Electronic Supplementary Information (ESI)

Surface faceting and compositional evolution of Pd@Au core−shell nanocrystals during in situ annealing

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Details of Methods

Preparation of Pd@Au core-shell cubic NPs[1]

Synthesis of Pd 10.0 nm nanocubes. The Pd cubic seeds with an average edge length of 10.0 nm were prepared according to the previously reported method. In a typical synthesis, 105 mg of PVP, 60 mg of AA, 300 mg of KBr, and 8.0 mL of DI water were mixed in a 20 mL glass vial and the solution was preheated to 80 °C for 10 min under magnetic stirring. After that, 3 mL of DI water containing 57 mg of Na_2PdCl_4 was quickly injected into the preheated solution by a pipette. The vial was capped and the reaction was kept at 80 °C for 3 h. After the mixture had cooled to room temperature, the product was obtained by centrifugation, washed with ethanol and acetone for three times, and then re-dispersed in ethanol for further use.

Phase transfer of Pd 10.0 nm nanocubes. In a standard procedure, 8 mL of ethanol solution containing the Pd 10.0 nm nanocubes were mixed with 5 mL of OAm and 3 mL of toluene in a 20 mL glass vial. The phase transfer was conducted by magnetic stirring of the mixture at 80 °C for 9 h. The product was collected by centrifugation, washed with ethanol, and then re-dispersed in OAm serving as the seeds for the epitaxial growth of Au layers.

Epitaxial growth of Au layers on Pd 10.0 nm nanocubes with different shapes. In a standard preparation, 4 mL of OAm solution containing Pd 10.0 nm nanocubes seeds were added into a 25 mL single-necked flask and preheated to 130 $^{\circ C}$ in an oil bath for 10 min. After that, 2 mL of OAm solution containing a certain amount of $HAuCl_4$ was added into the flask by a pipette. The reaction was proceeded at 130 °C for 3 h. Finally, the final product was collected by centrifugation, washed with ethanol and cyclohexane for several times.

STEM characterizations

The in-situ HAADF-STEM analysis of the transformation of Pd@Au NPs from segregated core-shell structure to mixed alloy structure was performed in an aberration-corrected scanning transmission electron microscopy (Titan G2 80-200 ChemiSTEM, FEI), operating at 200 kV, which provides us a spatial resolution of ~0.8Å. In the HAADF imaging, the probe convergence angle was set for 21 mrad and the beam current was ~0.6 nA. The element analysis was acquired by detectors from Bruker (super X technique), and the data were dealt with Esprit software. A DENS SH30 TEM heating holder were used in in situ heating experiments.

Fitting of energy parameters

Galanakis et al. reported in their early works that NMBM describes well for the three low index ((100), (111), and (110)) surfaces of noble metals[2]. Herein, we adopted the calculated surface energies of the three low index surfaces in our previous work for the fitting[3], the value of which are shown in Table. S1. According to the assumption of the NMBM, the energy cost for separating two [hkl] surfaces from the bulk is response to the broken NNBs during the process. The surface energy of a unit cell of single [hkl] surface can be described as:

$$E_{hkl}^{surf} = \frac{1}{2} N_{hkl}\, \varepsilon \qquad (3).$$

N_{hkl} is the number of broken NNBs, which is different for different [hkl] surface. Special attention should be paid for (110) surface because N_{110} is 6 for 5 missing bonds of the surface atom and 1 missing bond of the subsurface atom.

DFT calculations

To calculate the separating energy, the Vienna Ab initio Simulation Package (VASP) was used in these spin unrestricted DFT calculations[4]. The exchange functional was chosen to be the generalized gradient approximation (GGA) with the projector augmented-wave method (PAW)[5-7]. A 400 eV cut-off of the plane-wave expansion was employed. The convergence for the electronic self-consistent and for the geometry optimization within a conjugate-gradient algorithm was 10-5 eV and 10-2 eV/ Å respectively. A (4×4) 2-D periodic slab was considered, which has 6 atomic layers. The atoms were allowed to relax except the ones in the bottom two layers. Two Pd atom were inset in the Au slab separately and in a pair, respectively.

