

Nanoscale Alloying, Phase-Segregation, and Core–Shell Evolution of Gold–Platinum Nanoparticles and Their Electrocatalytic Effect on Oxygen Reduction Reaction

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The design of active and robust bimetallic nanoparticle catalysts requires the control of the nanoscale alloying and phase-segregation structures and the correlation between the nanoscale phase structures and the catalytic properties. Here we describe new findings of a detailed investigation of such nanoscale phase structures and their structure–catalytic activity correlation for gold–platinum nanoparticles prepared with controllable sizes and compositions. The nanoscale alloying and phase-segregation were probed as a function of composition, size, and thermal treatment conditions using X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, electrochemical characterization, and density functional theory modeling. The results have provided the experimental evidence in support of the theoretically simulated dependence of alloying and phase segregation on particle size and temperature. More importantly, new insights have been gained into the control of the nanoscale phase properties of this bimetallic system among alloyed, partially alloyed, or partially phase segregated structures. In contrast to the largely alloyed character for the catalysts treated at 300–400 °C, the higher-temperature treated catalysts (e.g., 800 °C) are shown to consist of a Pt-rich alloy core and a Au shell or a phase-segregated Au domains enriched on the surface. This conclusion is further supported by the electrochemical and electrocatalytic data revealing that the catalytic activity is highly dependent on the nanoscale evolution of alloying and phase segregation. The thermal control of the nanoscale alloying, phase-segregation, and core–shell evolution of the nanoscale bimetallic catalysts provided the first example for establishing the correlation between the nanoscale phase structures and the electrocatalytic activity for oxygen reduction reaction correlation, which has profound implications to the design and nanoengineering of a wide variety of bimetallic or multimetallic nanostructures for advanced catalysts.

Introduction

Alloy and phase properties are key factors in determining the catalytic properties of bimetallic or trimetallic catalysts. In sharp contrast to the miscibility gap in a wide bimetallic composition range for bulk gold–platinum system,¹ our earlier work has demonstrated single-phase alloy properties for bimetallic AuPt nanoparticles prepared by sequential two-phase synthesis, assembly, and activation processes.² The alloy nanoparticles showed enhanced electrocatalytic activities for methanol oxidation reaction and oxygen reduction

reaction.^{3–5} The phase properties were recently supported by computation modeling showing a negative heat of formation for AuPt particles smaller than ~6 nm,⁶ and several recent experimental studies of different AuPt systems.^{7–19}

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For example, a study of the bimetallic nanoparticles prepared by microemulsion and impregnation showed an alloy phase whereas the colloidal approach resulted in phase-segregated particles.⁷ Thin films of AuPt prepared by co-sputtering were shown to exhibit alloy properties dependent on surface compositions and electrochemical conditions.⁹ Thin films of AuPt were also prepared by crossed-beam pulsed laser deposition where the metastable AuPt alloys are formed over the entire composition range.²⁰ The study of AuPt/C prepared by microemulsion showed segregation of Pt on the surface for low-Au particles but single-phase alloy properties on high-Au particles.¹⁴ Pt-rich alloy surfaces in different AuPt heteronanostructures prepared by depositing colloidal Pt on Au nanoparticles in organic solvents showed enhanced activity toward formic acid oxidation reactions.¹⁵ However, non-alloyed AuPt/C prepared by a polyol method was also shown to display electrocatalytic activity for oxygen reduction reaction and methanol oxidation reaction.¹⁶ Our recent in situ real time X-ray diffraction study revealed that the AuPt system could be alloyed or phase-segregated depending on support properties.¹² For example, SiO₂-supported AuPt nanoparticles exhibited a single-phase alloy structure after extensive annealing at high temperature whereas Al₂O₃-supported particles exhibited phase segregation.¹² The phase structure of this nanoscale system is evidently complex.

The design and control of spatial arrangement of Au and Pt in AuPt nanoparticles are critical for exploiting the nanoscale bifunctional catalytic activity where Pt provides a site for catalyzing methanol oxidation or oxygen reduction reactions and Au provides a site for adsorption of hydroxide groups or oxidation of CO to CO₂.^{17–19} Indeed, the importance of the bimetallic spatial arrangement was recently demonstrated for core-shell structured Au-core/Pt-shell, Pt-core/Au-shell and Fe₃O₄-core/Au-shell/Pt-shell nanoparticles in electrocatalytic oxygen reduction reaction and methanol oxidation reaction,¹⁸ and for dendritic Au-core/Pt-shell core-shell nanostructures prepared by ascorbic acid reduction in electrocatalytic methanol oxidation reaction.²¹ A partially alloyed AuPt catalyst was proposed to enhance the electrocatalytic activity for oxygen reduction reaction.¹³ The modification of Pt nanoparticles with gold clusters has also been demonstrated to enhance catalyst stability against dissolution in the electrocatalytic oxygen reduction reaction.²² For preformed Au-core/Pt-shell nanoparticles prepared by depositing Pt shell on Au core, surface mapping showed instability of the core-shell structure at high

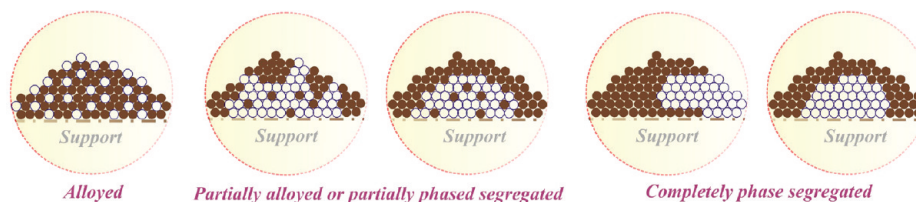
temperatures and transformation into two phases separated by an interface.²³ The partial substitution of Pt with Au was shown to improve the methanol oxidation reaction in alkaline electrolyte, but alloying had no significant effect on catalytic activity in acidic electrolyte.²⁴ This bimetallic structure of Au core and Pt shell synthesized by a successive reduction was shown to exhibit electrocatalytic activity for methanol oxidation reaction.²⁵ The possibility of the phase segregation forming core-shell nanoparticles by heating AuPt alloy nanoparticles to higher temperatures has been suggested by computation modeling.⁶ It is noteworthy that electrochemical studies of hydrogen adsorption-desorption charges and electrocatalytic reactions^{7,8,18,26–30} have indicated the close association of surface sites with the electrocatalytic activity, but little information has been obtained for assessing the correlation between the phase structures and the surface catalytic properties.

In this report, new experimental and theoretical findings are presented for establishing the correlation between the nanoscale phase structures and the catalytic activities of carbon-supported Au_nPt_{100–n} nanoparticles thermally processed at different temperatures. An important emphasis is to address the question how the nanoscale bimetallic system undergoes alloying, partial, or complete phase segregation (Scheme 1) under thermal control, from which we wish to develop the phase properties of a wide range of nanoscale bimetallic catalysts in catalytic reactions. The theoretical basis for the hypothesis of this type of phase properties as illustrated in Scheme 1 largely stems from two findings of the recent molecular dynamics simulations.⁶ One finding was the negative heat of formation for the gold-platinum particles smaller than ~6 nm which thermodynamically favors the formation of alloyed phase. The other finding was that a possible phase segregation of the gold-platinum particles could happen as a result of the larger surface free energy of Pt (2.48 J/m²) than Au (1.50 J/m²) and the lower melting point of smaller-sized nanoparticles than larger-sized particles ($\Delta T \propto 1/r_{(\text{particle radius})}$).^{31,32} As will be shown in this report, the results have provided not only the first experimental confirmation of the theoretical finding, but also the first experimental demonstration of the control of the phase properties of this nanoscale bimetallic system from alloyed to partially alloyed or partially phase segregated structures.

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Scheme 1. Idealized Illustrations of the Nanoscale Alloyed, Partially Alloyed/Partially Phase Segregated, Or Completely Phase Segregated Bimetallic Metals on a Support



Experimental Section

Chemicals. Hydrogen tetrachloroaurate (HAuCl_4 , 99%), tetraoctylammonium bromide (TOABr, 99%), hydrogen hexachloroplatinate (IV) ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, 99.995%) obtained from Alfa Aesar. Decanethiol (DT, 96%), oleylamine (OAM, 70%), sodium borohydride (NaBH_4 , 99%), methanol (99.9%), ethanol (99.9%), and Nafion (5 wt %) were purchased from Aldrich and used as received. Other chemicals included hexane (99.9%) and toluene (99.8%) from Fisher. Carbon Black (Vulcan XC-72) was obtained from Cabot. Water was purified with a Millipore Milli-Q water system.

