

# Synthesis-Atomic Structure-Properties Relationships in Metallic Nanoparticles by Total Scattering Experiments and 3D Computer Simulations: Case of Pt-Ru Nanoalloy Catalysts

Binay Prasai,<sup>1</sup> Yang Ren,<sup>2</sup> Shiyao Shan,<sup>3</sup> Yinguang Zhao<sup>3</sup>, Hannah Cronk<sup>3</sup>, Jin Luo,<sup>3</sup> Chuan-Jian Zhong<sup>3</sup> and Valeri Petkov<sup>1</sup>

<sup>1</sup> Department of Physics, Central Michigan University, Mt. Pleasant, Michigan 48859, USA.

<sup>2</sup> X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA.

<sup>3</sup> Department of Chemistry, State University of New York at Binghamton, New York 13902, USA.

## COMPUTATIONAL METHODS AND EXPERIMENTAL DATA

### *Classical Molecular Dynamics (MD) Simulations*

MD simulations were carried out with the help of computer program DL-POLY [S1] under canonical NVT ensemble in the absence of periodic boundary conditions. Velocity Verlet algorithm with a time step of 2 fs was used. Initial model atomic configurations were equilibrated for 200 ps at 400 °C, which is just about the temperature at which Pt-Ru NPs were post-synthesis treated as to be activated for catalytic applications. The models were then cooled down to room temperature (300 K) in steps of 50 °C and again equilibrated for 100 ps.

### *Reverse Monte Carlo (RMC) Simulations*

Reverse Monte Carlo (RMC) simulations were used to refine further MD generated structure models for Pt-Ru NPs shown in Figure S5 below. In the spirit of traditional RMC simulations [S2, S3] positions of atoms in MD models were adjusted as to minimize the difference between the RMC model computed and respective experimental atomic PDFs. During the simulations Pt and Ru atoms were constrained to maintain as maximal (i.e. as close to 12) as possible coordination numbers thus taking into account the close packed (fcc/hcp-type) nature of the atomic structure in Pt-Ru NPs studied here. Also, Pt and Ru atoms were constrained not to come closer than pre-selected distances of closest approach thus taking into account the fact that metal atoms may not approach each other much closer than the sum of their radii  $R_{ij}$ . Radii of Pt and Ru atoms used in the RMC simulations were determined from the positions of the first peak in the partial atomic PDFs computed from the respective MD models. A relatively new feature [S4, S5], turning the simulations into a hybrid between traditional RMC and MD, was the optimization of model's energy. The simultaneous minimization of model's energy and the difference between model computed and experimental PDF data is important since if the former or latter are minimized alone some inherent to NPs structural features (e.g. local structural

disorder) may end up under or overestimated, respectively. Model's energy was described by a simplistic yet scientifically sound pair-wise (Lennard-Jones type) potential the parameters of which were taken from literature sources [S6]. The simulations were considered completed when no significant changes in model's goodness-of fit indicator  $R_{wp}^{PDF}$ , described below, were observed. Simulations were done with the help of a new version of the program RMC++ [S7]. Note hybrid RMC described here is distinctly different from the so-called Empirical Potential Structure Refinement (EPSR) simulations featuring somewhat disordered but continuous atomic configurations subjected to 3D periodic boundary conditions [S8, S9].

### *Evaluation the quality of 3D structure models for Pt-Ru NPs*

The quality of structure models for  $Pt_xRu_{100-x}$  NPs ( $x=31, 49$  and  $75$ ) was evaluated by computing a goodness-of-fit indicator  $R_{wp}^{PDF}$ , defined as [S10-S12]:

$$R_{wp}^{PDF} = \left\{ \frac{\sum w_i (G_i^{exp.} - G_i^{calc.})^2}{\sum w_i (G_i^{exp.})^2} \right\}^{1/2} \quad (1)$$

where  $G^{exp.}$  and  $G^{calc.}$  are the experimental and model computed atomic PDFs, respectively, and  $w_i$  are weighting factors reflecting the experimental uncertainty of individual  $G^{exp.}$  data points. Here  $w_i$  were considered to be uniform which, as predicted by theory [S12] and largely corroborated by experiment [S13], is a reasonable approximation in the case of high quality  $G^{exp.}$  data such as ours. Note  $R_{wp}^{PDF}$  is conceptually very similar to the weighted profile agreement factor  $R_{wp}$  [S14,S15] used for evaluating the quality of structure models for 3D periodic polycrystalline materials defined as:

$$R_{wp} = \left\{ \frac{\sum w_i (y_i^{exp.} - y_i^{calc.})^2}{\sum w_i (y_i^{exp.})^2} \right\}^{1/2} \quad (2)$$

where  $y_i^{exp}$  and  $y_i^{calc}$  are, respectively, the observed and model calculated Bragg intensities at the step  $i$  in the polycrystalline powder diffraction pattern, and  $w_i$  are weighting factors reflecting the quality of this pattern. Typical values of  $R_{wp}^{PDF}$  are, however, in the range of 15-30 % thus appearing somewhat high when compared to  $R_{wp}$  values which, usually, are smaller than 10 % [S14, S15]. This mostly reflects the fact that atomic PDFs analysis takes both Bragg-like features and the strong diffuse component of the experimental diffraction patterns for NPs into account while crystal structure determination from powder diffraction data focuses on sharp Bragg peaks alone. The inherently higher absolute values of the goodness-of-fit indicator  $R_{wp}^{PDF}$ , however, do not affect its functional purpose as a quantity allowing evaluating the quality of NP structure models unambiguously.

