

---

Erik Jonsson School of Engineering and Computer Science

---

2013-10-17

*Enhanced Shape Stability of Pd-Rh Core-frame  
Nanocubes at Elevated Temperature: In Situ Heating  
Transmission Electron Microscopy*

UTD AUTHOR(S): Ning Lu, Jinguo Wang and Moon J. Kim

©2013 The Royal Society of Chemistry. This article may not be further made available or distributed.

## Enhanced shape stability of Pd–Rh core–frame nanocubes at elevated temperature: *in situ* heating transmission electron microscopy†

Cite this: *Chem. Commun.*, 2013, **49**, 11806

Received 23rd August 2013,  
Accepted 15th October 2013

DOI: 10.1039/c3cc46465b

www.rsc.org/chemcomm

Ning Lu,<sup>a</sup> Jinguo Wang,<sup>a</sup> Shuifen Xie,<sup>b</sup> Younan Xia<sup>bc</sup> and Moon J. Kim<sup>\*ad</sup>

**Shape stability of Pd–Rh core–frame nanocubes was studied by *in situ* heating transmission electron microscopy. Pd–Rh nanocubes could maintain cubic shape at elevated temperature compared with pure Pd. The surface diffusion process of Rh onto {100} side surfaces is believed to postpone the degradation to higher temperature.**

Nanosize metallic particles have long been recognized as important heterogeneous catalytic materials.<sup>1</sup> Recent studies show that the atomic characteristics of metallic nanoparticles, including particle size, shape and surface composition, are critical to catalytic activity and selectivity.<sup>2,3</sup> It has been proven that the catalytic activities of noble metals are highly dependent on their surface structures in many reactions.<sup>4</sup> Given that the surface structures of nanocrystals have a strong correlation with their morphologies, morphology control of nanocrystals has become a central theme of research with an ultimate goal to tune the catalytic performance of nanocrystals. However, the stability of nanocatalysts especially the single crystal nanoparticles with high index surface planes forming regular shapes under realistic technical conditions is a well documented inherent problem. Different capping agents, such as organic and other agents, have been widely used in colloidal chemistry to stabilize nanoparticles under mild conditions. Unfortunately, these capping agents decompose at relatively low temperatures, 300–400 °C, which is well below the temperature required for many industrially important catalytic processes.<sup>5</sup>

On the other hand, even though bimetallic nanocatalysts, composed of two different metallic elements, are the focuses of intense research efforts in catalysis,<sup>3,6</sup> there are very few reports

on the thermal stability of bimetallic nanoparticles, especially on the evolution of single bimetallic nanoparticles at the atomic scale. Recently, Cao and Vesper demonstrated that the Pt–Rh alloying nanoparticles could maintain exceptional thermal stability by using the impact of alloying Pt with Rh.<sup>7</sup> A theoretical study on the alloying bimetallic Pd–Au nanoparticles has shown that the surface diffusion played an important role in the thermal stability.<sup>8</sup> Here, we demonstrate the possibility of enhancing the shape stability of Pd–Rh core–frame nanocubes at elevated temperature by using the high melting point element Rh as a capping agent coated on the corner and the frame of the Pd nanocube. We study the enhanced shape stability of the Pd–Rh nanocubes by *in situ* heating transmission electron microscopy. The Pd–Rh core–frame nanocubes could maintain the cubic shape after annealing for 1 hour at 500 °C in contrast to the apparent truncation of pure Pd nanocubes at 400 °C for 8.5 min. We believe that the diffusion of the high melting point metal (Rh) coated on the corners and edges onto {100} side surfaces plays an important role in the stabilization of the nanoparticle at the atomic scale. The high melting point metal (Rh) could be used as a metallic capping agent to stabilize the embedded low melting point metal (Pd).

Pd–Rh bimetallic nanocubes were synthesized by site-specific growth. The details of the synthesis process can be found in our previous work.<sup>9</sup> Transmission electron microscopy (TEM), high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectrometry (EDS) mapping were performed in a JEOL ARM200F with a STEM aberration (Cs) corrector operated at 200 kV. *In situ* heating experiments were performed using a MEMS-based localized heating specimen holder (by Protochips). The holder allows the specimen to be heated to 1200 °C within milliseconds.

For comparison, Pd nanocubes were used as baseline samples in the *in situ* heating experiment. Fig. 1 shows a series of TEM images taken from the same region at different stages as the temperature was increased from room temperature (*RT*) to 700 °C. As the thermal holder can heat the specimen to the targeted temperature within milliseconds, one could determine the annealing time at setting temperature more accurately. Pd particles showed intact cubic shape with 18 nm in edge length at room temperature (Fig. 1a).