Synthesis of Nanoparticles and Catalysts. The $\text{Au}_n\text{Pt}_{100-n}$ nanoparticles were prepared by a molecular encapsulation approach based on a modified two-phase protocol.² The synthesis of AuPt nanoparticles involved first transfer of AuCl_4^- and PtCl_6^{2-} from aqueous solution of HAuCl_4 and H_2PtCl_6 into toluene solution using a phase transfer reagent (TOABr). Thiols (e.g., decanethiol, DT) and amine compounds (e.g., oleylamine, OAM) were added to the organic solution as capping agents. An excess of aqueous NaBH_4 was slowly added for the reduction reaction. The resulting DT/OAM-encapsulated AuPt nanoparticles in toluene were collected by removing the solvent through evaporation in vacuum, and were dispersed in hexane. The bimetallic composition of the AuPt nanoparticles was determined by DCP-AES. The control of AuPt composition in the desired proportion and high monodispersity ($< \pm 0.5$ nm) was achieved by manipulating the precursor feed ratio.

The preparation of the carbon-supported catalysts followed our earlier protocols² with slight modifications. Briefly, the protocol involved assembly of the as-synthesized nanoparticles on carbon support, followed by thermal treatment under controlled temperature and atmosphere. The thermal treatment involved heating the catalyst at from room temperature (RT) to 280 °C under 20% O_2 and holding at this temperature for 60 min for sample series -A and for 30 min for sample series -B and -C, followed by cooling to RT before annealing in a temperature range of 300–800 °C under 15% H_2 over a time length of 2 h. The actual loading was controlled in the range 20 to 24% by mass.

Preparation of Catalysts on Electrodes. Glassy carbon disks (geometric area: 0.196 cm^2) were polished with 0.005 μm Al_2O_3 powders. The geometric area of the substrate electrode (glassy carbon), not the surface area of the catalyst itself, provides a measure of the loading of catalyst on the electrode surface. A typical suspension of the catalysts was prepared by adding 15 mg of catalyst (AuPt/C) to 12 mL of deionized water, 3 mL of isopropanol and 60 μL of 0.25% Nafion solution, and ultrasonication for 10 min. The suspension was then quantitatively transferred to the surface of the polished glassy carbon disk.

Direct current plasma-atomic emission spectroscopy (DCP-AES) was employed to analyze the composition of the as-synthesized bimetallic nanoparticles using an ARL Fisons SS-7 DCP-AES instrument; the measurements were made on emission peaks at 267.59 and 265.95 nm for Au and Pt, respectively. The

nanoparticle samples were dissolved in concentrated aqua regia, and then diluted to concentrations in the range of 1 to 50 ppm for analysis. Calibration curves were made from dissolved standards with concentrations from 0 to 50 ppm in the same acid matrix as the unknowns. Standards and unknowns were analyzed 10 times each for 3 s counts. Instrument reproducibility, for concentrations greater than 100 times the detection limit, results in $< \pm 2\%$ error.

Transmission electron microscopy (TEM) was performed on a Hitachi H-7000 electron microscope (100 kV). For TEM measurements, samples were suspended in hexane solution and were cast by dropping the nanoparticle solution onto a carbon-coated copper grid followed by solvent evaporation in air at room temperature.

X-ray Powder Diffraction (XRD) data were collected on two instruments; (a) a Philips X'Pert diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406$ Å). The measurements were done in reflection geometry and the diffraction (Bragg) angles 2θ were scanned at a step of 0.025°. Each data point was measured for at least 20 s and several scans were taken of each sample for $\text{Au}_{22}\text{Pt}_{78}/\text{C}$ sample A series and $\text{Au}_{49}\text{Pt}_{51}/\text{C}$ samples series; (b) a Scintag XDS2000 θ - θ diffractometer using $\text{Cu K}\alpha$ $\lambda = 1.5406$ Å, equipped with a Ge (Li) solid state detector for $\text{Au}_{22}\text{Pt}_{78}/\text{C}$ sample B series. The XRD data was collected from 20 to 90 degree 2θ at a rate of 0.58 degrees/min at room temperature. The diffraction data was compared to the XRD database of International Centre for Diffraction Data for both instruments.

X-ray Photoelectron Spectroscopy (XPS) measurements were made by using a Physical Electronics Quantum 2000 scanning ESCA microprobe. This system uses a focused monochromatic $\text{Al K}\alpha$ X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. The X-ray beam used was a 100W, 100- μm diameter beam that is rastered over a 1.4 mm by 0.2 mm rectangle on the sample. The X-ray beam is incident normal to the sample, and the X-ray detector is at 45° away from the normal. The binding energy (BE) scale is calibrated using the $\text{Cu}2\text{p}_{3/2}$ feature at 932.62 eV and $\text{Au}4\text{f}_{7/2}$ at 83.96 ± 0.05 eV for known standards. The sample experienced variable degrees of charging low energy electrons at ~ 1 eV, 20 μA , and low energy Ar^+ ions were used to minimize this charging. The percentages of individual elements detected were determined from the relative composition analysis of the peak areas of the bands.

Thermogravimetric analysis (TGA) was used to determine the actual loading of metal nanoparticles on the carbon black support. TGA analysis of the catalysts was performed using Perkin-Elmer Pyris 1 TGA instrument. Typical samples weighed ~ 5 mg and were heated in a platinum pan under 20% O_2 atmosphere at a rate of 30 °C/min

Electrochemical Measurements (Cyclic Voltammetry and Rotating Disk Electrode) measurements were performed using a microcomputer-controlled electrochemical analyzer (CHI600a, CH Instruments). The experiments were performed in three-electrode electrochemical cells at room temperature. All electrolytic (0.5 M H_2SO_4) solutions were deaerated with high purity

nitrogen before the cyclic voltammetry (CV) measurements, or saturated with oxygen before the rotating disk electrode (RDE) measurements. The potentials are given with respect to a reversible hydrogen electrode (RHE).

Results and Discussion

The discussion of the results is divided into four sections. In the first section, we describe the characterization of the composition and morphological properties of the bimetallic nanoparticles and supported catalysts derived from our synthetic and thermal processing approaches. In the second section, we focus on the detailed characterization of the nanoscale phase properties of the bimetallic catalysts in terms of alloying and phase segregation. In addition to extensive use of XRD technique for the characterization, DFT-based computational modeling approach was utilized to aid the fundamental understanding. In the third section, the detailed thermal evolution of the bimetallic composition of the catalysts was further assessed by XPS analysis in terms of the nanoscale core and shell structures. The final section focuses on a detailed assessment of the electrocatalytic activity of the composition-, size-, and phase-controlled bimetallic catalysts for oxygen reduction reaction, aiming at understanding the correlation between the nanoscale phase structures and the catalytic properties.

1. Composition and Morphology. The bimetallic composition of both as-synthesized and carbon-supported AuPt nanoparticles was determined by the DCP-AES technique. The control of the bimetallic composition in the entire bimetallic composition range and the particle size with high monodispersity ($< \pm 0.5$ nm) was achieved by manipulating the precursor feed ratio. The as-synthesized nanoparticles were supported on different support materials, including carbon, silica, and other materials, followed by thermal treatment under controlled temperature and atmosphere.^{2,33} The thermal treatment involved heating the catalyst at 280 °C under 20% O₂ followed by treatment at 300–800 °C under 15% H₂, as detailed in the Experimental Section. The oxidation step under oxygen was followed by reduction under hydrogen which also removed possible oxidized species produced by the oxidation process. For the as-synthesized Au_nPt_{100-n} nanoparticles, the bimetallic composition was shown to be fully controllable by the synthetic feeding composition. This is demonstrated by the 1:1 linear relationship between the feeding composition and the nanoparticle composition in Figure 1, which were obtained from the experimentally determined feed and nanoparticle compositions. The particle size and monodispersity were also shown to be controllable. Au_nPt_{100-n} nanoparticles with average sizes ranging from 1.6 ± 0.4 nm to 3.4 ± 0.4 nm depending on the composition were obtained. For example, Au₂₂Pt₇₈ (error for composition: $\pm 1\%$) nanoparticles showed an average size of 2.4 ± 0.4 nm.