### Basics of SC method and derivation of SC parameters for Ru species

In brief, SC method treats atomic pair interactions in metals and alloys as a sum of two constituents. One accounts for the repulsion between metal atom cores and the other - for the attractive force between metal atoms due to the delocalized electrons surrounding them [S16-S18]. Accordingly, the energy,  $E$ , of atomic-level models based on SC method appears as a sum of an atomic pair potential  $V(r_{ij})$  term and a local electron density ( $\rho_i$ ) term defined as follows:

$$U = \sum_i \left[ \sum_{j \neq i} \frac{1}{2} \epsilon_{ij} V(r_{ij}) - h_i \epsilon_{ij} (\rho_i)^{\frac{1}{2}} \right] \quad (3)$$

where

$$V(r_{ij}) = \left( \frac{a_{ij}}{r_{ij}} \right)^{n_{ij}} \quad \text{and} \quad \rho_i = \sum_{j \neq i} \left( \frac{a_{ij}}{r_{ij}} \right)^{m_{ij}} \quad (4)$$

The so-called “energy” parameter  $\epsilon_{ij}(meV)$  and the dimensionless parameter  $h_i$  are used to scale appropriately the interatomic repulsive  $V(r_{ij})$  and attractive ( $\rho_i$ ) interactions, respectively. Parameters  $m_{ii}$  and  $n_{ii}$  are positive integers such that  $n_{ii} > m_{ii}$ . On the other hand, SC parameter  $a_{ij}$  is a quantity used to scale appropriately distances  $r_{ij}$  between  $i$  and  $j$  type atoms in structure models, including first atomic neighbor distances. Essentially, the latter set the radii/size of metal atoms involved. SC parameters for Pt species adopting fcc-type structure in bulk were taken from literature sources [S17, S18]. Parameters are listed in Table S1 below. SC parameters for Ru species adopting hcp-type structure in bulk were derived following a procedure described in [S19]. According the procedure, at equilibrium,

$$\frac{\partial E}{\partial a} = 0 \quad (5)$$

yielding

$$c = \frac{n S_n}{m \sqrt{S_m}} \quad (6)$$

where

$$S_n = \sum \left( \frac{a}{r} \right)^n \quad \text{and} \quad S_m = \rho_i \quad (7)$$

Also, it may be shown [S19] that model's energy,  $E$ , can be expressed as:

$$E = \frac{\epsilon S_n}{2m} (2n - m) \quad (8)$$

and model's bulk modulus,  $B$ , as:

$$B = \frac{4}{9a} \frac{\partial^2 E}{\partial a^2} = \frac{(2n - m) n \epsilon S_n}{36 \Omega} \quad (9)$$

where  $\Omega = \frac{a^3}{\sqrt{2}}$  is the volume of atoms involved.

Furthermore, eqs. (8) and (9) lead [S19] to the following useful relation:

$$\frac{\Omega B}{E} = \frac{mn}{18} \quad (10).$$

SC parameters for Ru were obtained on the basis of equations (6), (8) and (10) using experimental values for the atomic volume ( $\Omega$ ), bulk modulus ( $B$ ) and cohesive energy ( $E$ ) of bulk Ru [S20]. As obtained parameters are shown in Table S2. Their values were validated against experimental and theoretically predicted data for the hcp-lattice parameters,  $a$  and  $c$ , (see Table S3 below) and elastic constants of bulk Ru.

**Table S1. SC parameters for Pt species taken from literature sources [S18].**  
**Note parameters are validated against data for bulk Pt. Accordingly, SC parameter  $a_{ii}$  is nothing but the fcc-lattice parameter of bulk Pt.**

| Metals | $m_{ii}$ | $n_{ii}$ | $\epsilon_{ii}$ | $a_{ii}$ (Å) | $h_i$  |
|--------|----------|----------|-----------------|--------------|--------|
| Pt     | 8        | 10       | 0.0197          | 3.920        | 34.428 |

**Table S2. SC parameters for Ru species derived as explained above.**

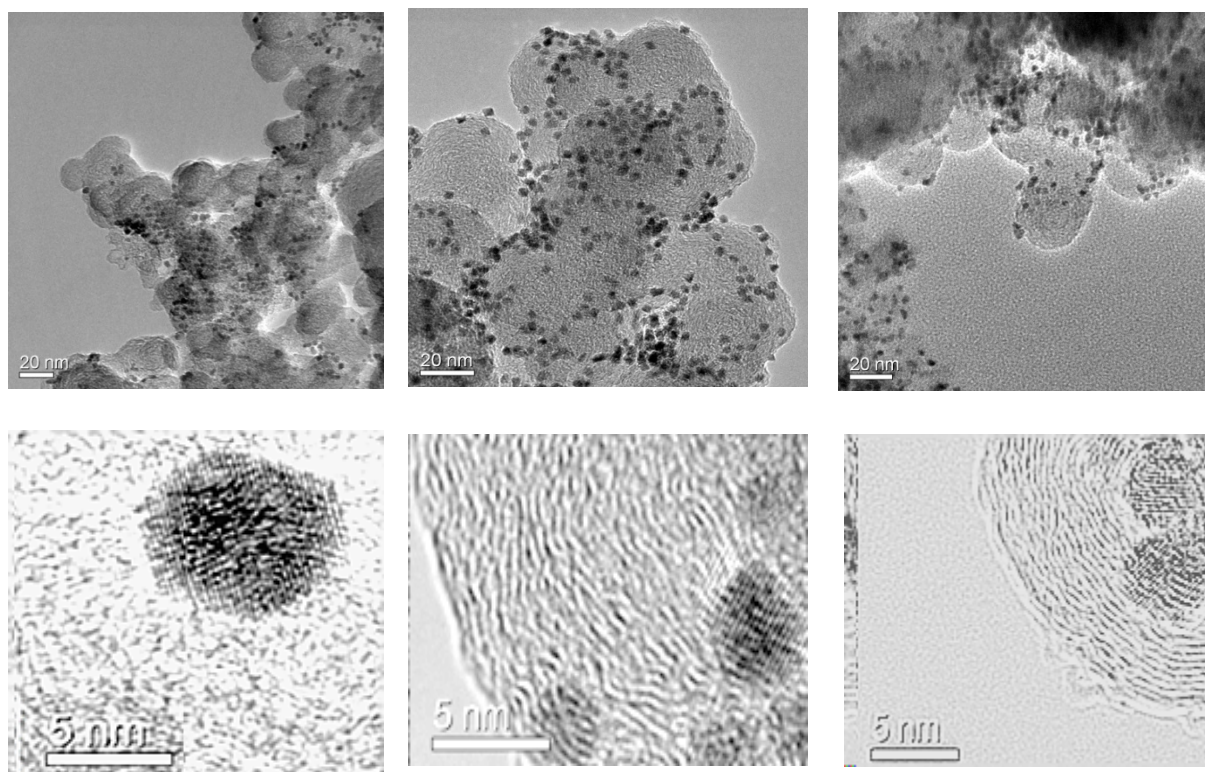
| Metals | $m_{ii}$ | $n_{ii}$ | $\epsilon_{ii}$ | $a_{ii}$ (Å) | $h_i$ |
|--------|----------|----------|-----------------|--------------|-------|
| Ru     | 8        | 9        | 0.7880          | 2.707        | 4.133 |