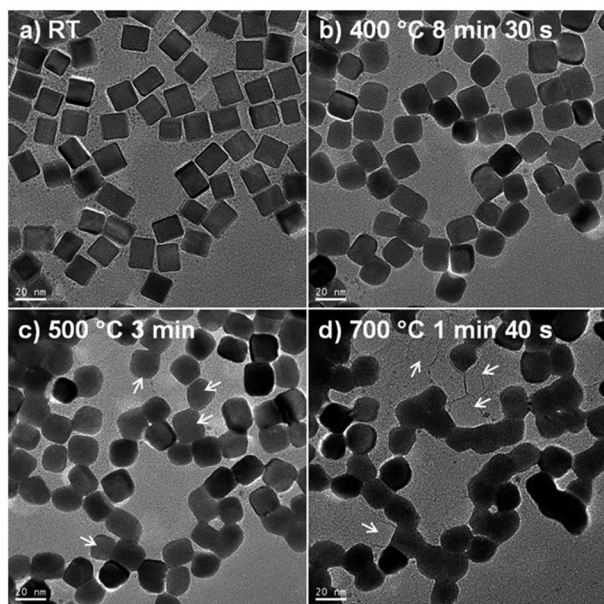
<sup>a</sup> Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, USA. E-mail: moonkim@utdallas.edu; Fax: +1-972-883-5725; Tel: +1-972-883-6635

<sup>b</sup> The Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, GA 30332, USA

<sup>c</sup> School of Chemistry and Biochemistry and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

<sup>d</sup> Department of Nanobio Materials and Electronics, World Class University, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea

† Electronic supplementary information (ESI) available: EDS spectrum extracted from EDS mapping of Pd–Rh cubes after 60 min annealing at 500 °C. See DOI: 10.1039/c3cc46465b



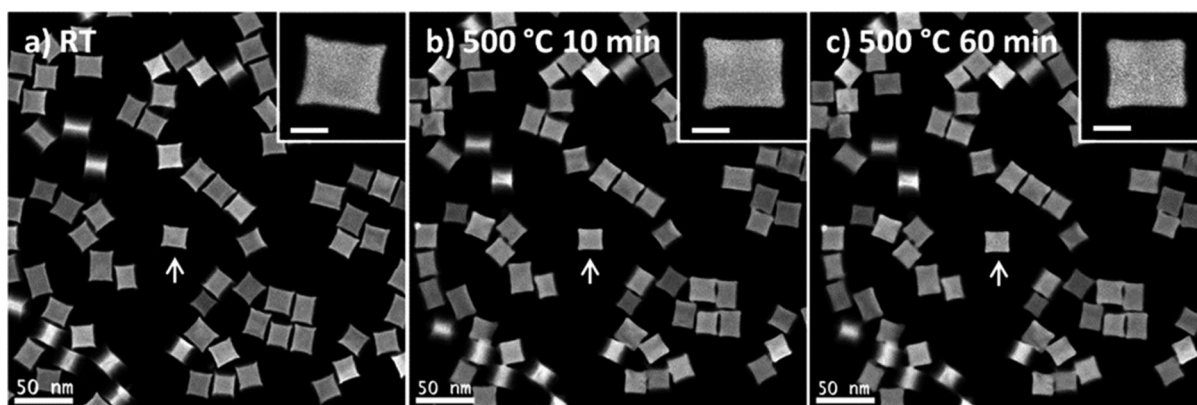
**Fig. 1** *In situ* TEM images of Pd nanocubes recorded from the same region with varying duration and temperature for the thermal treatment: (a) at room temperature, (b) 8 min 30 s at 400 °C, (c) 3 min at 500 °C, and (d) 1 min 40 s at 700 °C. The arrows in (c) and (d) show the corresponding positions of migrated particles.