As shown in Figure 2A, the particles were well dispersed on the carbon support. The particle sizes of the

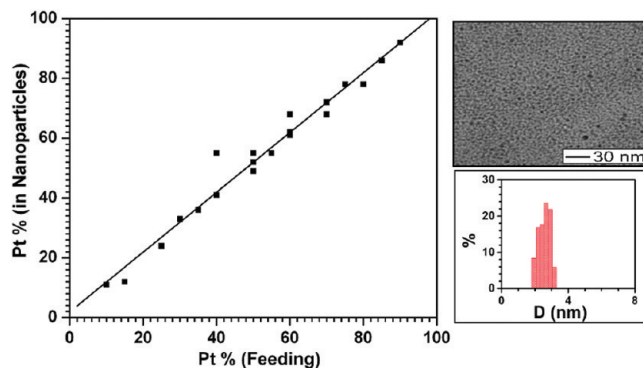


Figure 1. Correlation between the Pt composition in nanoparticles (from DCP-AES analysis) and the synthetic feeding composition. The solid line represents the linear fitting to the experimental data ($y = 1.906 + 0.999x$, $r^2 = 0.9848$). Right graphs: TEM and size distribution (2.4 ± 0.4 nm) of Au₂₂Pt₇₈ as an example.

carbon-supported bimetallic nanoparticles (AuPt/C) after the thermal treatment were found to depend on the thermal treatment temperature. For example, Au₂₂Pt₇₈/C after hydrogen treatment at temperatures ranging from 300 to 800 °C showed a gradual increase in size from 4 to 7 nm (Figure 2B). This size increase is approximately linear versus the thermal treatment temperature. Lower temperature (300 °C) results in small sized nanoparticles, whereas higher temperature (800 °C) results in large sized nanoparticles. A similar size evolution has also been observed for the nanoparticles of the other compositions studied in this work (see Supporting Information). The fact that the slightly larger slope in the 600–800 °C region than in the 300–500 °C region may reflect a difference in surface sintering mechanism. As shown by the HRTEM images for samples treated at 400 and 800 °C (Figure 2C), the observation of the indicated lattice fringes, 0.232 (or 0.235) and 0.204 nm, corresponding to 111 and 100 planes, indicate that the carbon-supported nanoparticles are highly crystalline with a subtle difference in interatomic distance between these two treatment temperatures. Similar results were also observed for samples from different thermal treatment temperatures and with different compositions (e.g., Au₄₉Pt₅₁).

Our ability to control the size and composition of the nanoscale bimetallic system was further substantiated by preparing a series of Au_nPt_{100-n}/C catalysts with different thermal treatment temperatures and different bimetallic compositions. These catalysts were examined in our investigation in terms of nanocrystal phase properties, surface composition, and electrocatalytic properties. In the following subsections, several representative types of samples will be emphasized to illustrate our major findings, including catalysts with the same composition but treated at different time lengths under O₂ atmosphere, for example, Au₂₂Pt₇₈/C catalysts treated for 60 min (Sample-A series) and for 30 min (Sample-B series), and catalysts with the same treatment conditions but different composition, for example, Au₄₉Pt₅₁/C catalysts (Sample-C series). The results for other compositions and conditions will be also discussed to aid the comprehensive understanding of this nanoscale bimetallic system.

2. Nanocrystal Phase Properties. In contrast to the bulk AuPt counterparts which display a miscibility gap

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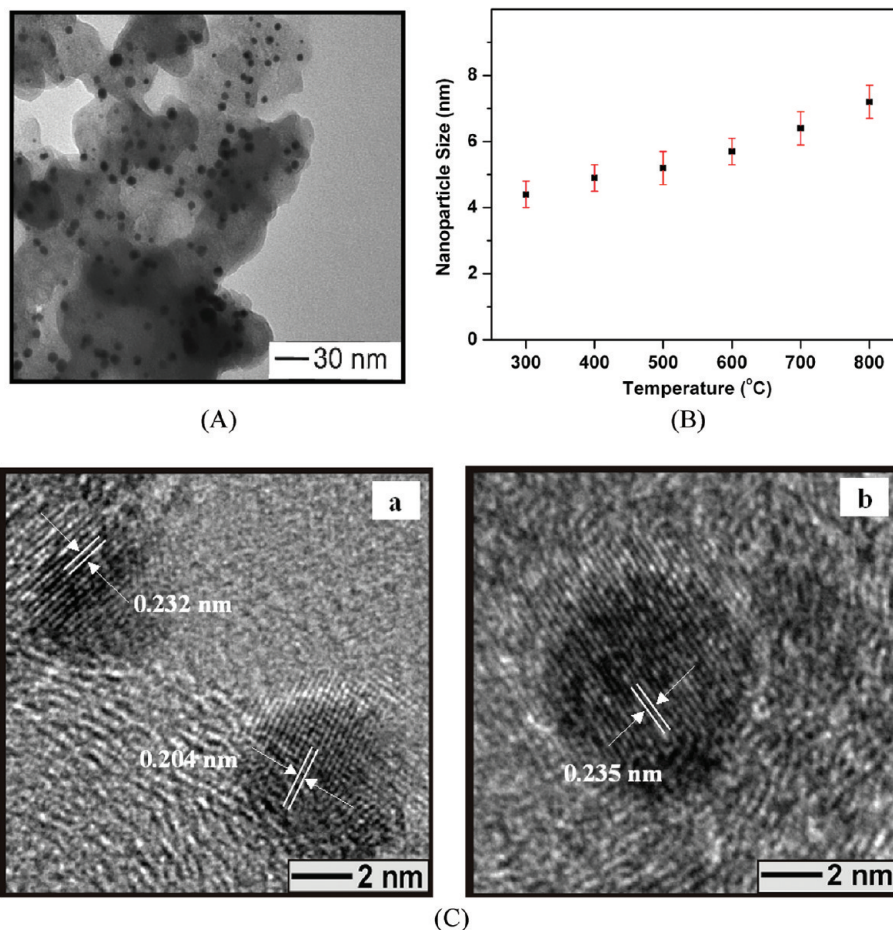


Figure 2. Size and morphology of carbon-supported AuPt nanoparticles. (A) TEM of a sample of Au₂₂Pt₇₈ nanoparticles supported on carbon (400 °C). (B) Correlation between particle size and the thermal treatment temperature. (C) HRTEM for samples treated at 400 (a) and 800 °C (b). (The indicated lattice fringes, 0.232 (or 0.235) and 0.204 nm, correspond to 111 and 100 planes).

at 20–90% Au,¹ our earlier work² showed that the lattice parameters of the alloyed AuPt nanoparticles scale linearly with composition (Vegard's law) demonstrating the alloy properties.² In the present work, the question of how the temperature influences the alloy, partial alloy, or phase segregation was investigated by examining a series of carbon-supported Au_nPt_{100-n} nanoparticles as a function of thermal treatment temperatures. The Au₂₂Pt₇₈/C samples were systematically examined under two thermal treatment conditions, one for 30 min (Sample-B series) and another for 60 min (Sample-A series) under 20% oxygen at 280 °C before further treatment under hydrogen at temperatures ranging from 300 to 800 °C (for 2 h). Figure 3 shows a representative set of XRD patterns for Sample-A (A), -B (B), and -C (C) series as a function of treatment temperature. There is a clear evolution of the diffraction peaks as the temperature increases, showing a gradual splitting of a single-peak pattern at low temperature into a two-peak overlapping pattern upon increasing the treatment temperature. There are also subtle differences in the degree of peak splitting at the high temperatures for these samples with different treatment conditions or different compositions, suggesting differences in phase segregation of the bimetallic nanoparticles.

To understand the correlation between the XRD pattern evolution and nanoscale phase segregation, the detailed

XRD characteristics were compared with those for Au/C, Pt/C, and alloyed AuPt/C systems.^{2,9,20} In Figure 4A, the 111-peak characteristics for the AuPt/C catalysts treated at 400 and 800 °C (as shown in Figure 3) are compared with those for Pt/C and Au/C catalysts. It is evident that the peak positions of the 400 °C treated samples clearly fall in between those for Au/C and Pt/C. For the 800 °C treated samples, it appears that the low-angle peaks match well with that for Au/C, whereas the high-angle peaks still fall in between Au/C and Pt/C but close to Pt/C. On the basis of the linear relationship between the lattice parameter and the bimetallic composition (Vegard's law) derived from fitting to experimental data for alloyed AuPt nanoparticles (a),² AuPt thin films (b and c),^{9,20} and bulk AuPt metals (d)² (see Figure 4B), the results indicate that the 400 °C treated samples are largely characteristic of alloyed AuPt whereas the 800 °C treated samples were largely characteristic of partially segregated phases.