**Table S3. HCP-lattice parameters  $a$  and  $c$ , hcp-lattice unit cell volume and cohesive energy (per atom) for bulk Ru derived on the basis of SC parameters of Table S2 as compared to experimental data [S20] and the theoretical predictions of Chen. et al [S19] and Fast et al. [S21].**

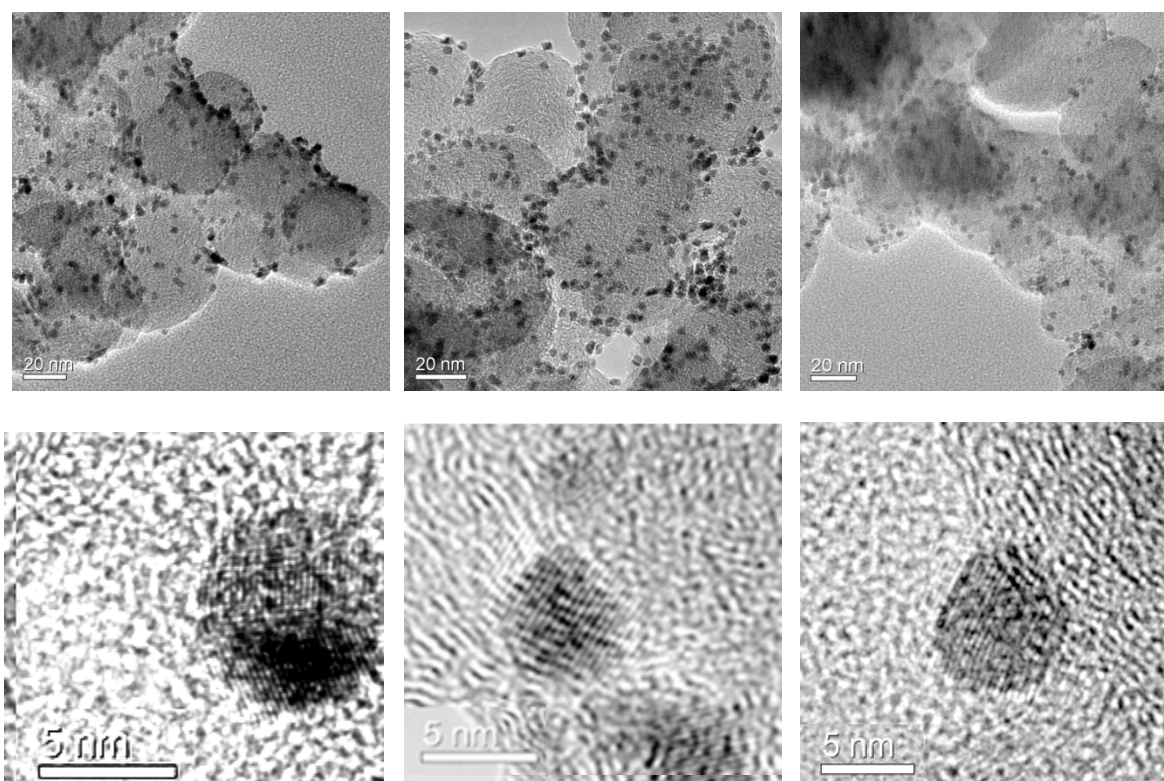
|                     | $a$ (Å) | $c$ (Å) | Volume (Å <sup>3</sup> ) | $E_{\text{coh}}$ (eV) |
|---------------------|---------|---------|--------------------------|-----------------------|
| SC-derived          | 2.707   | 4.288   | 13.607                   | 6.74                  |
| Experiment          | 2.704   | 4.281   | 13.552                   | 6.74                  |
| Theory/Chen et al.  | 2.751   | 4.352   |                          | 6.78                  |
| Theory/ Fast et al. |         |         | 13.24                    |                       |

**Table S4. Elastic Constants (in eV) for bulk Ru derived on the basis of SC parameters of Table S2 as compared to experimental data [S22] and the theoretical predictions of Chen. et al [S19] and Fast et al. [S21].**

