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Evolution of Au@Pt core–shell nanoparticles at high temperatures

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Abstract: Bimetallic Pt nanoparticles play a critical role in various applications, including catalysis, chemical production, fuel cells, and biosensing. In this study, we start with Au@Pt core–shell structure and investigate the evolution of these nanoparticles at elevated temperatures. Our in-situ X-ray diffraction study at elevated temperatures concluded that the onset of Au–Pt alloying occurs between 500 and 600 °C. At higher temperatures, the nanoparticles gradually approached the state of a solid solution, but the composition across the nanoparticles was not uniform even at 1,000 °C. Our results suggest that the alloyed nanoparticles at high temperatures are dominated by one solid solution but contain distinct regions with slightly different compositions.
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Key words: X-ray diffraction, Nanoparticles

I. INTRODUCTION

Bimetallic platinum nanoparticles demonstrate exceptional potential in various applications, including catalysis, chemical production, fuel cells, and biosensing (Kristian et al., 2009; Ataee-Esfahani et al., 2010; Tan et al., 2017; Fu et al., 2021). Recently, gold-core platinum-shell (Au@Pt) nanoparticles have attracted significant attention. Compared to pure Pt nanoparticles, such core–shell nanostructures enhance the performance efficiency of platinum while substantially reducing Pt usage across most applications (He et al., 2017; Shim et al., 2019; Villa-Manso et al., 2023).

The stability of the Au@Pt nanoparticles is crucial for their performance (Braidy et al., 2008; Chung et al., 2020; Borysiuk et al., 2023). The formation of Au_xPt_{1-x} alloy can decrease the activation surface area of these nanoparticles, thereby reducing their electrochemical efficiency. Therefore, understanding the evolution of the Au@Pt nanostructures at elevated temperatures is essential for their applications. This study employs in-situ X-ray diffraction (XRD) to investigate the structural changes of Au@Pt nanoparticles under high-temperature conditions.

II. EXPERIMENTAL

The average diameter of the Au@Pt nanoparticles used in this study is about 50 nm, with the gold core measuring about 40 nm in diameter and the platinum shell thickness around 5 nm. The Au@Pt nanoparticles suspended in a solvent were dropped on a quartz substrate and allowed to dry before XRD measurements. The XRD measurements were performed on a Rigaku SmartLab diffractometer equipped with a Cu-sealed tube and a HyPix-3000 pixel array detector. In-situ temperature-dependent measurements were carried out using a Rigaku high-temperature stage vacuumed with an oil rotary pump.

III. RESULTS AND DISCUSSION

The room-temperature XRD measurement was taken at 25 °C. The result is shown in Figure 1, where gold and platinum peaks appearing in pairs are observed and identified. No signs of alloying are present within the resolution limit of the XRD measurement.

XRD measurements at elevated temperatures were taken from 100 to 1,000 °C in 100 °C increments and the temperature rate was 10 °C/min. Upon reaching each target temperature, an XRD measurement was taken after a 5-minute holding time. The results are collectively shown in Figure 2. Initial observations indicate that from 100 to 500 °C, gold and platinum peaks remained as pairs as those at 25 °C, except for the peak shift due to thermal expansion effects. This is clearly shown in Figure 3, where the (111) peaks of gold and platinum are displayed. This indicates that the Au@Pt nanoparticles remain phase-separated up to 500 °C.

At 600 °C, the two (111) peaks have clearly shifted toward each other, suggesting that the onset of the alloying occurred between 500 and 600 °C. Due to this alloy formation, we will refer to these two (111) peaks as Peak-1 and Peak-2, respectively, and a comparison of these peaks at 500, 600, and 700 °C is shown in Figure 4. Notably, from 500 to 600 °C,

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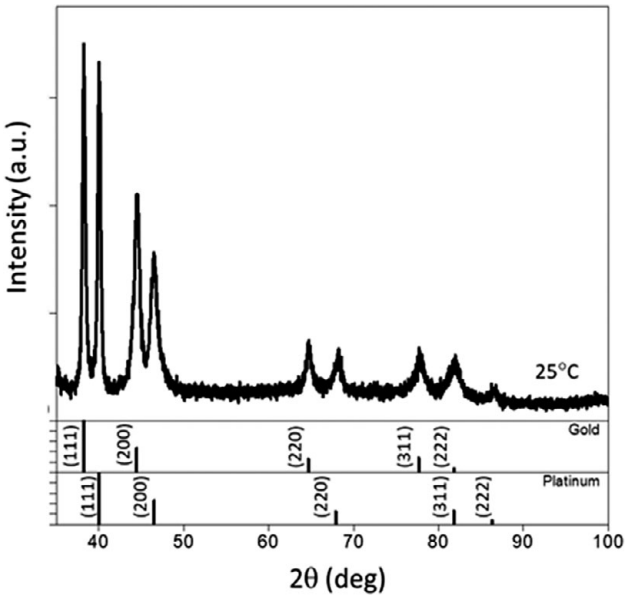


Figure 1. The XRD pattern of Au@Pt nanoparticles at room temperature. Separate gold and platinum phases are identified.

