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Direct Observation of Carbon Nanostructure Growth at Liquid-solid Interfaces

Linfeng Fei,^{*a*} Tieyu Sun,^{*a*} Wei Lu,^{*a*} Xiaoqiang An,^{*b*} Zhuofeng Hu,^{*b*} Jimmy C. Yu,^{*b*} Renkui Zheng,^{*c*} Xiaomin Li,^{*c*} Helen L. W. Chan,^{*a*} and Yu Wang*^{*a*}

^a Department of Applied Physics and Material Research Center, The Hong Kong Polytechnic University, Hong Kong SAR, P.R. China E-mail: <u>Yu.Wang@polyu.edu.hk</u>

^b Department of Chemistry and Institute of Environment, Energy and Sustainability, The Chinese University of Hong Kong, Hong Kong SAR, P.R. China.

^c State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China

S1. Experimental methods

Synthesis of Pt_3Co Nanoparticles. Pt_3Co nanoparticles with an average diameter of ~9.5 nm were synthesized from the reduction of Pt^{4+} and Co^{2+} salts simultaneously with ethylene glycol at high temperature. Typically, 5.72 mg H₂PtCl₆ and 0.66 mg CoCl₂ were dissolved into 20 mL ethylene glycol (pH value was adjusted to 11 by adding NaOH) to form a homogeneous light-green solution. The solution was then transferred to a 30 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h. The black precipitates were then filtered and washed with deionized water, acetone and absolute alcohol alternatively to remove soluble species before drying at 70 °C in a vacuum oven overnight.

Transmission Electron Microscope (TEM) Observations. The *in situ* heating experiment described here was conducted on a Protochips AduroTM platform with heating E-Chip specimen support that provides atomic resolution at thermal ramp rates of up to 10^6 °C/s with highly accurate temperature control of specimen inside a TEM. The TEM sample was prepared for imaging by dispersing Pt₃Co nanoparticles onto a lacy carbon film supported by a ceramic membrane from a nanoparticle-ethanol suspension and was allowed to dry in air. TEM observation was conducted on a JEM 2100F field-emission transmission electron microscope operating at 200 kV, equipped with STEM and EDS. The sample was quickly heated to 350 °C and stayed at this temperature for ~10 minutes to remove any possible organic residuals before subsequent observations. During the observation, the image was recorded using a Gatan SC1000 ORIUSTM CCD with a short exposure time (0.1 s), and the electron beam was blanked whenever possible to minimize beam effects on the nanoparticles.

Density-functional Theory (DFT) Calculations. The relaxed progresses and calculations of self-consistent fields were all performed with Quantum ESPRESSO.¹ All structures have been relaxed with BFGS method with $1 \times 1 \times 1$ k-points. A unit cell with 4 layers of atoms in which the uppermost layer is imperfect to simulate the steps. The convergence threshold on total energy and forces is 10^{-5} and 10^{-3} (in a.u.), the kinetic energy cutoff for wavefunctions is 25 Ry, and the kinetic energy cutoff for charge density and potential is 200 Ry.The energy change in diffusion progress was calculated with nudged elastic band method (NEB). The crystal plane index of the surface was (111), and the structure was the same as that of Pt₃Co. The lower two layers were fixed during the process to simulate a bulk crystal, and only the top two

layers of atoms were allowed to travel to simulate the surface reconstruction of the steps and the attachment of the carbon atom.





Figure S1. XRD profile of as-synthesized Pt₃Co nanoparticles.

Discussion:

The crystal structure of the as-synthesized nanoparticles was examined by means of X-ray diffraction (XRD). The as-measured XRD pattern was shown in **Figure S1**, with a bulk Pt₃Co crystal (cubic, JCPDS card No.: 29-0499, space group: $Pm\bar{3}m(221)$) attached as a reference. It can be seen that pure Pt particles reached diffraction peaks at 2θ of 39.6, 46.3 and 67.4 with d values of 2.26, 1.96 and 1.39 Å (corresponding to (111), (200), and (220) facets of Pt), respectively. However, diffraction peaks from Pt₃Co particles as shown in Figure S1 were found to have shifted in the XRD pattern towards the high degree angle region whereas diffraction peaks at 2θ of 40.5, 47.1 and 68.8 with d values of 2.22, 1.92 and 1.36 Å were assigned to Pt₃Co. Apparently, the lattice of Pt₃Co is smaller than that of Pt particles. This result could be attributed to the substitution of Pt with smaller Co atoms. The full width at half maximum (FWHM) of the diffraction peak of Pt₃Co at 40.5 was found to be 0.835 degree, thus, the average diameter of the Pt₃Co particle was found to be approximately 10.0 nm based on Scherrer Equation. Using similar methods, the peak at 47.1 was 9.58 nm, and the peak at 68.8 was 9.35 nm. The average diameter of the as-synthesized nanoparticles was estimated to be ~9.5 nm.

S3. Transmission electron microscopy (TEM) characterizations of Pt₃Co nanoparticles



Figure S2. TEM characterizations of as-synthesized Pt_3Co nanoparticles. (a) Brightfield TEM images and (b) HAADF-STEM image of Pt_3Co nanoparticle clusters. (c) HRTEM image and (d) EDS elemental mapping of a small number of nanoparticles.