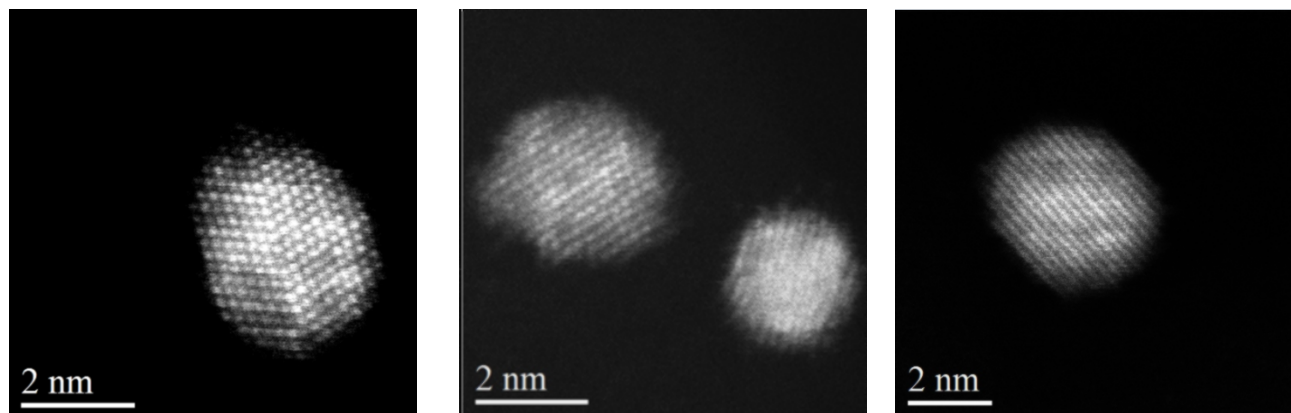
|                    | B     | C <sub>11</sub> | C <sub>12</sub> | C <sub>13</sub> | C <sub>33</sub> | C <sub>55</sub> |
|--------------------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SC-derived         | 1.978 | 3.211           | 1.121           | 1.468           | 3.266           | 1.021           |
| Experiment         | 2.002 | 3.596           | 1.168           | 1.044           | 3.997           | 1.180           |
| Theory/Fast et al. | 2.301 | 4.347           | 1.224           | 1.169           | 4.833           | 1.498           |
| Theory/Chen et al. | 2.136 | 3.137           | 1.266           | 1.252           | 3.705           | 1.184           |



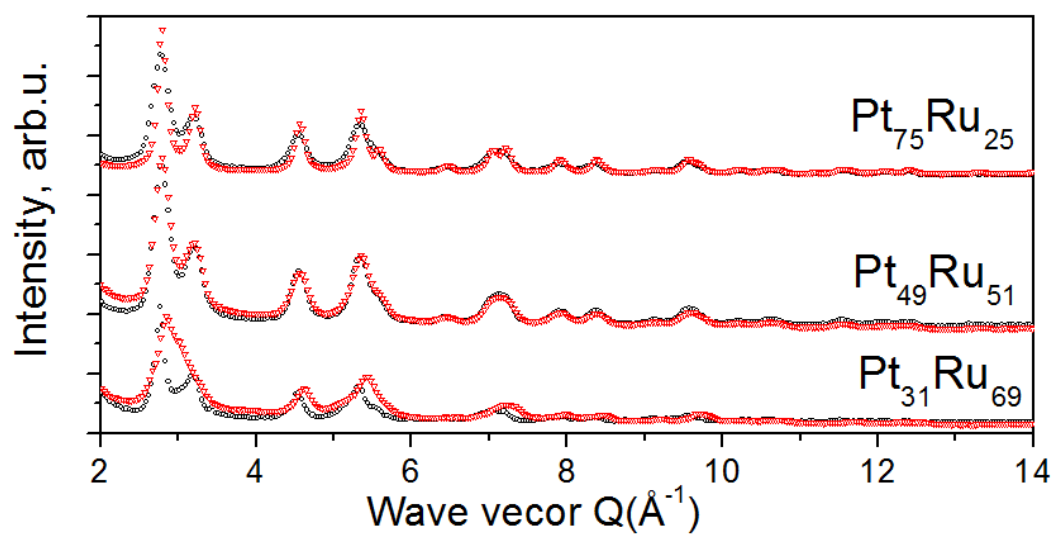
**Figure S1.** Representative TEM (first row) and HR-TEM (second row) images of carbon supported as-synthesized Pt<sub>x</sub>Ru<sub>100-x</sub> NPs (x=31, left column); (x=49, middle column) and (x=75; right column). NPs appear spherical in shape and with an average size of approximately 4.3 ( $\pm$  0.6) nm. Note the “ $\pm$ ” deviation from the average NP size is the full width at half maximum of a gaussian-like distribution of sizes extracted from populations of several hundred NPs sampled by different TEM images. HR-TEM images show clear lattice fringes inside the NPs. However, fringes appear distorted and/or are missing close to NP surface indicating the presence of usual for metallic NPs surface structural disorder.



**Figure S2.** Representative TEM (first row) and HR-TEM (second row) images of carbon supported, post-synthesis treated as to be fully activated for catalytic applications  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31$ , left column); ( $x=49$ , middle column) and ( $x=75$ ; right column). NPs appear spherical in shape and with an average size of approximately  $4.6 (\pm 0.7)$  nm. Note the “ $\pm$ ” deviation from the average NP size is the half width at full maximum of a gaussian-like distribution of sizes extracted from populations of several hundred NPs sampled by different TEM images. HR-TEM images show clear lattice fringes inside the NPs. However, fringes appear distorted and/or are missing close to NP surface indicating the presence of usual for metallic NPs surface structural disorder.