Supporting Table

Table S1 Surface tension of Au and Pd surfaces, the unit is eV/Å^2

Pd	γ_{hkl}	Au	γ_{hkl}
(111)	0.08	(111)	0.04
(100)	0.09	(100)	0.05
(110)	0.10	(110)	0.06

Supporting Figures

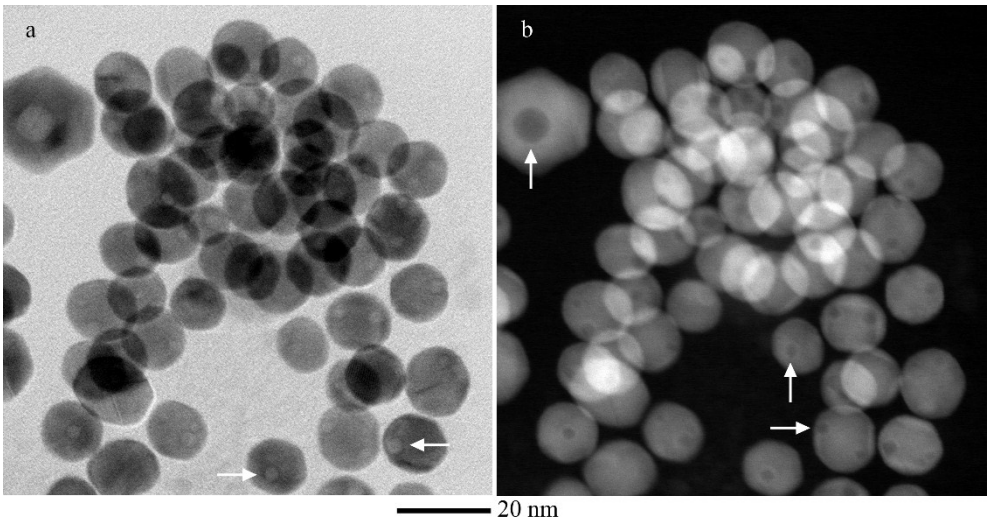

Fig. S1 Pd@Au NPs annealing at 300 °C for 30 minutes. (a) and (b) are BF and STEM images taken in the same position at the same time, respectively. Voids (marked by white arrows) can be seen in most of particles, indicating a diffusion between Pd and Au.

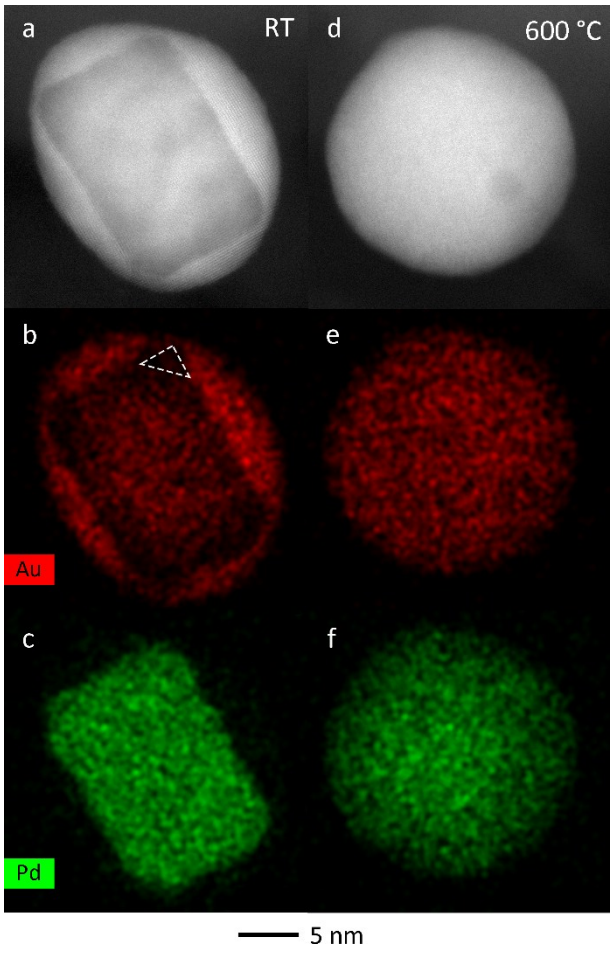

Fig. S2 HAADF-STEM images of Pd@Au core-shell nanoparticle and corresponding EDX maps at room temperature (a-c) and after heating at 600 °C (d-f). Since little Au signal was detected at corner as marked by dashed triangular in b, we think that Pd atoms were partial exposed. After heating at 600 °C, we can conclude from both the uniform contrast of HAADF-STEM image and EDX maps that the nanoparticle turned into a random mixed alloy.