Obvious truncated cubic particles were found when the annealing temperature was increased to 400 °C, which is indicated by the disappearance of sharp corners (Fig. 1b). When the temperature reached 500 °C, the cubic particles became close to spherical, and most of the neighbouring particles started to melt together at the adjacent areas (Fig. 1c). Immediately after the temperature reached 700 °C, significant interparticle coalescence was observed (Fig. 1d). Some particles migrated out of view, as marked by arrows in Fig. 1c and d, respectively. The shape transformation of the Pd nanocubes from RT to 500 °C (Fig. 1a–c) could be induced by surface diffusion, which would lead to a three dimensional atomic rearrangement.<sup>10</sup> Liquid-like properties of surface layers of the Pd nanoparticles played an important role in the coalescence process at 700 °C (Fig. 1c and d).<sup>11</sup> Our observation of heating Pd

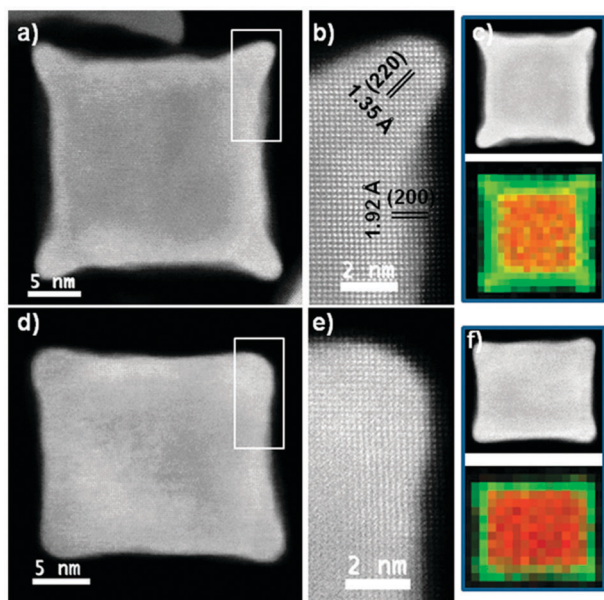
nanocubes is similar to the report of *in situ* thermal experiments of Pt nanocrystals.<sup>10</sup> Since the Pd nanocubes start to dramatically degrade at 500 °C, changing into spherical-like shape, we chose 500 °C as the heat treatment temperature to investigate the shape stability of Pd–Rh core–frame nanocubes.

The Pd nanocubes shown in Fig. 1 were used as seeds for confined overgrowth of Rh atoms at the corners and edges. Fig. 2a shows a HAADF-STEM image of the Pd–Rh core–frame nanocubes. The out-extending corners of Pd–Rh nanocubes have a pod-like appearance in the projection along the  $\langle 100 \rangle$  directions. The specimen was directly heated up to 500 °C and annealed for 1 hour. The images in Fig. 2b and c were recorded from the same region as shown in Fig. 2a at different stages of the annealing process. The enlarged insets in Fig. 2a–c clearly illustrate the details of the evolution of an individual Pd–Rh nanocube annealed for 60 min at 500 °C. In the earlier stage, 10 min (Fig. 2b), the sharp corners of the nanocubes turned into round ones. After the continuous annealing for 50 min, the shape of nanocubes showed no significant change; except that the out-extending corners became smaller. The Pd–Rh nanocubes could maintain the cubic shape very well after annealing at 500 °C for 1 hour. The shape stability of Pd nanocubes is significantly enhanced by coating the high melting point metal (Rh) on the corners and edges.

To perform the stabilization mechanism of the bimetallic Pd–Rh core–frame nanocubes, the atomic structure and composition of the nanocubes before and after 60 min annealing at 500 °C were further investigated using atomic HAADF-STEM images and EDS mapping, as shown in Fig. 3. All nanocubes in Fig. 3 were projected along  $\langle 100 \rangle$  zone axes. The atomic HAADF-STEM image taken at RT (Fig. 3b) reveals the continuous lattice fringes from the Pd core to the Rh frame, which indicates an epitaxial relationship between the core and frame metals. The (200) and (220) planes of face-centered cubic (fcc) Rh are marked in Fig. 3b. It is worth noting that the surfaces of the out-extending edges were nearly parallel to the  $\{220\}$  planes. The atomic numbers of Pd and Rh are 46 and 45, respectively, and they are very close. There is no distinct difference in contrast between core Pd and frame Rh in the HAADF-STEM images, so-called Z-contrast images.<sup>12</sup> Thus, EDS mapping was used to determine the distributions of Pd and Rh in the



**Fig. 2** *In situ* HAADF-STEM images of Pd–Rh core–frame nanocubes recorded from the same region at room temperature (a) and at 500 °C after different annealing times of 10 min (b) and 60 min (c). The enlarged insets in (a–c) show the evolution of an individual Pd–Rh nanocube, indicated by arrows in (a–c), annealed for 60 min at 500 °C. The scale bars in the insets are all 10 nm.