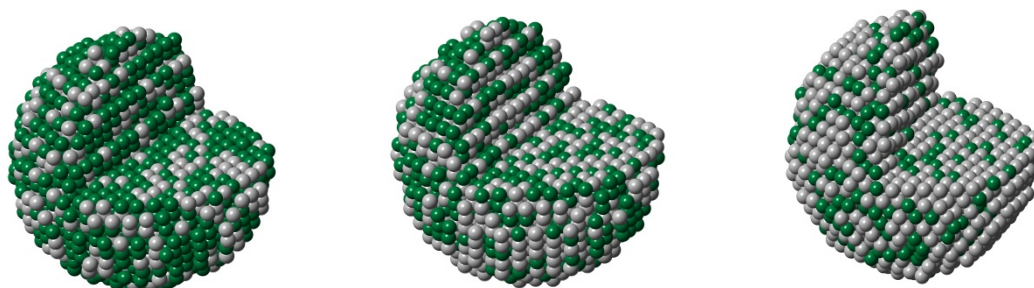
**Figure S3.** HAADF-STEM images of carbon supported, catalytically fully activated  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31$ , left); ( $x=49$ , middle) and ( $x=75$ ; right). The image for  $\text{Pt}_{31}\text{Ru}_{69}$  nanoparticle shows a somewhat sharp, bright/dark contrast pattern indicating NP segregation into Pt(bright)- and Ru(dark)-rich domains. Images for  $\text{Pt}_{49}\text{Ru}_{51}$  and  $\text{Pt}_{75}\text{Ru}_{25}$  NPs are rather uniform indicative of a homogeneous alloy-type chemical pattern.



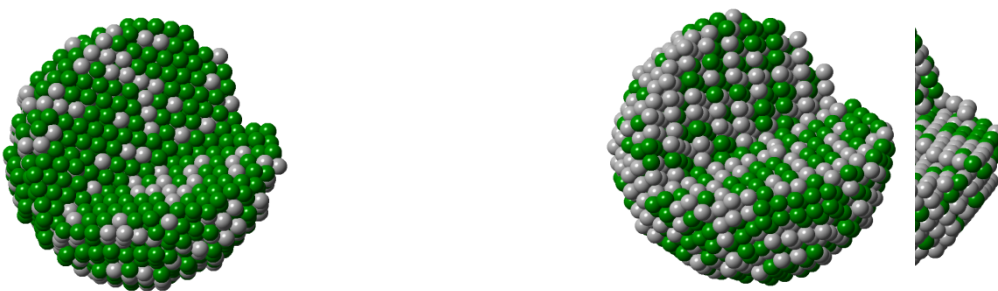


**Figure S4.** Background & carbon support scattering corrected experimental high-energy synchrotron XRD patterns for as-synthesized (symbols in black) and fully activated (symbols in red)  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31, 49$  and  $75$ ). XRD patterns exhibit a few broad, strongly overlapping peaks at low diffraction (Bragg) angles and almost no distinct features at high diffraction angles, i.e. are rather diffuse in nature. Such patterns are typical for nanometer-size materials. Also, note, positions and intensities of several major peaks in the XRD patterns for as-synthesized and respective fully activated NPs differ significantly. The difference indicates that the atomic-scale structure of as-synthesized Pt-Ru NPs changes significantly when NPs are subjected to post-synthesis treatment (see

text). Hence, the latter can be used as a tool for fine-tuning the

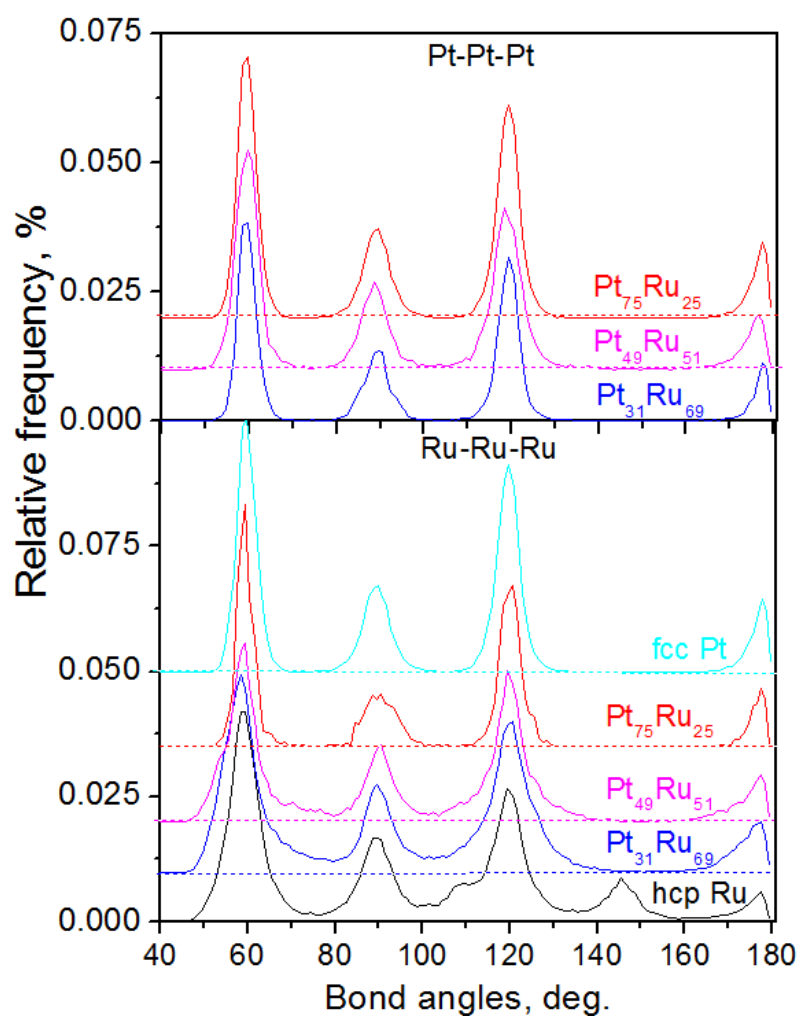


former.