The nature of the gradual phase segregation as a function of temperature was further analyzed by peak deconvolution. On the basis of a two-peak model for the partially segregated phases, the deconvolution results (Figure 5) reveal a clear pattern from the single peak at the low temperature to double peak pattern at the high temperatures. The lattice parameters extracted from the deconvolution results (Figure 5) also shows a clear split-

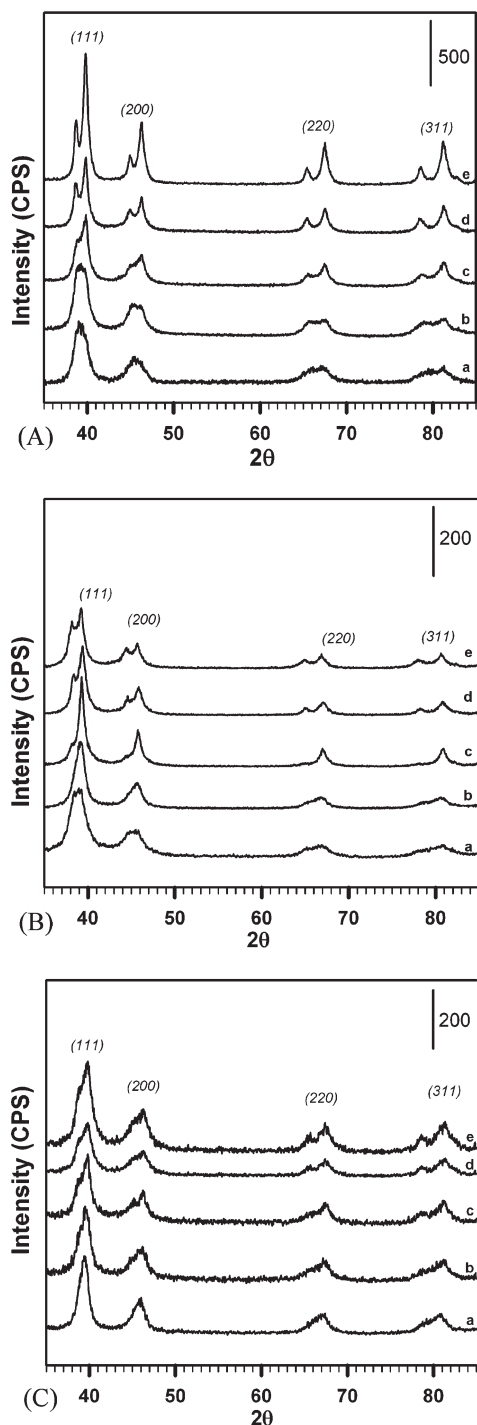


Figure 3. XRD patterns for several catalysts treated at different temperatures: Sample-A series (A) treated at 300 (a), 400 (b), 500 (c), 600 (d), and 800 °C (e). Sample-B series (B) treated at 400 (a), 500 (b), 600 (c), 700 (d), and 800 °C (e), and Sample-C series (C) treated at 400 (a), 500 (b), 600 (c), 700 (d), and 800 °C (e).

ting of the lattice parameter toward the single metal directions (lattice constants: 0.4075 nm for Au/C and 0.3915 nm for Pt/C). Where there are subtle differences in the actual values of the lattice parameter, a clear trend is found for all three types of samples in terms of their general feature in temperature dependence. The lattice parameters characteristic of single-phase alloy at the low temperature gradually approach those for the pure Au and Pt nanoparticles with the increase in temperature. In

contrast to the 400 °C treated samples largely characteristic of alloys with a lattice parameter: $0.3915 \text{ nm} < a < 0.4075 \text{ nm}$, the higher-temperature treated samples show that one component closely matches the lattice parameter of Au, where the other is shift toward Pt/C but larger than 0.3915 nm. By comparing the data for Sample-A, -B and -C series (Figure 5), the subtle differences of the lattice parameters include degree of splitting and the exact values of the lattice parameters. Note that the deconvolution based on three-peak model (see Supporting Information, Figure S2) also reached similar conclusions about the alloying and partial phase segregation characters. In addition, similar partial phase-segregation trends were also observed for samples of other compositions such as $\text{Au}_{89}\text{Pt}_{11}/\text{C}$ and $\text{Au}_{56}\text{Pt}_{44}/\text{C}$ catalysts.

In general, the degree of the temperature-dependent phase segregation depends not only on the bimetallic composition but also on the thermal treatment time length. For Sample-B series, the lattice parameter for the Au-rich phase evolves from the alloy to the partial phase-segregation at a higher temperature than that for Sample-A series. This is reflected by the differences in slopes in the temperature dependence of the lattice parameter. The Pt-rich alloy phase showed a similar trend of evolution from the alloy to the partial phase-segregation for Sample-A and -B series. The extent of phase segregation from alloy phase at low temperature to two phases at higher temperatures clearly depends on the thermal treatment conditions. For Sample-C series, the partial phase segregation is similar to that for Sample-B series. The longer time duration of thermal treatment under oxygen was evidently more favorable for an increased tendency of partial phase segregation than the shorter time duration.

To aid the understanding of the above results, the stability, lattice constant, and phase segregation of AuPt nanoparticles were also assessed by Density Functional Theory (DFT) computation of small AuPt nanoparticles ($\sim 1.2 \text{ nm}$). Seventeen 55-atom AuPt nanoparticles ($\sim 1.2 \text{ nm}$), six $\text{Au}_{24}\text{Pt}_{76}$ (13 Au atoms and 42 Pt atoms), five $\text{Au}_{49}\text{Pt}_{51}$ (27 Au atoms and 28 Pt atoms), and six $\text{Au}_{76}\text{Pt}_{24}$ (42 Au atoms and 13 Pt atoms) were studied using DFT calculations. These calculations were carried out using the spin-polarized DFT method that is implemented in Vienna Ab-initio Simulation Package (VASP).^{34–36} The exchange and correlation energies were calculated using the generalized gradient approximation of Perdew and Wang (PW91).³⁷ The electron-ion interactions were described by Projector Augmented Waves (PAW) method.³⁸ A plane wave basis set was used with a cut off energy of 400 eV. Only the Γ point is needed for these finite systems and therefore was used. Furthermore, the size of the unit cell was chosen such that the nearest distance between neighboring images was more than 10 Å. The above computational techniques have been used in our previous

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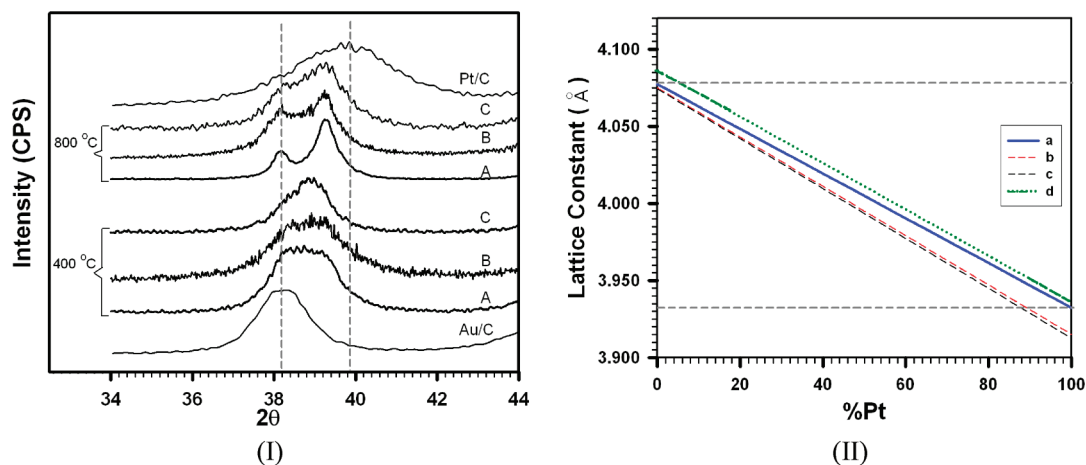


Figure 4. (I) Comparison of the 111-peak characteristics among Au/C catalyst, Pt/C catalyst, and AuPt/C catalysts (A, B, and C) treated at two temperatures. (II) Plots based on linear fitting (Vegard's law) to experimental data for the lattice constant–bimetallic composition correlation for alloyed AuPt nanoparticles treated below 400 °C (a),² AuPt thin films (b),⁹ AuPt thin films (c),²⁰ and bulk AuPt metals (d). Note that the dash line originates from data whereas the dotted only represent the linear trend.² The two horizontal dashed lines represent the lattice parameters corresponding to Au/C and Pt/C, respectively.

studies of transition metal clusters, such as Pt,³⁹ Au,^{40,41} and AuPt.^{42–44} A full geometry relaxation without any symmetry constraints was also performed to all the systems. The structures and the corresponding stability of these nanoparticles are shown in Supporting Information, Figure S3.