**Fig. 3** Atomic structure and compositional analysis of Pd-Rh core-frame nanocubes at room temperature (a–c) and at 500 °C after annealing for 60 min (d–f): (a), (d) HAADF-STEM images; (b), (e) atomic resolution HAADF-STEM images of the regions marked in (a) and (d), respectively; (c), (f) EDS mapping together with corresponding HAADF-STEM images of individual Pd-Rh nanocubes (red = Pd, green = Rh).

core-frame nanocubes. Fig. 3c demonstrates an EDS mapping of Pd-Rh nanocubes at RT. The mapping confirms that the out-extending corners and edges were dominated by Rh, while the cubic core was essentially made of pure Pd. Fig. 3d shows a HAADF-STEM image of an individual Pd-Rh nanocube annealed for 60 min at 500 °C. The high resolution image (Fig. 3e) clearly presents that the annealed cube still maintained the epitaxial relationship between core and shell metals. The out-extending corners and edges degraded into slightly truncated ones. It seems that the overgrown Rh atoms on the corners diffused to the side surfaces and/or the core of the nanocube. From the thermodynamic aspect, surface diffusion requires less energy than body diffusion. The Rh atoms should mainly migrate to {100} side surfaces. This has been confirmed by the EDS mapping of an annealed Pd-Rh cube (Fig. 3f). The mapping indicates that Rh mainly dominated along the {100} side surfaces, and was no more enriched on the corners and edges. The EDS spectrum extracted from the Fig. 3f mapping in the projection (001) plane shows that Rh distributes on the side surfaces, which further confirms that Rh migrated to {100} surfaces at elevated temperature (Fig. S1 in ESI†). The difference in Rh concentration between Fig. 3c and f is because the two EDS mappings were obtained from two nanocubes. In addition, the Pd-Rh cubes with slight degradation retained the annealed shape at 500 °C, when the temperature was set back to RT.

Surface layers of nanoparticles tend to become liquid-like before the melting transition, the so-called pre-melting stage.<sup>8</sup> The surface of nanoparticles melts at a lower temperature compared with the melting point of nanoparticles.

Therefore, to resist the surface pre-melting could be an effective strategy to improve the shape stability of nanoparticles. The high melting point metal (Rh) coated on corners and edges as a capping agent suppressed the surface pre-melting of the low melting point core metal (Pd) at 500 °C. Rh has higher activation energy for self-surface diffusion [84.95 kJ mol<sup>−1</sup> on the (100) surface]<sup>13</sup> than Pd [58 kJ mol<sup>−1</sup> on the (100) surface].<sup>14</sup> With Rh coated at corners and edges as a capping agent, a relatively higher energy barrier needs to be overcome to melt the surface layers of Pd-Rh core-frame nanocubes. Thus, the Pd-Rh core-frame nanocubes can present improved shape stability at elevated temperature.

In summary, using *in situ* heating transmission electron microscopy, we have demonstrated one effective approach to enhance shape stability of Pd nanocubes at elevated temperature by coating high melting point metal Rh on corners and edges to form core-frame bimetallic nanocubes. The Pd-Rh core-frame nanocubes could maintain cubic shape after annealing for 1 hour at 500 °C in contrast to the apparent truncation of pure Pd nanocubes at 400 °C for 8.5 min. Surface pre-melting of Pd is suppressed by the surface diffusion of Rh from corners and edges to {100} side surfaces. This strategy of shape stabilization can be extended to the development of other multi-metallic nanocrystals for broad high temperature applications.

This work was supported by AOARD-AFOSR (FA2385-10-1-4066) and the World Class University Program (by MEST through NRF (R31-10026)). The synthesis work was supported in part by a grant from the NSF (DMR-1215034) and start-up funds from Georgia Institute of Technology.