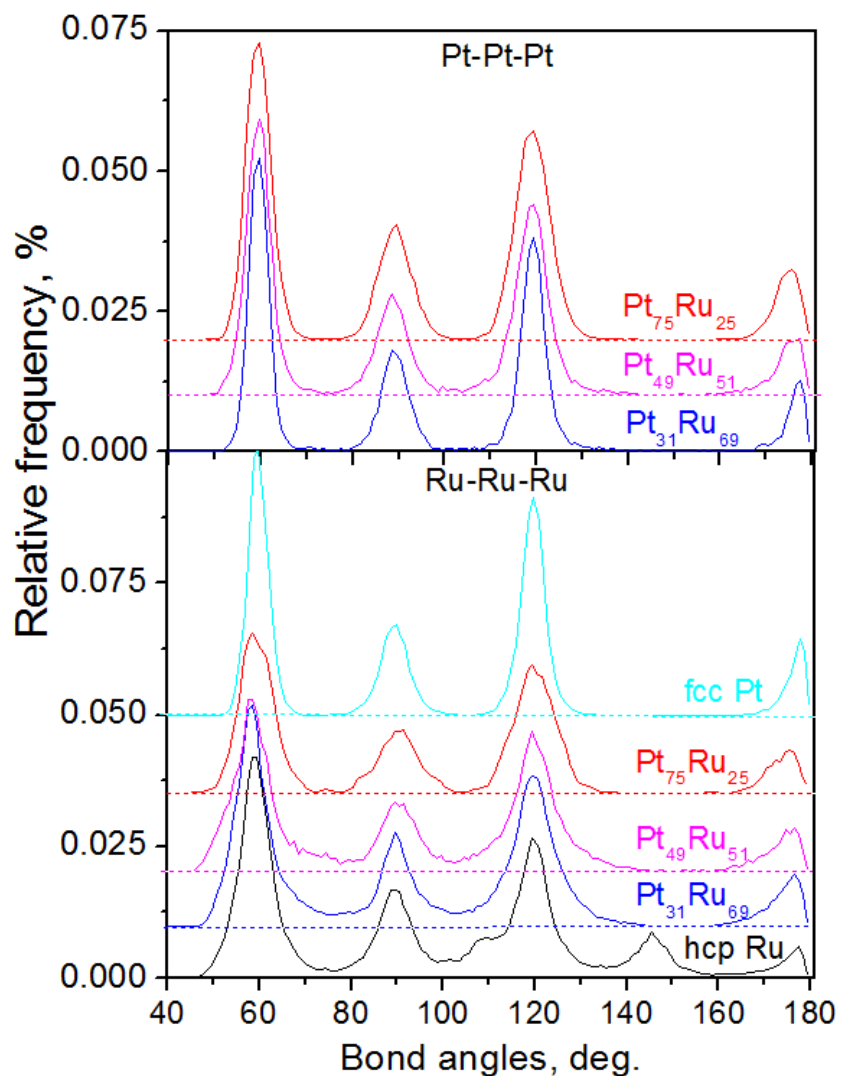


**Figure S5.** MD generated 3D structure models for as-synthesized (first row) and post-synthesis treated (second row)  $\text{Pt}_x\text{Ru}_{100-x}$  alloy NPs ( $x=31$ , left column); ( $x=49$ , middle column) and ( $x=75$ ; right column). Each model includes about 3500 atoms. Ru atoms are in green and Pt – in gray.

