1632
doi:10.1017/S1431927614009891
Microsc. Microanal. 20 (Suppl 3), 2014

In-Situ Studies of Thermal Stability of Core–Frame Cubic Pd–Rh Nanocrystals at Elevated Temperatures

Ning Lu[1], Jinguo Wang[1], Shuifen Xie[2], Younan Xia[2], Moon J. Kim[1]

[1.] Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas 75080 USA
[2.] The Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, School of Chemistry and Biochemistry and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332 USA

Nanosize metallic particles have long been recognized as important heterogeneous catalytic materials. Recent studies show that the atomic characteristics of metallic nanoparticles, including particle size, shape and surface composition, are critical to catalytic activity and selectivity. It has been proven that the catalytic activities of noble metals are highly dependent on their surface structures. Given that the surface structures of nanocrystals have a strong correlation with their morphologies, the control of nanocrystal morphology has become a central theme of research with an ultimate goal to tune the nanocrystal catalytic performance. Bimetallic nanocubes synthesized by seed-mediated growth have the advantage of coupling the catalytic properties of one metal with those of another metal and form multifunctional nanocrystals. Herein, we demonstrate a potential method to enhance the thermal stability of Pd-Rh core-frame nanocubes investigated by in-situ heating transmission electron microscopy.

Pd-Rh bimetallic nanocubes were synthesized by site-specific growth. [1] Transmission electron microscopy (TEM), high-angle annular dark-field scanning (HAADF)-scanning transmission electron microscopy (STEM) and energy dispersive X-ray (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). Pd-Rh cubes obtained at different stages of a synthesis were investigated at elevated temperatures.

Since the Pd nanocubes start to dramatically degrade at 500 °C, changing into spherical-like shape, we choose 500 °C as the heating treatment temperature to investigate the thermal stability of Pd-Rh core-frame nanocubes. [2] Figure 1 presents the results of the Pd-Rh nanocubes obtained in the initial stage of synthesis. Figures 1a-1c show in-situ HAADF-STEM images of Pd-Rh core-frame nanocubes recorded from the same region at room temperature (RT) and 500°C. The Pd-Rh nanocubes maintained the cubic shape very well up to annealing at 500 °C for 1 hour. The thermal stability of Pd nanocubes is significantly enhanced by coating high melting point metal (Rh) on the corners and edges. Figure 1d and 1e show the atomic HAADF-STEM images of typical nanocubes at RT and 500°C annealing 1 hr, respectively. The atomic numbers of Pd and Rh are 46 and 45, respectively. They are very close. Thus, there is no distinct contrast difference between core Pd and frame Rh in the HAADF images, as shown in Figure 1d-1e. STEM/EDS mapping was used to determine the distributions Pd and Rh in the nanocubes at RT and 500 °C.

In summary, using in-situ heating transmission electron microscopy, we have demonstrated one effective approach to enhance thermal stability of Pd nanocubes at elevated temperatures by coating high melting point metal Rh on corners and edges to form core-frame bimetallic nanocubes. The Pd-Rh core-frame cubes maintained cubic shape after annealing 1 hour at 500 °C. Surface pre-melting of Pd is suppressed by the surface diffusion of Rh from corners and edges to {100} side surface. This strategy of shape stabilization can be extended to the development of other multi-metallic nanocrystals for broad high temperature applications. [2]

References:

[1] S. F. Xie, N. Lu, Z. X. Xie, J. G. Wang, M. J. Kim and Y. N. Xia, *Angewandte Chemie – International Edition* ***51*** (2012), 10266.

[2] N. Lu, J. G. Wang, S. F. Xie, Y. N. Xia and M. J. Kim, Chemical Communication **49** (2013), 11806.

[3] This work was supported by Leading Foreign Research Institute Recruitment Program through NRF funded by MSIP, Korea (2013K1A4A3055679). The synthesis work was supported in part by a grant from the NSF (DMR-1215034) and start-up funds from Georgia Institute of Technology.

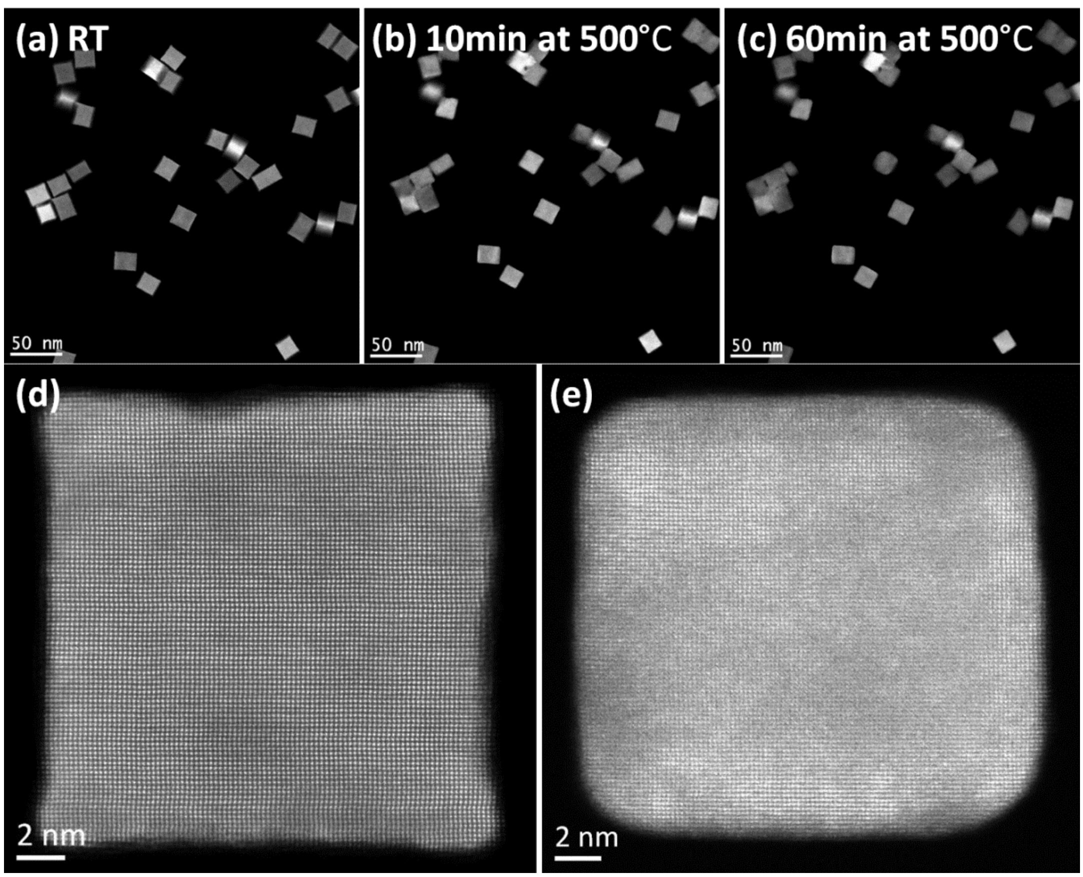

Figure 1. HAADF-STEM images of Pd-Rh core-frame nanocubes as synthesized. In-situ images recorded from the same region (a) at room temperature and (b, c) at 500 °C after different annealing time of 10 min and 60 min. (d) and (e) are the atomic HAADF-STEM images of typical nanocubes at RT and 500 °C annealing 1 hr, respectively.

https://doi.org/10.1017/S1431927614009891 Published online by Cambridge University Press