## Notes and references

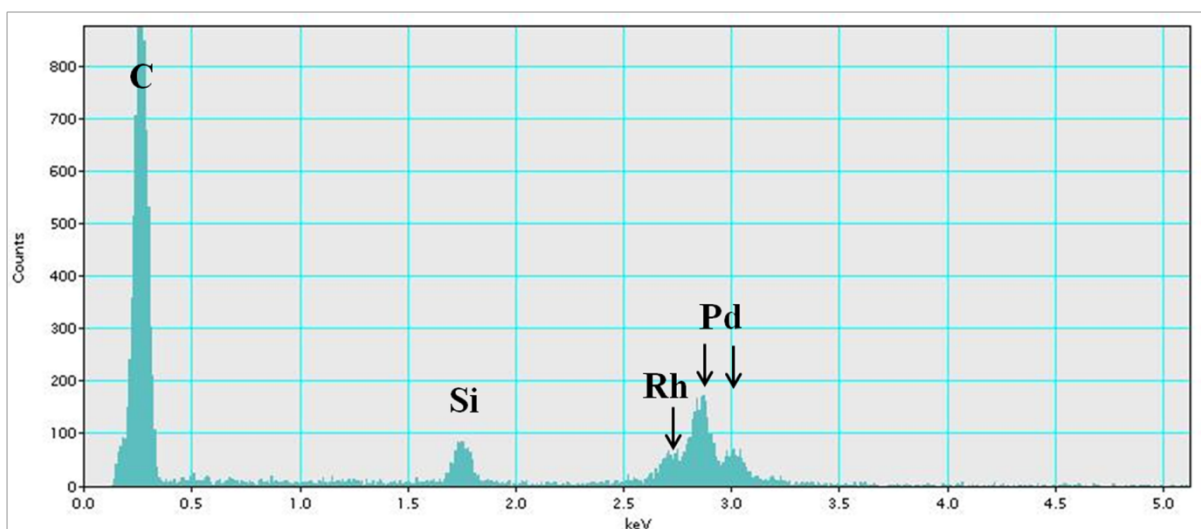
- 1 M. A. Van Hove, *Catal. Today*, 2006, **113**, 133–140; R. Schlogl and S. B. Abd Hamid, *Angew. Chem., Int. Ed.*, 2004, **43**, 1628–1637; A. T. Bell, *Science*, 2003, **299**, 1688–1691.
- 2 U. Heiz and U. Landman, *Nanocatalysis*, Springer, 2007; G. A. Somorjai and Y. G. Borodko, *Catal. Lett.*, 2001, **76**, 1–5.
- 3 N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, **22**, 1179–1201.
- 4 L. Ma, C. M. Wang, M. Gong, L. W. Liao, R. Long, J. G. Wang, D. Wu, W. Zhong, M. J. Kim, Y. X. Chen, Y. Xie and Y. J. Xiong, *ACS Nano*, 2012, **6**, 9797–9806.
- 5 S. H. Joo, J. Y. Park, C. K. Tsung, Y. Yamada, P. D. Yang and G. A. Somorjai, *Nat. Mater.*, 2009, **8**, 126–131; L. S. Ott and R. G. Finke, *Coord. Chem. Rev.*, 2007, **251**, 1075–1100; R. Narayanan and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2003, **125**, 8340–8347.
- 6 V. Ponec, *Appl. Catal., A*, 2001, **222**, 31–45.
- 7 A. Cao and G. Vesz, *Nat. Mater.*, 2010, **9**, 75–81.
- 8 S. J. Mejia-Rosales, C. Fernandez-Navarro, E. Perez-Tijerina, J. M. Montejano-Carrizales and M. Jose-Yacamán, *J. Phys. Chem. B*, 2006, **110**, 12884–12889.
- 9 S. F. Xie, N. Lu, Z. X. Xie, J. G. Wang, M. J. Kim and Y. N. Xia, *Angew. Chem., Int. Ed.*, 2012, **51**, 10266–10270; X. H. Xia, S. F. Xie, M. C. Liu, H. C. Peng, N. Lu, J. G. Wang, M. J. Kim and Y. N. Xia, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 6669–6673.
- 10 Z. L. Wang, J. M. Petroski, T. C. Green and M. A. El-Sayed, *J. Phys. Chem. B*, 1998, **102**, 6145–6151.
- 11 M. Jose-Yacamán, C. Gutierrez-Wing, M. Miki, D. Q. Yang, K. N. Piyakis and E. Sacher, *J. Phys. Chem. B*, 2005, **109**, 9703–9711.
- 12 P. Hartel, H. Rose and C. Dinges, *Ultramicroscopy*, 1996, **63**, 93–114.
- 13 G. Ayrault and G. Ehrlich, *J. Chem. Phys.*, 1974, **60**, 281–294; A. Winzer, *Krist. Tech.*, 1979, **14**, 857–876.
- 14 I. Beszede, E. G. Gontier-Moya and D. L. Beke, *Surf. Sci.*, 2003, **547**, 229–238.



Electronic Supplementary Information for

**Enhanced shape stability of Pd-Rh core-frame nanocubes at elevated temperature: in-situ heating transmission electron microscopy**

*Ning Lu, Jinguo Wang, Shuifen Xie, Younan Xia, and Moon J. Kim\**



**Fig. S1** EDS spectrum extracted from EDS mapping of Pd-Rh cube after 60 min annealing at 500 °C. The chosen area of the EDS spectrum is from the projection (001) plane. Rh distributes on the side surfaces. Carbon signal comes from supporting film, and silicon signal from in-situ heating E-chips.