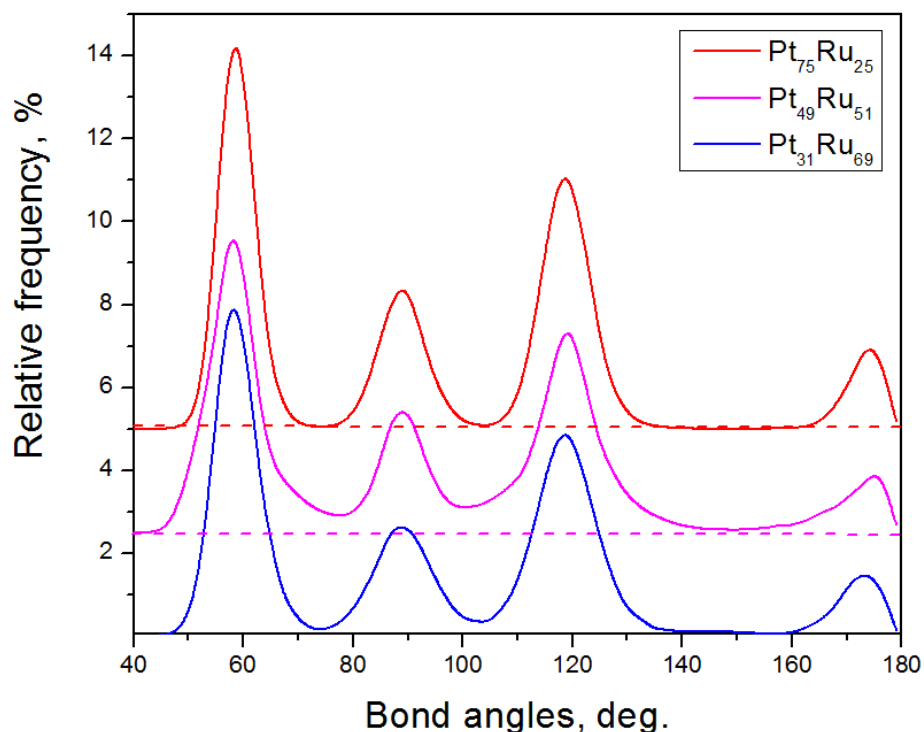




**Figure S6.** Distribution of Ru-Ru-Ru and Pt-Pt-Pt bond angles in as-synthesized  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31, 49$  and  $75$ ). Distributions of bond angles in pure Ru and pure Ru NPs, derived by independent studies, are also shown as benchmarks of the distribution of bond angles in NPs of entirely hcp- and fcc-type atomic structure, respectively. Data sets are shifted by a constant factor (marked with a horizontal broken line) for clarity. Note, bond angles in NPs of a fcc-type structure (pure Pt NPs) are clustered around 60, 90, 120 and 180 degs. and those in NPs of a hcp-type structure (pure Ru NPs) are clustered around 60, 90, 109, 120, 146 and 180 degs. As a result the distribution of bond angles in the latter appears broader, i.e. covers a wider range of angles, than that in the former. Data in the Figure indicate that Pt species in all as-synthesized  $\text{Pt}_x\text{Ru}_{100-x}$  alloy NPs ( $x=31, 49$  and  $75$ ) are fcc-type ordered locally. Ru species in as-synthesized  $\text{Pt}_{75}\text{Ru}_{25}$  alloy NPs are also fcc-type ordered locally. On the other hand, Ru species in as-synthesized  $\text{Pt}_{31}\text{Ru}_{69}$  and, to a certain extent, in as-synthesized  $\text{Pt}_{49}\text{Ru}_{51}$  NPs appear hcp-type ordered locally.

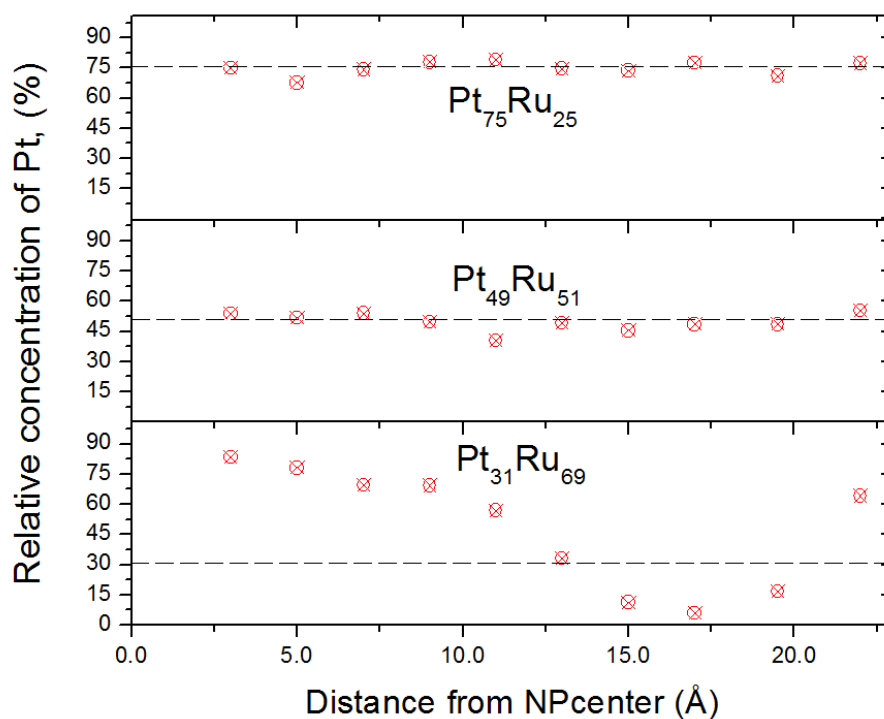


**Figure S7.** Distribution of Ru-Ru-Ru and Pt-Pt-Pt bond angles in post-synthesis treated  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31, 49$  and  $75$ ). Distributions of bond angles in pure Ru and pure Pt NPs, obtained by independent studies, are also shown as benchmarks of the distribution of bond angles in NPs of entirely hcp- and fcc-type atomic structure, respectively. Data sets are shifted by a constant factor (marked with a horizontal broken line) for clarity. Note, bond angles in NPs of entirely fcc-type structure (pure Pt NPs) are clustered around 60, 90, 120 and 180 degs. and those in NPs of entirely hcp-type structure (pure Ru NPs) - around 60, 90, 109, 120, 146 and 180 degs. As a result the distribution of bond angles in the latter appears broader, i.e. covers a wider range of angles, than that in the former. Data in the Figure indicate that Pt species in all post-synthesis treated  $\text{Pt}_x\text{Ru}_{100-x}$  alloy NPs ( $x=31, 49$  and  $75$ ) are fcc-type ordered locally. Ru species in post-synthesis treated  $\text{Pt}_{75}\text{Ru}_{25}$  alloy NPs are also fcc-type ordered locally. On the other hand, Ru species in  $\text{Pt}_{31}\text{Ru}_{69}$  and, to a certain extent, in post-synthesis treated  $\text{Pt}_{49}\text{Ru}_{51}$  alloy NPs appear hcp-type ordered locally.



**Figure S8.** Distribution of bond angles between all metallic species forming the top three layers in post-synthesis treated  $\text{Pt}_x\text{Ru}_{100-x}$  alloy NPs ( $x=31, 49$  and  $75$ ). Data sets are shifted

by a constant factor (marked with a horizontal broken line) for clarity. Data in the Figure indicate that metal species forming the top three layers in post-synthesis treated  $\text{Pt}_{31}\text{Ru}_{69}$  and  $\text{Pt}_{75}\text{Ru}_{25}$  NPs are fcc-like ordered locally, i.e. that near surface atomic layers in these NPs are largely stacked in a fcc-type (ABCABC-type) manner. On the other hand, metal species forming the top three layers in post-synthesis treated  $\text{Pt}_{49}\text{Ru}_{51}$  NPs appear hcp-like ordered locally indicating that near surface atomic layers in these NPs are largely stacked in a hcp-like (ABAB-type) manner. Results may not come as a big surprise since the surface both of  $\text{Pt}_{31}\text{Ru}_{69}$  and  $\text{Pt}_{75}\text{Ru}_{25}$  NPs is populated mostly ( $\sim 60$ - $75$  %) with Pt atoms (see Figure 3, second row and Figure S9, top and bottom panels) that tend to order fcc-like (see Figure S7) locally. The surface of  $\text{Pt}_{49}\text{Ru}_{51}$  NPs is uniformly (50:50) populated with Pt and Ru atoms and, obviously, retains the characteristic for the latter hcp-type structure to a great extent.