On the basis of comparison of the results for the Au₂₄Pt₇₆ isomers (see Supporting Information, Figure S3), which is close to the experimental composition Au₂₂Pt₇₈ for this study, the stability of alloy structures was found to lie in between the core–shell structures. The complete Pt-core/Au-shell structure is the most stable among all isomers. The least stable isomer has the least number of surface Au atoms. When temperature increases, the alloy nanoparticles evolve in such a way that the outer shell Pt atoms migrate into the inner shell. This is further supported by molecular dynamics simulations,⁶ where upon heating above 600 K such Pt migration takes place in an alloy nanoparticle of ~3.6 nm. The computational results further indicate that thermal treatments of alloy AuPt nanoparticles should be below certain temperatures to prevent the loss of outershell Pt atoms. Figure 6 shows the DFT-calculated lattice constants, which are indeed smaller than that of bulk. This finding is in agreement with our earlier finding of the nanoscale phase properties for the alloyed AuPt/C catalysts (see Figure 4–(II)).² The computation results supported the observed overall lattice shrinking of the metal and bimetallic nanoparticles in comparison with the bulk counterparts, and showed the possibility of an evolution of the alloy nanoparticles in such a way that the outer shell Pt atoms migrate into the inner shell when temperature increases, which is qualitatively consistent with the XRD analysis results. Although the computational results agree with the experimental observation, a further investigation is needed to determine how the results correlate with the particle homogeneity.

3. Nanocrystal Surface Composition. The relative change of Au and Pt distribution on the nanoparticle surface as a function of the treatment temperature was assessed by determining the relative surface composition using XPS.^{45,46} Figure 7 shows the XPS spectra in the Pt 4f and Au 4f region comparing samples annealed at 400 (a) and 800 °C (b), and the peak values are shown in Table 1. For Sample-A series, the Pt 4f_{7/2} and Pt 4f_{5/2} bands were observed at 71.90 and 75.25 eV for 400 °C, and 71.75 and 75.10 eV at 800 °C, respectively. The Au 4f_{7/2} and Au 4f_{5/2} bands were observed at 84.45 and 88.10 eV for 400 °C, and 84.53 and 88.30 eV at 800 °C, respectively. Similar results were obtained for Sample-B series annealed at 400 and 800 °C. On the basis of surface composition analysis, Au₂₇Pt₇₃ (400 °C) and Au₅₉Pt₄₁ (800 °C) were obtained for Sample-A series, and Au₃₄Pt₆₆ (400 °C) and Au₄₅Pt₅₅ (800 °C) were obtained for Sample-B series.

While the presence of Au in Pt increases the lattice distance of Pt, the higher electronegativity of Au (2.54) than Pt (2.20) could cause a partial charge transfer from Pt to Au. This expectation was supported by high-resolution XPS data showing binding energy (BE) of Au 4f_{7/2} at 83.32 eV for Au/Pt and 83.87 eV for bulk-like Au samples,⁴⁷ and consequently an increase of the d-orbital vacancy in the AuPt.⁴⁷ In Table 1, the BE values and the atomic ratios of Au and Pt (based on 4f peaks) for AuPt/C samples treated at 400 and 800 °C are compared. Indeed, a subtle increase of the Au 4f peak from 400 to 800 °C by 0.1–0.2 eV was found for Sample-A series (a). In this case, the Pt/Au ratio was decreased by a factor of 4. In comparison, a smaller change was found for the Au 4f peak from 400 to 800 °C for Sample-B series (b), and the Pt/Au ratio was decreased by a smaller factor (1.6). Similarly, a smaller change was found for the Au 4f peak from 400 to 800 °C for Au₄₉Pt₅₁/C, and the Pt/Au ratio was decreased by

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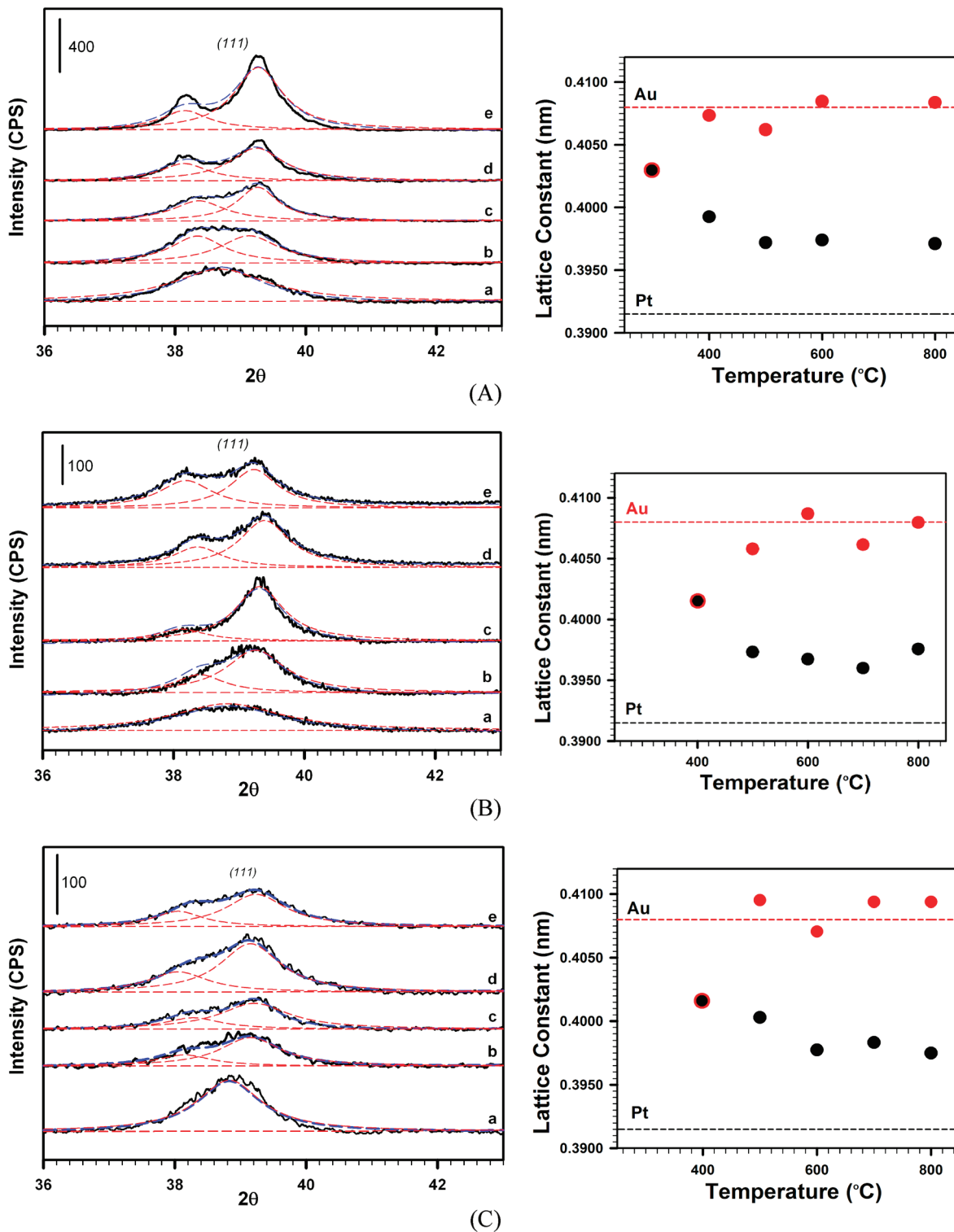


Figure 5. Deconvolution (two-peak model) results for XRD patterns (in the left, obtained from Figure 3) and lattice parameters (in the right) of catalysts treated at different temperatures for Sample-A (A), Sample-B (B), and Sample-C series (C). (In the right graphs, the upper and bottom dotted horizontal lines represent the values of lattice parameters for Au/C and Pt/C obtained from Figure 4, respectively).

a smaller factor (1.2). For Sample-C series, the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ bands were observed at 71.90 and 75.20 eV for 400 °C, and 71.75 and 75.05 eV at 800 °C, respectively. The Au $4f_{7/2}$ and Au $4f_{5/2}$ bands were observed at 84.50 and 88.20 eV for 400 °C, and 84.30 and 88.05 eV at 800 °C respectively. A smaller change was found for the Au 4f peak from 400 to 800 °C for Au₄₉Pt₅₁/C, though the Pt/Au ratio was decreased

by a smaller factor (1.2) in sample-C series as for sample B catalyst.