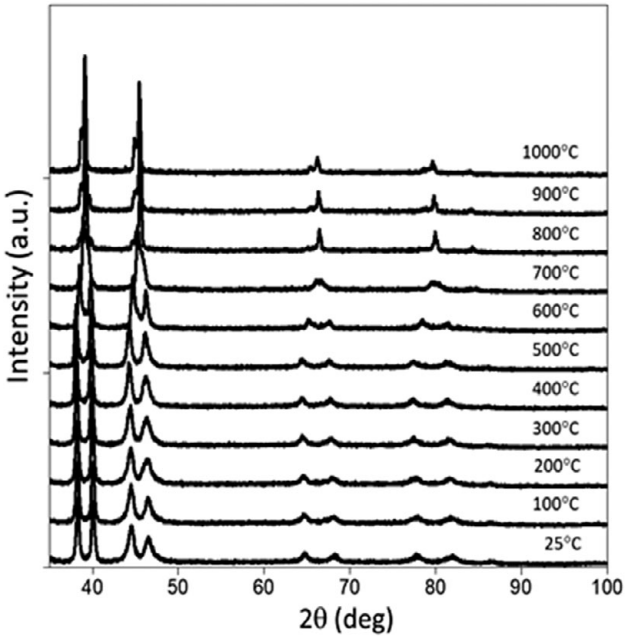


Figure 2. XRD patterns of the Au@Pt nanoparticles from room temperature to 1,000 °C.

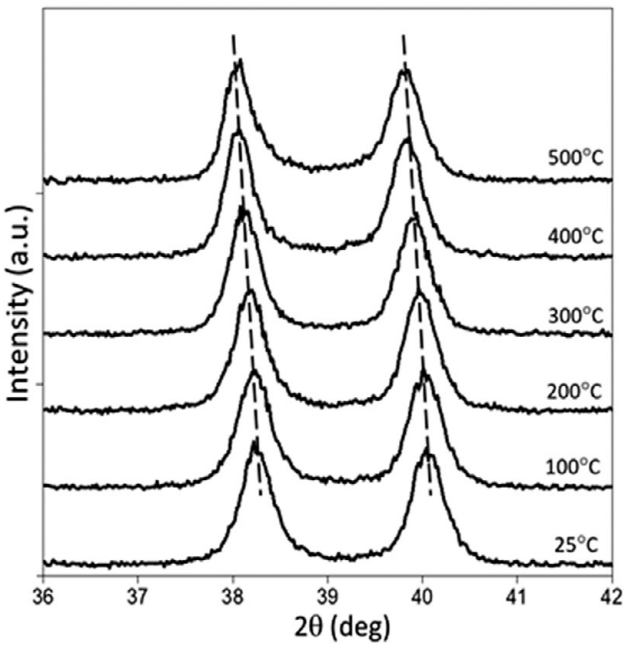


Figure 3. The (111) peaks of gold (Peak-1) and platinum (Peak-2) from 25 to 500 °C. The left shift of peaks is due to thermal expansion effects.

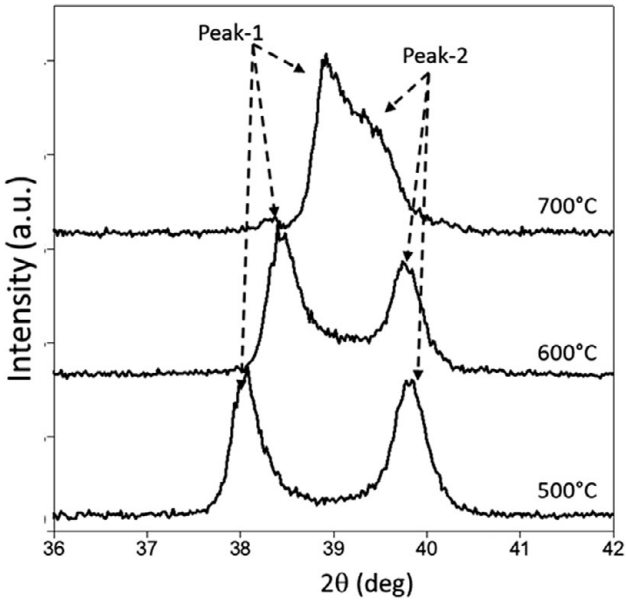


Figure 4. A comparison of the (111) peaks at 500, 600, and 700 °C.

