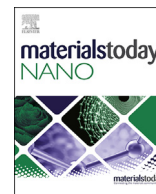




Contents lists available at ScienceDirect

Materials Today Nano

journal homepage: <https://www.elsevier.com/profile/#/MTNANO/login>Pd–Pt nanoalloy transformation pathways at the atomic scale[☆]M. Tang^{a, c}, B. Zhu^{b, c}, J. Meng^b, X. Zhang^a, W. Yuan^a, Z. Zhang^a, Y. Gao^{b, **}, Y. Wang^{a, *}^a State Key Laboratory of Silicon Materials and Center of Electron Microscopy, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027 China^b Division of Interfacial Water and Key Laboratory of Interfacial, Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Science, Shanghai 201800 China

ARTICLE INFO

Article history:
Available online xxxKeywords:
Transformation pathways
Palladium–platinum core-shell
nanoparticles
In-situ STEM
Alloying

ABSTRACT

Nanoalloys have attracted considerable attention for their wide applications in materials, optics, catalysis, and biomedicine, which largely rely on their composition-, size-, and shape-dependent properties. Because these properties change dynamically with working conditions, the knowledge of the complex transformation pathway of nanoalloys is highly demanded. Herein, we combined the in-situ aberration-corrected scanning transmission electron microscopy and multiscale modeling to fully resolve the whole transformation trajectory of a bimetallic nanoalloy (Pd–Pt) at the atomic level. The transformation from core-shell to solid-solution structure is a multistep and temperature-dependent pathway, which includes monometallic-surface refacetting, bimetallic-surface refacetting, and alloy mixing, owing to the different atomic activation barriers of surface diffusion and bulk migration. The critical role of shell thickness in determining the transformation pathway was also revealed and explained. In particular, a unique partial core-shell structure with an anisotropic surface pattern was observed in the annealing process of ultrathin core-shell nanoparticles. This study offers a fundamental insight into the structure evolution of nanoalloys, which is beneficial for the development of functionalized nanoparticles with kinetic stability.

© 2018 Elsevier Ltd. All rights reserved.

Nanoalloys have attracted extensive attention for their potential applications in nanocatalysis, nano-engineering, and nanomedicine [1,2]. The unique properties of nanoalloys are determined not only by their morphologies and sizes, as for other nanomaterials, but also by their unique chemical compositions and atomic distributions [1–9]. For Pt-based bimetallic alloys, the solid solution structures and core-shell structures exhibit distinct properties. The Pd–Pt solid-solution alloy nanoparticles (NPs) have a higher hydrogen-storage capacity than the core-shell-type NPs [10], and their core-shell NPs have been widely employed as model catalysts for oxygen reduction reaction in fuel cells [11–15]. In particular, the core-shell Pd–Pt NPs with controlled shell thickness and morphology have attracted great interests because of their distinct catalytic properties [16–18]. Interestingly, recent in-situ

experiments have shown that both structures and compositions of nanoalloys may considerably transform during thermal treatment and under real reaction conditions [19–26]. For instance, Vara et al. recently reported that both the shape and the mixing pattern of Pd–Pt core shell NPs change at a high temperature, consequently changing their catalytic activities [27]. As a result, understanding how the structure of a controlled core-shell nanoalloy changes under a given condition is crucial for the effective tuning of properties, which requires detailed information about the complex transformation pathways.

In the past decade, much effort has been contributed to study the complex pathways of formation [28], transformation [29–32], and dissolution [33,34] of individual nanoscale building blocks. Chi et al. identified the distinct stages of surface element rearrangements of Pt₃Co NPs under thermal treatment [35]. Very recently, Ye et al. presented a breakthrough work for mapping the short-lived intermediate state of single gold NPs [36] to provide the possibility of designing a kinetically stabilized surface. However, despite the above achievements, only limited information is available on the transformation pathways of nanoalloys because it remains a challenge to monitor the structure evolution of a single NP during the long-time annealing process at the atomic scale.

[☆] Given his role as Editor-in-Chief, Ze Zhang had no involvement in the peer-review of this article and has no access to information regarding its peer-review. Full responsibility for the editorial process for this article was delegated to Zhifeng Ren of Materials Today Physics.

* Corresponding author.

** Corresponding author.

E-mail addresses: gaoyi@sinap.ac.cn (Y. Gao), yongwang@zju.edu.cn (Y. Wang).

^c These authors give the same contributions to this work.

In this study, we employed in situ scanning transmission electron microscopy (STEM) annealing experiments to fully monitor the whole pathway of the transformation of Pd–Pt NPs from segregated core-shell structures to randomly mixed structures. The dynamic evolution of morphology, elemental diffusion, and alloy mixing for individual NPs during annealing was tracked as a function of temperature and time, by high-angle annular dark-field (HAADF) STEM imaging. The temperature-dependent transformation pathways were identified and rationalized by the density functional theory calculations and multiscale modeling. This study facilitates the tailoring of the physical and chemical properties of nanoalloys for catalytic applications.

The core-shell Pd–Pt cubic NPs were prepared by a chemical method reported in a previous work [37] (see [Supplemental Material](#) for details). The highly monodispersed Pd–Pt NPs (to prevent the nanoparticle coalescence) were heated on a silicon nitride film using a double-tilt DENS TEM holder [38]. Because the core-shell structures are not the equilibrium states of NPs, the structures will transform during the annealing process. The in situ annealing experiments were performed in an aberration-corrected STEM (Titan ChemiSTEM, FEI). During the long-time heating process, special attention has been paid to obtain atomic-resolution HAADF-STEM images as NPs rotate frequently at a high temperature. Besides, EDX mapping has also been performed at the same temperature to acquire in-situ information of the elemental distribution of Pd–Pt alloys.