It is known that the penetration depth for XPS measurements is typically in the range of a few nanometers. However, there is an electron attenuation or depth profiling. Thus, XPS data can infer the structure of the nanoparticle surface. The way we approached this issue in our work was

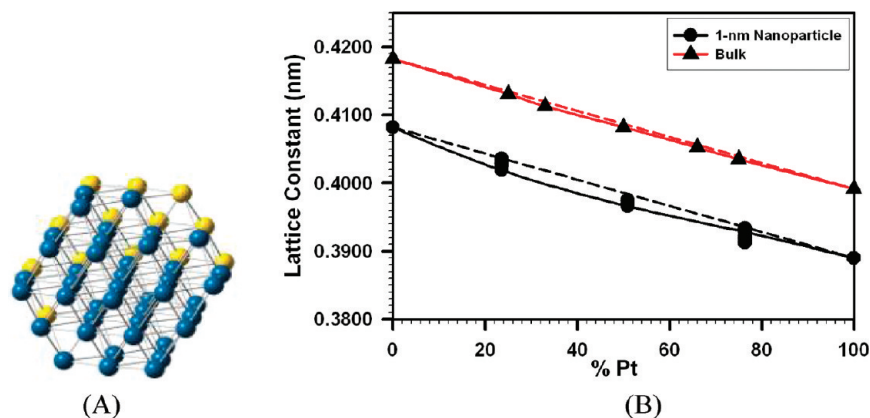


Figure 6. (A) Model built from 55-atom nanoparticle with a minimum-energy (corresponding to a composition of Au₂₄Pt₇₆). The blue and yellow balls represent Pt and Au atoms, respectively (B) DFT-calculated lattice constant–composition relationship for the nanoscale and bulk bimetallic systems.

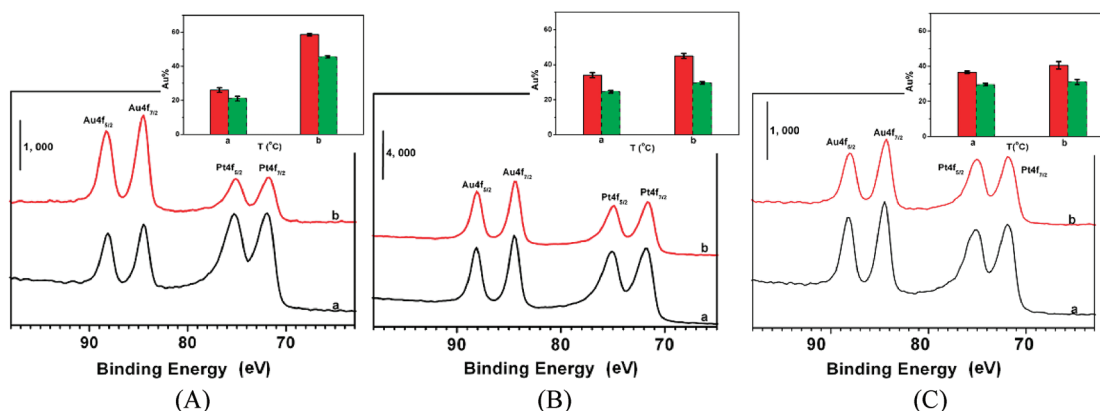


Figure 7. XPS spectra comparing catalysts after different thermal treatment temperatures: Sample-A (A), -B (B), and -C (C) series treated at 400 (a) and 800 °C (b). Insets: comparison of XPS-determined Au% (red) and the Au% calculated (green) based on idealized Pt (core)/Au (shell) nanoparticle (eqs 1–2). (The standard deviation in the y-axis is indicated on top of the bar).

Table 1. Comparison of Binding Energy Values (in eV) and Atomic Ratios for Sample-A and -B Series^a

XPS bands	from Sample-A series				from Sample-B series			
	400 °C (BE)	Pt/Au ratio	800 °C (BE)	Pt/Au ratio	400 °C (BE)	Pt/Au ratio	800 °C (BE)	Pt/Au ratio
Au 4f _{5/2}	88.10	2.85	88.30	0.71	88.08	1.93	88.08	1.21
Au 4f _{7/2}	84.45		84.53		84.40		84.40	
Pt 4f _{5/2}	75.25		75.10		75.05		74.90	
Pt 4f _{7/2}	71.90		71.75		71.75		71.65	

^aThe standard deviation is ±0.05 eV for binding energy value, and ±0.05 for the ratio.

2-fold. One involved XPS measurement of the relative changes of the two metal components as a function of temperature. The other was to apply electron attenuation theory to model the relative changes of the two metal components and compare them with the experimental data. The relative change of the Au/Pt atomic ratio was modeled based on an ideal Pt(core)/Au(shell) nanoparticle considering the electron attenuation effect.^{48,49} The composition derived from XPS depends on the core–shell structural arrangement because of the attenuation of photoelectrons escaping from the core and the shell, $I = I_0 \exp(-d/\lambda)$, where d represents a medium with a finite thickness d , and λ is the

attenuation length. The attenuation length depends strongly on the kinetic energy of the photoelectrons and also on the density of the medium because of the attenuation of the photoelectrons as they traverse the core and the shell (the density of Au (0.096 mol/cm³) obtained from bulk density of Au (18.9 g/cm³), and density of Pt (0.110 mol/cm³) from bulk density of Pt (21.4 g/cm³)). The intensity of a photoelectron peak for a spherical cluster is given by⁵⁰

$$S = \pi\lambda^3 \{x^2 + [(2x + 1)e^{-2x} - 1]/2\} \quad (1)$$

where $x = r/\lambda$ (r , particle radius). The calculation of the intensity of the concentric gold shell involves considering the radius of core–shell particle and core separately, and then

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taking their difference. For Pt core, the calculation involves a simple attenuation factor through the shell

$$S(\text{core}) = e^{-d/\lambda_s} \times \pi \lambda_C^3 \{x^2 + [(2x + 1)e^{-2x} - 1]/2\} \quad (2)$$

where d is the thickness of gold shell, and λ_C and λ_s are the attenuation lengths of core and shell, respectively (attenuation lengths for Pt 4f peak in Pt and Au 4f peak in Au are given as 0.9 and 1.7 nm).⁵¹ The ratio of $S(\text{Au})/S(\text{Pt})$ was calculated from the peak intensity in XPS spectra. Under the assumption of a core–shell structure, the radius of Pt core and the thickness of Au shell were estimated, and the results are shown in insets of Figure 7. For Sample-A (Figure 7A), the trend of the increase in Au% with temperature indicates that the surface treated at 800 °C is enriched with a Au shell in comparison with that treated at 400 °C. In this case, a Pt-rich core with Au shell structure is believed to be predominant for the 800 °C treated sample, which is consistent with partial phase segregation revealed by the XRD data. For Sample-B series, there is a surface enrichment of Au at 800 °C in comparison with that treated at 400 °C (Figure 7B). The degree of the surface Au enrichment is less significant than that for Sample-A series. In this case, a partial coverage of the Pt phase by the Au phase is likely for the 800 °C treated sample which is partially phase segregated. It is evident that the longer time of thermal treatment under oxygen was more favorable for the Pt alloy core–Au shell formation than the shorter duration. The results for sample-C series (Figure 7C) were found to be quite similar to the case for Sample-B series. The surface composition analysis revealed the ratio of Au/Pt as 38:68 for 400 °C and 41:59 for 800 °C. Note that the BE values for Sample-B series were found to be quite close to those for Sample-C series.

In comparison with the findings from XRD characterization, the above modeling based on XPS results provided additional insights into the relative surface-enrichment for partial phase segregation for the high temperature treated samples. It is concluded that upon the treatment at 800 °C, Sample-A consists of a Pt-rich alloy core and a Au shell whereas Sample-B and -C consist of a Pt-rich alloy core with phase-segregated Au domains enriched on the surface. This conclusion is further supported by the electrochemical and electrocatalytic data described below.