Peak-1 experienced a significant shift to higher 2θ, while Peak-2 remained almost unchanged in position, although its intensity decreased considerably. This behavior suggests that alloying was initiated at the Au–Pt interface, where the Pt atoms were the first to be thermally activated and diffuse into the Au core. Since only the interfacial Pt atoms participated in the alloying process at this stage, the outer layers of the Pt shell remain intact. As a result, the intensity of the platinum peak (Peak-2) at 600 °C diminished as the amount of pure Pt decreased.

Conversely, the shift of Peak-1 indicates that the interfacial Pt atoms have penetrated the Au core, forming an Au–Pt alloy. At 700 °C, Peak-1 and Peak-2 shifted toward each other and began to overlap, suggesting that the entire core–shell structure has become an alloy, albeit with distinct regions of different compositions. These findings are further corroborated by the d-spacing corresponding to Peak-1 and Peak-2 as a function of temperature, as shown in Figure 5a, b. Clearly, the d-spacing for Peak-1 initially increases linearly up to 500 °C due to thermal expansion, followed by a sharp decrease from 600 to 700 °C due to the formation of Au_xPt_{1-x} alloy in the core. In contrast, the d-spacing for Peak-2 initially increases linearly up to 600 °C, then jumps sharply at 700 °C.

The thermal effects responsible for the linear increase in d-spacing below 600 °C can be corrected using a linear fit of the data. After correction, the d-spacing for Peak-1 and Peak-2

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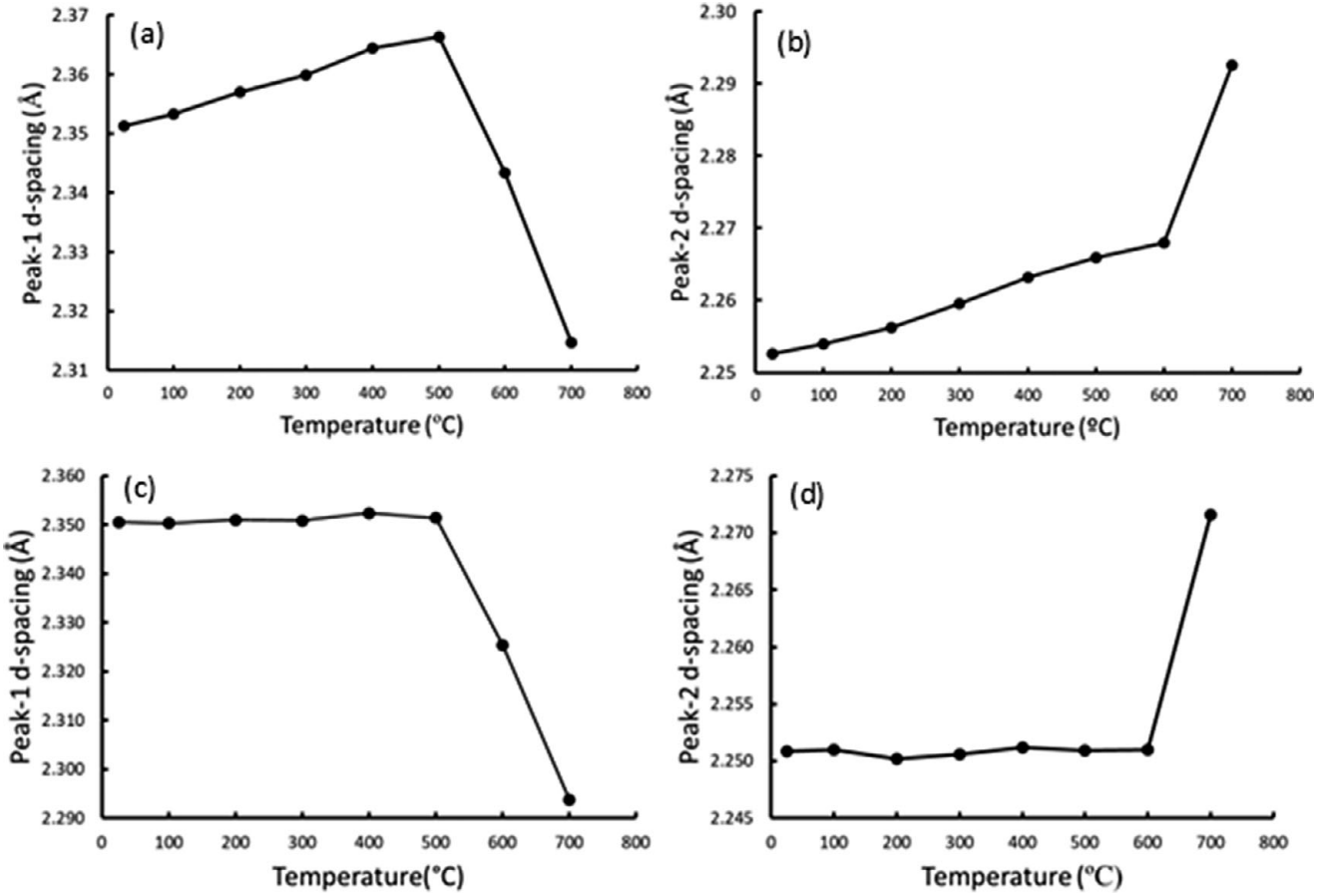


