

## TEM and EDX Studies on the Structural and Compositional Evolution of PtNi<sub>3</sub> Concave Nanocubes

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It has been demonstrated that the optical, biological, and chemical properties of metal nanoparticles are highly influenced by size, composition and morphology [1]. These systems are promising candidates for a wide variety of applications in catalysis, sensing, electronics, photonics, and medicine. Pt and its alloys have been receiving a great deal of attention because of their unique catalytic properties and a wide variety of economically driven applications. Recent work on Pt<sub>3</sub>Co nanocubes [2] and Pt<sub>3</sub>Ni nanoframes [3] showed enhanced catalytic activity with a strong dependence on the structure and composition of the nanocrystals. In this work we utilize high-resolution transmission electron microscopy (HRTEM) and electron dispersive X-ray (EDX) spectroscopy to study the structural and compositional evolution of PtNi<sub>3</sub> concave nanocubes before and after annealing in order to understand the difference in their electrochemical properties. High-resolution TEM images of as prepared PtNi<sub>3</sub> concave nanotubes were observed along three representative zone axes [001], [110], and [111], and showed that the initial PtNi<sub>3</sub> concave nanocubes are fcc nanocrystals (Fig.1 a-c), while after annealing most PtNi<sub>3</sub> concave nanocubes become hollow nanocrystals (Fig.1 d-f). EDX elemental mapping results showed that in as prepared nanocubes, Pt forms a cubic frame and the Ni EDX map indicates that it forms a sphere located inside and outside of the Pt cubic frame (Fig.2 a-c). After annealing, it was found that Pt-rich frame still exists but Ni EDX map shows much less Ni than initial nanocubes, and the Pt/Ni ratio after annealing is much higher than in initial nanocubes (Fig.2 d-f). We conclude that the PtNi<sub>3</sub> concave nanocubes developed from Ni-rich nanocrystals to Pt-rich nanoframes after annealing. The detail of the structure and composition evolution of PtNi<sub>3</sub> nanocubes before and after annealing will be discussed.

### References

- [1] Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.* 2009, 48, 60–103.
- [2] Chenyu Wang, Cuikun Lin, Lihua Zhang, Zewei Quan, Kai Sun, Bo Zhao, Feng Wang, Nathan Porter, Yuxuan Wang, and Jiye Fang. *Chemistry a European Journal*. 2014, 20 (6), 1753-1759.
- [3] C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, M. Chi, K. L. More, Y. Li, N. M. Markovic, G. A. Somorjai, P. Yang, V. R. Stamenkovic, *Science*, 2014, 343, 1319.
- [4] The HRTEM and STEM/HAADF-EDS studies were carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the US Department of Energy, Office of Basic Energy Sciences, under contract no. DE-SC0012704.