The steps in the annealing process are shown in Fig. 1(a), where the temperature was increased to 600 °C over 400 min. Fig. 1(b) shows the atomic HAADF-STEM image of a corner of a typical Pd–Pt

NP, which reveals the continuous lattice fringes from the Pd core to the Pt shell, indicating an epitaxial relationship between them. As shown in Fig. 1(b), the interplanar spacing of 1.945 and 1.415 Å on the edge and corner of the cubic NP can be indexed to FCC Pt {100} and {110} planes, respectively. No misfit dislocation was observed because the lattice mismatch between Pt and Pd is 0.8% only. The distribution of chemical components in the bimetallic Pd–Pt cubic NPs at room temperature was assessed using STEM/EDX mapping, as shown in Fig. 1(c and d), respectively. As there is a relatively large difference in the atomic number of $_{78}\text{Pt}$ and $_{46}\text{Pd}$, the contrast present in the atomic-scale HAADF-STEM images can be used to analyze the elemental distribution of Pt and Pd [39,40]. Further quantification of the distribution is very challenging for large-sized nanoalloy particles. It is out of the scope of this work and needs further studies in the future [41,42].

Fig. 2(a) shows the STEM image of a Pd–Pt cube kept at 300 °C for 140 min. No obvious structural change was observed. With the increase in temperature to 400 °C, a refaceting of the core-shell NP without alloy mixing was observed. As shown in Fig. 2(b, d), the morphology of the monitored NP became more and more round with time. The ultra-high resolution images (see the second and third rows of Fig. 2) clearly show that the surface refaceting resulted from the changes in the Pt shell thickness on the {110} and {100} surfaces. In the beginning, the thicknesses of the atomic layers of Pt shell were the same on the {110} and {100} facets. The Pt shell thickness on the {100} facet increased from 4 atomic layers at 300 °C to 6 layers, 9 layers, 11 layers after 30, 35, and 55 min at 400 °C, respectively. Furthermore, the Pt shell thickness on the {110} facet decreased from 4 atomic layers to 0 atomic layers. The

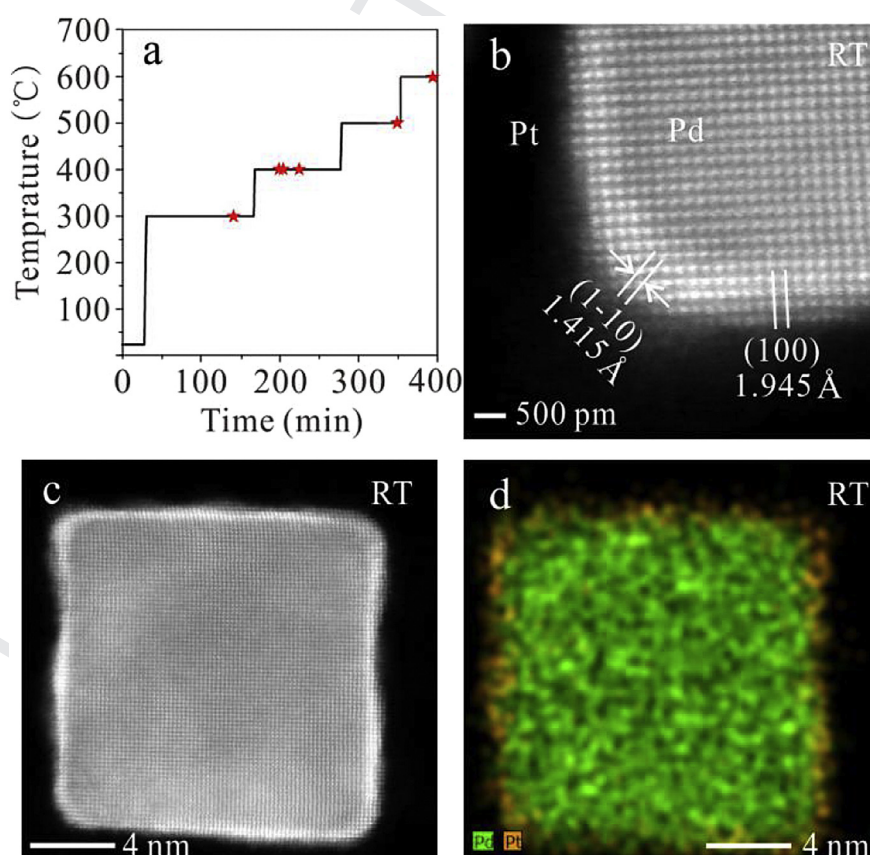


Fig. 1. (a) Annealing sequence for in situ experiments, plotted as the thermal annealing temperature with respect to time. The specific annealing conditions for the HAADF-STEM images shown in Fig. 2 are labeled with red stars in this plot. (b) Atomic-resolution HAADF-STEM image of a corner of a typical Pd–Pt NP at room temperature. (c–d) HAADF-STEM image and corresponding EDX elemental map of a Pd–Pt NP at RT.

Download English Version:

<https://daneshyari.com/en/article/6482696>

Download Persian Version:

<https://daneshyari.com/article/6482696>

[Daneshyari.com](https://daneshyari.com)