Figure 5. *d*-spacing calculated from the peak positions. (a) From 2θ of Peak-1. (b) From 2θ of Peak-2. (c) After thermal expansion corrected Peak-1. (d) After thermal expansion corrected Peak-2.

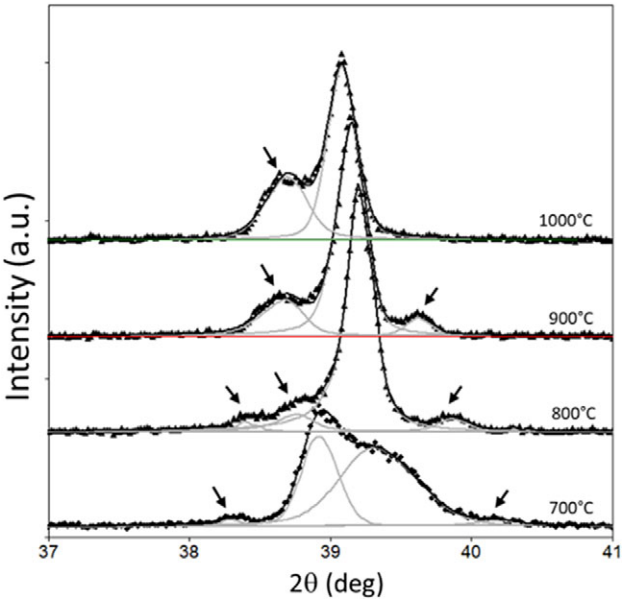


Figure 6. Components of the (111) peak from 700 to 1,000 °C. Gray lines show the decomposed component peaks at each temperature. Minor peaks are marked by arrows. From two major and two minor components at 700 °C, alloyed nanoparticles gradually evolved to one major and one minor component at 1,000 °C.

is illustrated in Figures 5c,d. As expected, the corrected d-spacing was nearly constant up to 500 and 600 °C for Peak-1 and Peak-2, respectively.

XRD patterns at 700 °C and higher also reveal minor peaks adjacent to the main peaks, as shown in Figure 6. Each component of these (111) peaks is presented as gray lines. Notably, at 700 °C, two minor peaks appear alongside two overlapping major peaks. This suggests that within the alloyed nanoparticles, regions with distinct compositions coexist. As the temperature rises to 800 °C, it becomes one major peak accompanied by three minor peaks, indicating the alloy becomes more uniform, but minor regions of different compositions still exist. At 900 °C, only two minor peaks are observed, suggesting the alloy nanoparticles have grown more uniformly in composition. At 1,000 °C, only one small peak is observed next to the major peak, indicating further increased uniformity. This trend indicates that the alloy nanoparticles become increasingly uniform with rising temperatures. However, a completely uniform alloy has not yet been achieved in our experiment, possibly due to the limited temperature range and the short duration of XRD measurement at each temperature.

IV. SUMMARY

In-situ XRD study of Au@Pt core–shell nanoparticles from room temperature to 1,000 °C shows that the onset of Au–Pt alloying occurs between 500 and 600 °C. Pt atoms at the Pt–Au interface rapidly diffuse through the entire Au core at 600 °C, while the outer Pt shell remains intact. Above 600 °C, alloying occurs throughout the entire nanostructure, though

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distinct regions of varying compositions persist. As the temperature continues to rise, the alloyed nanoparticles tend to grow more uniformly. Although the time dependence of the alloying process was not studied here, we anticipate that holding time at each temperature will also play an important role in the alloy structure.

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