4. Electrocatalytic Activity for Oxygen Reduction Reaction. The evolution of the relative surface composition of Pt and Au in the AuPt nanoparticles as a function of temperature was further substantiated by cyclic voltammetric analysis of electrochemical active area (ECA) associated with the hydrogen adsorption/desorption characteristics on surface Pt sites of the catalysts on glassy carbon electrode (Figure 8). For Sample-A series treated at 300–800 °C (Figure 8A), there is a clear trend of decrease of the hydrogen adsorption/desorption peaks in the 0.0–0.3 V region as the treatment temperature is increased. The adsorption/desorption

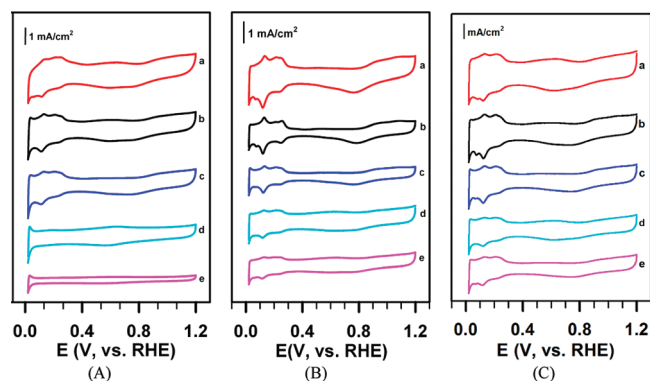


Figure 8. CV curves for catalysts from Sample-A series (A), -B series (B), and -C series (C treated at 400 (a), 500 (b), 600 (c), 700 (d), and 800 °C (e)) (Glassy carbon electrode (0.196 cm²); 0.5 M H₂SO₄; catalyst loading: 10 μg; scan rate: 50 mV/s).

peaks characteristic of (100) (at ~0.20 V) and defects/steps (at ~0.10 V),⁵² decrease with increasing temperature. The complete disappearance of the peaks for 800 °C is indicative of the absence of Pt on the surface. The peak features for Sample-B series (Figure 8B) showed a similar trend as a function of temperature. However, the peak features characteristic of (100) (at ~0.23 V) and defects/steps (at ~0.12 V) are more pronounced, and are still detectable for 800 °C, indicative of the presence of Pt on the surface. The peak features for Sample-C series (Figure 8C) are quite similar to those for Sample-B series.

The experimentally determined ECA values were also compared with that for Pt/C catalyst^{53,54} which provided an assessment of the Pt-specific active surface area on the AuPt/C catalysts treated under different temperatures. As shown in Table 2 for the Pt-specific surface area obtained by normalizing the ECA values against the ECA value of Pt/C catalyst (see also the Supporting Information, Figure S4 and Table S1), it was found to decrease as the temperature increases. This finding is suggestive of significant temperature dependence for the relative Pt- or Au-enrichment on the surface. In contrast to Sample-A series where Au-surface enrichment occurred at a temperature above 400 °C and the surface Pt % approached zero at 800 °C, Sample-B series showed Au-surface enrichment at a higher temperature (~600 °C). There is a small but detectable surface Pt% at 800 °C for Sample-B series. For Sample-C series, the surface area–size correlation appears to fall in between Sample-A and Sample-B series, but it closely resembles that for Sample-B series. The above findings are consistent with the conclusions from both XRD and XPS characterizations described in the previous subsections. Another important finding is that the Pt-specific surface area was found to be larger than that for Pt/C with similar particle

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Table 2. Pt-Specific Active Surface Areas of AuPt/C Catalysts That Are Normalized by That for Pt/C Catalyst^{53,54}

sample series	treatment temperature (°C) ^a					
	300	400	500	600	700	800
A (Au ₂₂ Pt ₇₈ /C)	2.3	1.5	1.4	1.4	0.2	0.1
B (Au ₂₂ Pt ₇₈ /C)	2.4	4.2	2.9	1.9	1.5	1.2
C (Au ₄₉ Pt ₅₁ /C)		3.1	3.3	2.5	1.7	1.9

^aNote: The thermal treatments: first treatment at 280 °C under 20% O₂ for 60 min for Sample-A series and for 30 min for sample-B and -C series, before further treatment at 300–800 °C under 15% H₂ for 2 h.

sizes by a factor of 2–4 for some of the bimetallic catalysts treated at low temperatures, which is shown in the Supporting Information, Figure S4 and Table S1. The ECA values for some of the AuPt/C catalysts are larger than the theoretical value (e.g., 70 m²/g_{Pt} for 3-nm particles⁵⁵ and for Pt/C and other alloy nanoparticle catalysts reported in our own earlier work^{53,54}). Note that a similar phenomenon was recently reported for a catalyst with a structure of Au core and Pt shell synthesized by a successive reduction method.²⁵ The results are suggestive of the possibility of a highly effective Pt-specific surface exposure for our carbon-supported AuPt nanoparticles. While further experiments are needed to determine the exact origin of this fact, we have considered three possible scenarios. The first is the possible contribution of electrical double layer charging or early hydrogen evolution currents to the total current in the H_{upd} region. However, our calculations and control experiments indicated that this contribution would not be sufficient to account for the larger charges observed. The second is a possible large loading of catalysts on the electrode surface. However, our careful and multiple repeating experimental examinations of the metal loading and the results ruled out this possibility. Third, it is possible that there is the presence of much smaller sized Pt-rich particles (e.g., < 0.5 nm) on the surface of the 3–4 nm particles or the carbon support which could increase Pt-specific surface area dramatically. Currently, we do not have evidence to support this possibility, but we are designing a systematic measurement to address this possibility.

RDE measurements were performed to assess the electrocatalytic activities of these catalysts for oxygen reduction reaction. As shown in Figure 9 comparing the RDE curves for catalysts with different compositions or phase structures, there are clear differences of the reduction currents in the kinetic region (0.8–0.9 V vs NHE). These differences demonstrated that both the bimetallic composition and the phase structures had profound effects on the electrocatalytic activity. To quantitatively assess the correlation between the nanoscale phase structures and the catalytic activity, the mass activity data were extracted from the kinetic currents of the RDE curves in the potential region of 0.8–0.9 V (Figure 10). It is evident that the mass activity depends on both thermal treatment temperature and condition. The data for Sample-A and -B series showed an increase of mass activity to a maximum at 400 °C and further decrease with increasing temperature. The decrease of the activity with temperature is

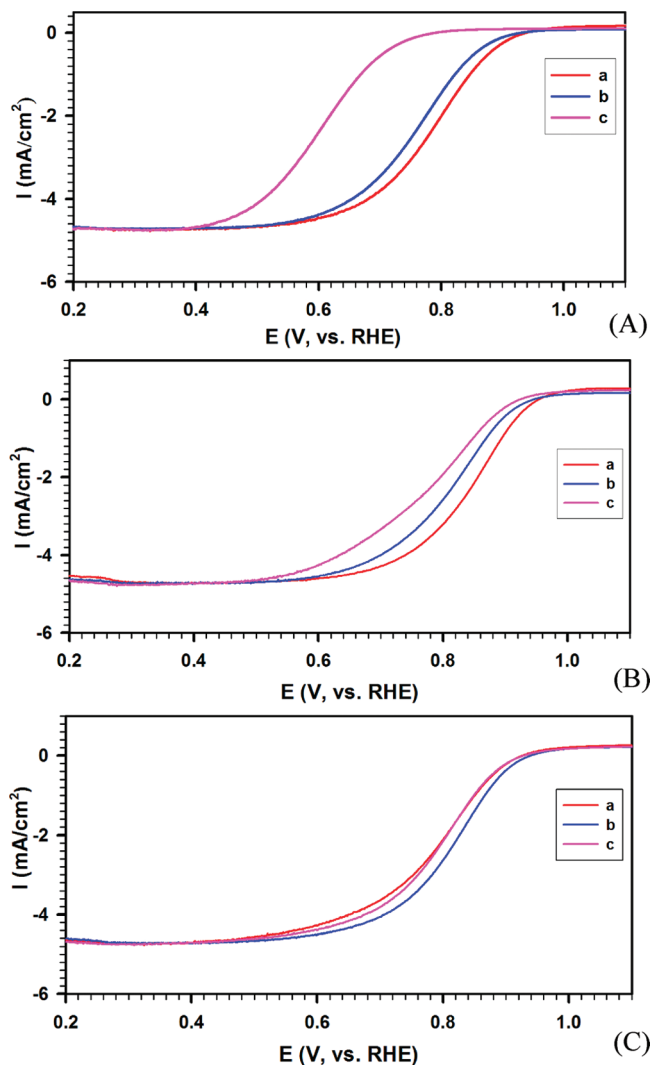


Figure 9. RDE curves for ORR for Samples-A (A), -B (B), and -C (C) series (normalized for comparison) treated at 400 (a), 600 (b), and 800 °C (c). (Glassy carbon electrode (0.196 cm²); 0.5 M H₂SO₄ saturated with O₂; catalyst loading: 10 μg; scan rate: 10 mV/s; speed: 1600 rpm).