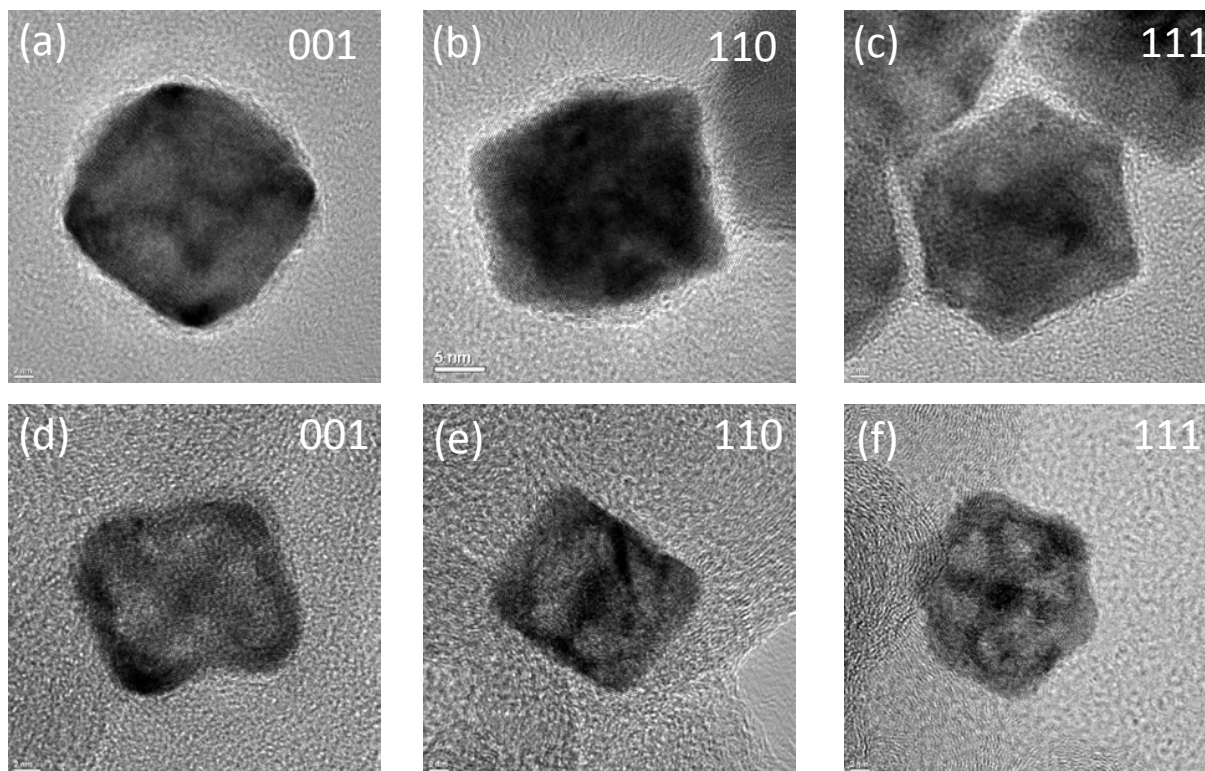


Figure.1 Bright field images from as prepared concave nanocubes (a)-(c), and from annealed nanocubes (d)-(f) along orientation [001], [110], and [111] respectively.

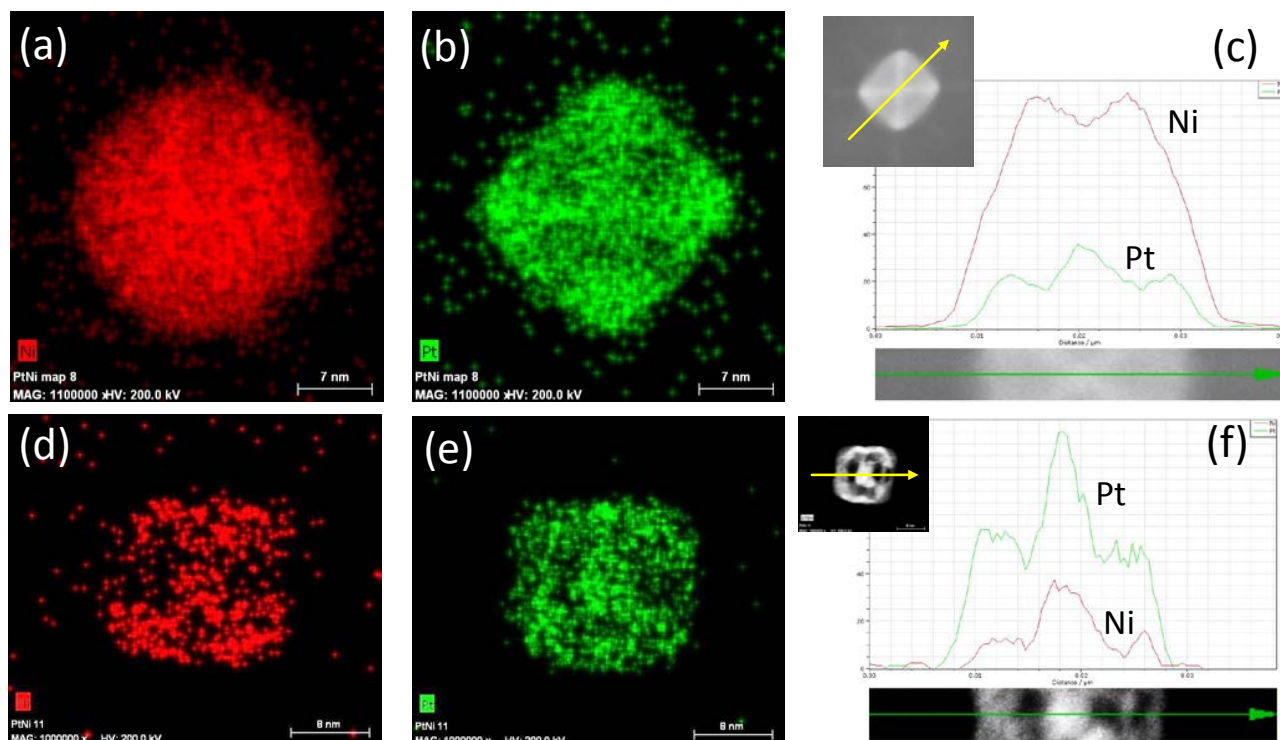


Figure.2 Elemental mapping and line scan of Ni and Pt from as prepared concave nanocube (a)-(c) and from annealed nanocube (d)-(f).