordingly, the ratio of surface area of used decahedra should be 1.57:1:0.65 from small size to large size order. If the catalytic ability difference is caused only by the surface area factor, the time needed for complete reduction of p-nitrophenol should theoretically match the ratio inversely. Practically, Fig. S17 shows that the result disagrees with that. The change of edge atoms with size might be another factor responsible for this difference. It has been demonstrated that the atoms on edges are more active than these on other positions.⁸⁷ The edge atoms number (A_e) can be calculated theoretically

with equation 3. Compared with large sized NPs, small sized ones have more edge atoms and possess high catalytic activity.

$$A_e = \frac{K}{a^2} \quad (11)$$

Where, K is a constant. According to equation 3, the edge atoms heavily decrease with size increasing. For example, the ratio of edge atom between 21 nm decahedra and 51 nm decahedra is about 5.896. Therefore, the edge atom difference, as well as the surface area, possibly causes the size-dependent catalytic activity.⁵

The catalytic performance of NSs (Fig. 6C, Fig. 7C, Fig. 7D and Fig. 7E) were also explored with the same reduction (Fig. S17 C). Nanobipyramids shown in Fig. 7 C exhibit excellent catalytic performance due to the presence of high index facet and large surface area.²⁶ The p-nitrophenol could be converted in 8 min completely when nanobipyramids were present (curve 1 in Fig. S17 C). 97% conversion rate was achieved by 2 nanobipyramids in 17 min (curve 2 in Fig. S17 C). The same conversion rate needs 28 min reaction time in the case of 3# NRs (curve 3 in Fig. S17 C). 4 # NRs only created 65% conversion rate even in 30 min (curve 4 in Fig. S17 C). The result demonstrates that the catalytic ability reduces with facet index because surface activity decreases.

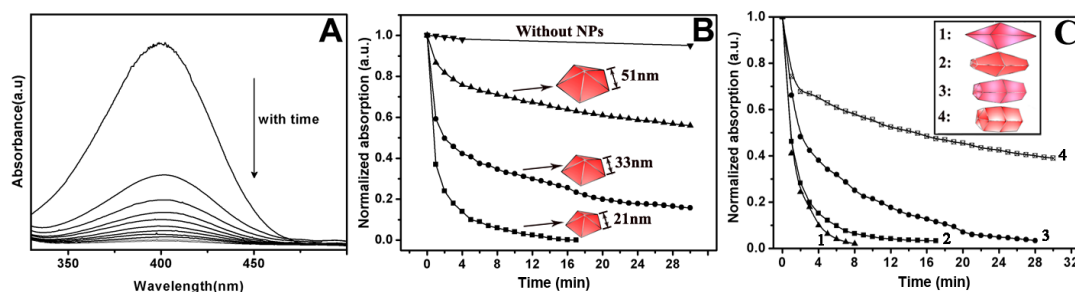


Fig. S17 (A) Time-dependent UV-vis absorption of the reaction mixture catalyzed by Au decahedron 21 nm. (B) Normalized absorption at the peak position of p-nitrophenol as a function of time when various sized Au decahedra were used as catalysts. (C) Normalized absorption at the peak position of p-nitrophenol as a function of reaction time when various shaped Au NSs were used as catalysts.

Reference

1. J. Zeng, Q. Zhang, J. Chen and Y. Xia, *Nano Lett.*, 2010, **10**, 30.
2. X. Zhang and Z. Su, *Adv. Mater.*, 2012, **24**, 4574.
3. X. Guo, Q. Zhang, Y. Sun, Q. Zhao and J. Yang, *ACS Nano*, 2012, **6**, 1165.
4. Y. Khalavka, J. Becker and C. Sonnichsen, *J. Am. Chem. Soc.*, 2009, **131**, 1871.

5. J. Wu, L. Qi, H. You, A. Gross, J. Li and H. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 1188