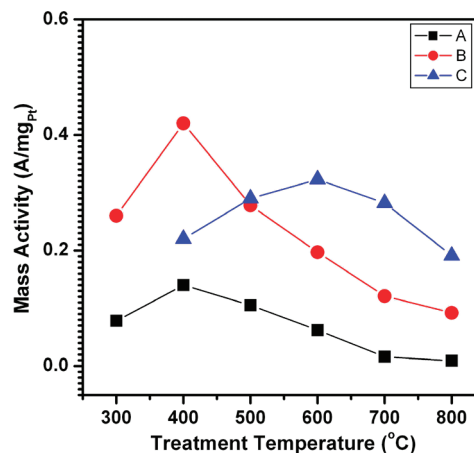


Figure 10. Plots of mass activity at 0.858 V as a function of thermal treatment temperature for samples -A (A), -B (B), and -C (C) series (C). (The size of symbols represents the standard deviation in the y-axis).

consistent with the findings of the increased phase segregation and the Pt core–Au shell formation. At any specific temperature

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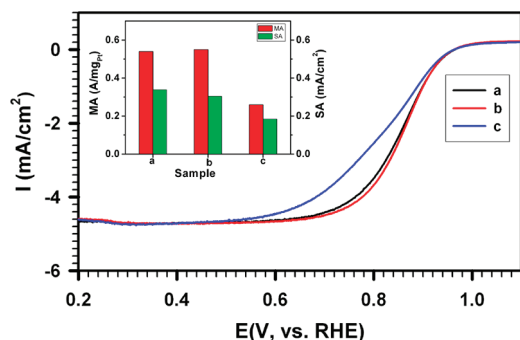


Figure 11. RDE curves for samples of Au₂₅Pt₇₅/C catalysts with different thermal treatment time lengths (15 (a), 30 (b), and 60 min (c)) under O₂ (Glassy carbon electrode (0.196 cm²); 0.5 M H₂SO₄ saturated with O₂; catalyst loading: 10 μg; scan rate: 10 mV/s; speed: 1600 rpm). (Inset: Bar charts comparing mass activity (MA) and specific activity (SA) for the different thermal treatment time lengths).

Sample-B series display a higher activity than Sample-A series by a factor of 2–3. This difference is believed to reflect the surface Au-enrichment effect on activity as a result of the difference in the thermal treatment conditions, as revealed by both XRD and XPS data. Note the difference in terms of time durations used for the organic shell removal under oxygen, and the difference in carbon burning temperatures for the two treatment conditions as observed by TGA. Moreover, the temperature for the maximum activity was also found to depend on the bimetallic composition, as supported by the observations of a maximum activity at 400 °C for Sample-A and -B series and a maximum activity at 600–700 °C for Sample-C series. A combination of lattice parameter and surface structural effects as a result of the differences in composition and treatment conditions is believed to be operative. Recent studies of AuPt thin films²⁰ showed that there is a stronger Pt–O binding energy for Au-rich alloys as compared with Pt-rich alloys. This study²⁰ and one of our earlier studies¹⁹ also revealed that the shift of the d-band center of the Pt atoms as a result of the presence of Au in close proximity to Pt atoms led to stronger bonds with CO- and O-containing species at the surface of the catalysts. The observed differences between Sample-A and -B series and between Sample-B and -C series indicate that there exists an optimized surface structure with an appropriate Pt–O bonding strength for achieving the enhanced electrocatalytic activity.

To confirm the possible surface structural effect as a result of the difference in the thermal treatment condition, another catalyst with the composition of Au₂₅Pt₇₅/C was treated at 400 °C under hydrogen, but different time lengths for the organic shell removal under oxygen gas, 15, 30, and 60 min (Figure 11) using the same temperature ramp as described in the Experimental Section. The Pt-specific active surface area normalized against that of Pt/C was found to exhibit a subtle increase (2.1 (60 min), 2.7 (30 min), and 2.4 (15 min)). Note that the difference of the particle sizes was found to be small for these three samples (4.4 ± 0.5, 4.4 ± 0.7, and 4.9 ± 0.7 nm). Again, ECA values larger than the theoretical values were observed, which is similar to the ECA results determined from Figure 8 as discussed earlier.

The finding is likely suggestive of the surface Au enrichment as a result of the increased time for the thermal treatment under oxygen. The mass activity and specific activity were found to yield 0.26 A/mg_{Pt} and 0.18 mA/cm² (60 min), 0.55 A/mg_{Pt} and 0.30 mA/cm² (30 min), and 0.54 A/mg_{Pt} and 0.34 mA/cm² (15 min), respectively. This finding clearly shows that both mass activity and specific activity increase with the decrease in the treatment time length for the thermal treatment under oxygen. This dependence is significant especially for the specific activity, which is believed to reflect a possible surface Au enrichment during the prolonged thermal treatment under oxygen, which involves a surface reaction of the capping species with oxygen and a subsequent Au-enrichment because of its lower surface free energy than that for Pt. XRD characterizations of the 15- and 30-min treated samples were found to exhibit single phase alloy character whereas the 60-min treated sample showed a partial phase segregation with an enrichment of Au domains on the surface. It further demonstrates the possibility of manipulating the thermal treatment temperatures and conditions for producing a significant effect of the surface metal-enrichment on the electrocatalytic activity.

Conclusions

In this work, the findings from the XPS and XRD characterizations have provided important information for us to pin down the changes of the alloying and phase segregation structures as a function of the thermal treatment temperature. In contrast to the largely alloyed character for the catalysts treated at 300–400 °C, the higher-temperature treated catalysts (e.g., 800 °C) are shown to consist of a Pt-rich alloy core and a Au shell or phase-segregated Au domains enriched on the surface. The electrochemical and electrocatalytic activities are highly dependent on the nanoscale evolution of alloying and phase segregation. In all these cases, the interaction remains between Au and Pt in the nanoparticles through either alloying bonding or phase boundaries. The question whether the particle completely phase segregated into monometallic Pt and Au particles at the high temperatures where the interaction between Au and Pt does not remain has been further addressed by the measurement of the Pt-specific active surface area. If the particle completely phase segregated into monometallic Pt and Au particles, the Pt-specific active surface area should be significant according to the bimetallic composition and the observed particle sizes determined. This assumption was, however, in contradiction to the experimental observation of an insignificant Pt-specific active surface area for the high temperature-treated catalysts. Therefore, the partially phase-segregated particles either exhibit a Pt-rich alloy core–Au shell structure, or a Pt-rich alloy core which is partially covered by phase-segregated Au domains as illustrated in Scheme 1. This conclusion is consistent not only with the fact that Au has a lower surface free energy than Pt but also with theoretical results including the DFT computation for small AuPt

clusters as shown in this work, and the earlier molecular dynamics simulations for AuPt nanoparticles of various sizes.⁶

Taken together, the experimental and theoretical results have led to new insights into the control of the nanoscale alloying, phase-segregation, and core-shell evolution of the AuPt nanoparticles of different composition. The demonstration of the unprecedented controllability of the alloying and partial, complete, or core-shell phase segregation of this nanoscale bimetallic system by a combination of bimetallic composition, size, thermal treatment temperature and duration provided an intriguing example for establishing the correlation between the nanoscale phase structures and the electrocatalytic activity for oxygen reduction reaction. These findings have constituted the basis for our expanded investigations

into other bimetallic or trimetallic nanoparticles and catalyst systems. The results are expected to have profound implications to developing advanced strategies for the design and nanoengineering of nanostructured multimetallic catalysts for a wide variety of catalytic reactions.

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Supporting Information Available: Additional information on the synthesis, TEM, XRD, DFT, and electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.