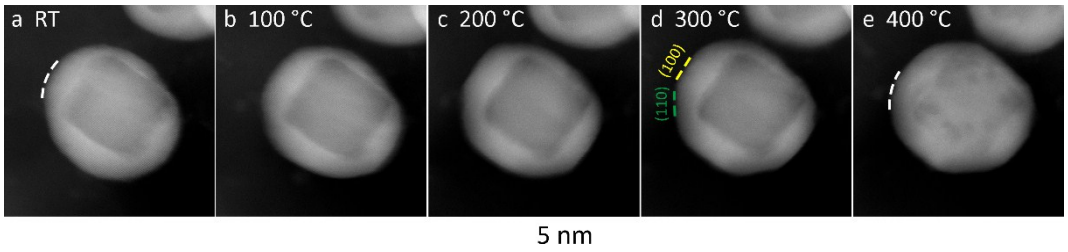

Fig. S3 Pd@Au HAADF-STEM images acquired every 100 °C from room temperature to 400 °C. The sample was not exposed to electron beam irradiation during the heating process. (a-e) are STEM images of room temperature, 100 °C , 200 °C , 300 °C and 400 °C respectively. The particle is spherical at room temperature. As temperature rising, the spherical surface become flat and Au(100) and Au(110) exposed. Keep heating to 400 °C, arcate surface shows up again.

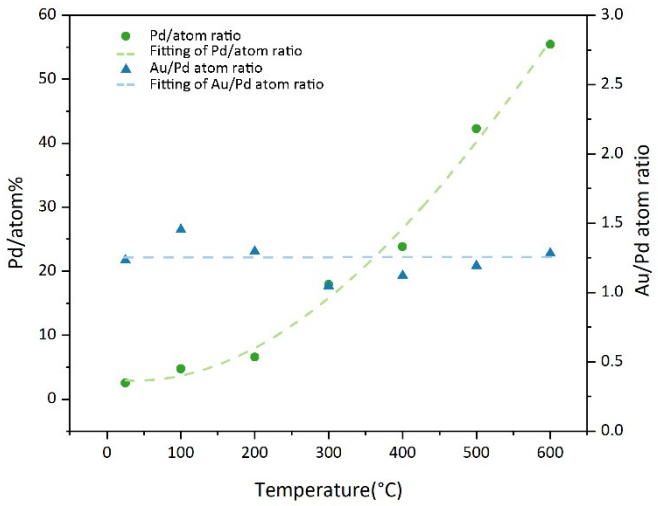

Fig. S4 Pd atomic composition (green dot) extracted from the EDX maps obtained from the shell of nanoparticle as a function of temperature and Au/Pd atomic ratio (blue dot) as a function of temperature extracted from the EDX maps of an entire particle. The Pd atom ratio changed extremely slowly at low temperature and fast at high temperature, revealing the slow bulk migration below 300 °C and fast inter-diffusion above 300 °C. Au/Pd atom ratio kept stable, indicating no apparent loss of atom happened.

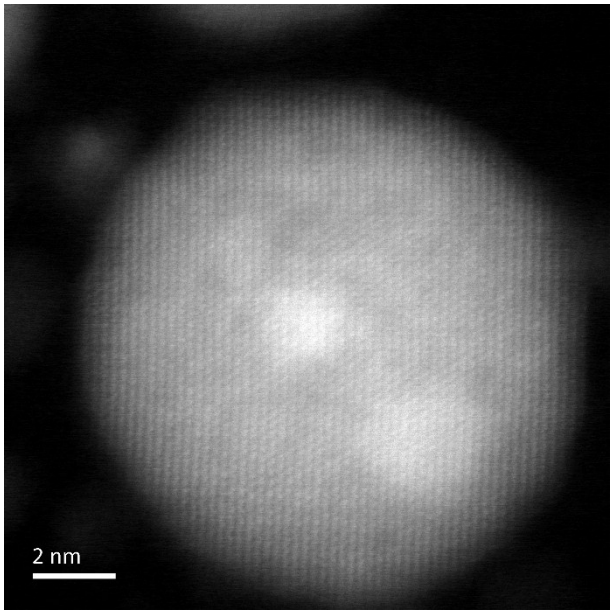

Fig. S5 Atomic resolution HAADF-STEM image of a typical AuPd alloying nanoparticle, showing no chemical ordered structure. (The brighter part in center is caused by long time e-beam irradiation)

References

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