**Figure S9.** Distribution of Pt species (symbols in red) in post-synthesis treated  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31, 49, 75$ ) as a function of NP radius. Broken lines mark the average concentration of Pt species in the respective NPs as determined by ICP-AES experiments. Note, the distribution of Pt species across  $\text{Pt}_{49}\text{Ru}_{51}$  and  $\text{Pt}_{75}\text{Ru}_{25}$  NPs is rather uniform reflecting the homogenous alloy-type character of these NPs. The distribution of Pt species in  $\text{Pt}_{31}\text{Ru}_{69}$  NPs is rather uninform showing a clear clustering/segregation of Pt species at the center and surface of NPs leading to an “onion-like” chemical pattern as shown in Fig. 3 (second row, left).

**Table S5. Metal-to-metal bond lengths in as-synthesized  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31, 49$  and  $75$ )**

| Bond length (Å) | $\text{Pt}_{75}\text{Ru}_{25}$ | $\text{Pt}_{49}\text{Ru}_{51}$ | $\text{Pt}_{31}\text{Ru}_{69}$ |
|-----------------|--------------------------------|--------------------------------|--------------------------------|
| NP Surface      |                                |                                |                                |
| Pt-Pt           | 2.73                           | 2.77                           | 2.76                           |
| Pt-Ru           | 2.69                           | 2.70                           | 2.71                           |
| Ru-Ru           | 2.66                           | 2.68                           | 2.67                           |
| NP Core         |                                |                                |                                |
| Pt-Pt           | 2.75                           | 2.78                           | 2.80                           |
| Pt-Ru           | 2.71                           | 2.69                           | 2.72                           |
| Ru-Ru           | 2.67                           | 2.65                           | 2.65                           |

**Table S6. Metal-to-metal bond lengths in post-synthesis treated  $\text{Pt}_x\text{Ru}_{100-x}$  NPs ( $x=31, 49$  and  $75$ )**

| Bond length (Å) | $\text{Pt}_{75}\text{Ru}_{25}$ | $\text{Pt}_{49}\text{Ru}_{51}$ | $\text{Pt}_{31}\text{Ru}_{69}$ |
|-----------------|--------------------------------|--------------------------------|--------------------------------|
| NP Surface      |                                |                                |                                |
| Pt-Pt           | 2.66                           | 2.63                           | 2.70                           |
| Pt-Ru           | 2.60                           | 2.64                           | 2.68                           |

|         |      |      |      |
|---------|------|------|------|
| Ru-Ru   | 2.62 | 2.68 | 2.65 |
| NP Core |      |      |      |
| Pt-Pt   | 2.74 | 2.77 | 2.76 |
| Pt-Ru   | 2.70 | 2.67 | 2.69 |
| Ru-Ru   | 2.66 | 2.63 | 2.63 |

**Table S7. First atomic neighbor CNs in as-synthesized  $\text{Pt}_x\text{Ru}_{100-x}$  NPs (x=31, 49 and 75)**

| First CN   | $\text{Pt}_{75}\text{Ru}_{25}$ | $\text{Pt}_{49}\text{Ru}_{51}$ | $\text{Pt}_{31}\text{Ru}_{69}$ |
|------------|--------------------------------|--------------------------------|--------------------------------|
| NP Core    |                                |                                |                                |
| Pt-Pt      | 8.8                            | 5.7                            | 7.2                            |
| Pt-Ru      | 2.9                            | 6.0                            | 4.6                            |
| Ru-Pt      | 8.8                            | 5.6                            | 2.2                            |
| Ru-Ru      | 3.0                            | 6.1                            | 9.7                            |
| On average | 11.7                           | 11.7                           | 11.8                           |
| NP Surface |                                |                                |                                |
| Pt-Pt      | 5.4                            | 3.9                            | 1.9                            |
| Pt-Ru      | 1.9                            | 3.3                            | 4.9                            |
| Ru-Pt      | 5.3                            | 3.4                            | 1.4                            |
| Ru-Ru      | 2.1                            | 3.9                            | 5.7                            |
| On average | 7.3                            | 7.3                            | 7.2                            |

**Table S8. First atomic neighbor CNs in post-synthesis treated  $\text{Pt}_x\text{Ru}_{100-x}$  NPs (x=31, 49 and 75)**



| First CN   | Pt <sub>75</sub> Ru <sub>25</sub> | Pt <sub>49</sub> Ru <sub>51</sub> | Pt <sub>31</sub> Ru <sub>69</sub> |
|------------|-----------------------------------|-----------------------------------|-----------------------------------|
| NP Core    |                                   |                                   |                                   |
| Pt-Pt      | 8.9                               | 5.8                               | 7.0                               |
| Pt-Ru      | 2.9                               | 5.9                               | 4.5                               |
| Ru-Pt      | 8.8                               | 5.7                               | 1.9                               |
| Ru-Ru      | 3.0                               | 6.1                               | 9.7                               |
| On average | 11.7                              | 11.8                              | 11.6                              |
| NP Surface |                                   |                                   |                                   |
| Pt-Pt      | 5.3                               | 3.8                               | 4.2                               |
| Pt-Ru      | 1.9                               | 3.5                               | 3.0                               |
| Ru-Pt      | 5.2                               | 3.5                               | 2.0                               |
| Ru-Ru      | 2.2                               | 3.8                               | 5.2                               |
| On average | 7.3                               | 7.3                               | 7.2                               |

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