Discussion:

The bright-field TEM image (**Figure S2a**) and the high angle annular dark-field (HAADF) STEM image (**Figure S2b**) show that most of the as-synthesized Pt₃Co nanoparticles are uniform in size and faceted in shape. An average size distribution of ~10 nm was identified, which is consistent with our XRD analysis (**Part S2**). The HRTEM image of the representative nanoparticles is shown in **Figure S2c**, revealing a well-crystallized nature. Lattice fringes with a periodic lattice spacing of 0.22₃ nm corresponding to the Pt₃Co (111) plane are clearly visible and dominant among repeated particles. The dominance of the exposed (111) planes is in accordance with earlier results on nanosized metal particles.² Additionally, EDS elemental mapping (**Figure S2d**) suggests a homogenous distribution of Pt and Co elements with a rough atomic ratio of 3.

S4. Temperature-dependent evolution on morphology and crystallography of Pt₃Co nanoclusters



Figure S3. Image sequences showing typical dynamics during heating of Pt_3Co nanoparticles. (**a-f**) illustrate the evaporation of organic residuals, and the coalescing and macroscopic melting of Pt_3Co nanocrystal agglomeration. The scale bar of (**a**) also applies to (**b-f**). (**g-k**) represent the corresponding selected-area electron diffraction (SAED) patterns upon image area at chosen temperatures. The scale bar of **g** also applies to (**h-k**).

Discussion:

A cluster of Pt_3Co nanoparticles was chosen for examining the morphology transformation induced by increasing temperature in the present study. The following intervals are derived from the observed changes as the temperature increases.

I. Evaporation of organic residuals (25 $^\circ C$ – 350 $^\circ C).$

To completely remove the organic residuals, i.e. to ensure a "clean" reaction environment for the following catalytic reaction, the sample was quickly heated to 350 °C and was kept at this temperature for about 10 minutes. In comparison with the image recorded at 25 °C (**Figure S3a**), it is rather obvious that the width of the agglomeration decreased when the temperature reached 350 °C while the edges of the nanoparticles became more visible (**Figure S3b**). These phenomena can be attributed to the vaporization of organic residuals between crystallites and the rearrangement of Pt₃Co nanoparticles located on the first layer adjacent to the supporting carbon film. Another interesting finding is that some organic passivating surface layers (~1 nm) could be identified through phase contrast imaging in **Figure S3a** (as indicated by black arrows) yet these layers all vanished in **Figure S3b**. This observation should verify the complete removal of organic residuals. Under such clean reaction environment, the configuration of the SAED patterns (**Figure S3g & Figure S3h**) remained mostly unchanged apart from some minor contrast enhancement, which can both be well indexed to cubic Pt₃Co and amorphous carbon as shown.

II. Coalescence of neighboring crystals *via* oriented attachment (350 °C – 550 °C). It should be noted that patches of dark contrast (as indicated by white dashed ovals) could be found in **Figure S3b**. These patterns, known as Moiré interference patterns,^{3,4} occur when two lattices overlap with a rotational mis-orientation. Several groups of Moiré fringes appeared abruptly between the adjacent crystals when the sample was heated to 350 °C as shown in **Figure S3b**. However, these fringes disappeared upon further heating to 450 °C (**Figure S3c**). It can also been seen that the contrast of the same area where the Moiré fringes used to appear at 350 °C in **Figure S3c** (as indicated by a white dashed oval) have become increasingly uniform, implying that the nanoparticles underwent a neighboring coalescing process *via* oriented attachment mechanism.^{5,6}

III. Melting of Pt₃Co nanoclusters (550 °C – 850 °C).

As shown in **Figure S3d**, when the sample was heated to 550 °C, the corresponding SAED pattern (**Figure S3i**) show three halo rings. An analysis of the halo rings

suggests that the two outer halo rings were due to the amorphous carbon film, whereas the inner one was resulted from the liquid Pt₃Co compound.⁷ Meanwhile, the cubic Pt₃Co crystals represented by bright Debye-Scherrer rings continue to be visible, suggesting initial surface melting could have occurred at this stage. In the subsequent sintering process, the temperature was increased very slowly. When the temperature reached 750 °C as shown in **Figure S3j**, the series of Debye-Scherrer rings became much weaker, leaving some bright spots which indicate the occurrence of further melting towards the core-part within the crystals. As shown in **Figure S3f** and Figure **S3k**, the Debye-Scherrer rings vanish completely at 850 °C while the contrast of the halo ring from liquid Pt₃Co has become rather dominant in the SAED pattern, implying the nanoclusters are fully melted at this point. Interestingly, another halo ring has become so visible that it could be clearly indexed to the graphite (002) planes. During the whole heating process, a continuous volume contraction (from **Figure S3a** to **S3f**) was observed originated from the evaporation of organic residuals, coalescence of adjacent crystals, melting of particles, and gradual loss of interspaces.

S5. Discussion on the decreasing eutectic temperature of Pt₃Co alloy nanoparticles



Figure S4. Normalized eutectic temperature T/T_0 versus inverse radius of Pt₃Co alloy nanoparticles.

Discussion:

The as-measured initial surface melting temperature (~550 °C) of as-synthesized Pt_3Co nanoparticles is much lower than bulk eutectic temperature (~750 °C). However, this is not surprising for Wang *et al.* have reported the surface melting of 8 nm pure Pt nanoparticles at ~600 °C.⁸ Although research on suppression of eutectic temperature by alloying in In-Sn,⁹ Pb-Bi,¹⁰ and Ag-Pb⁷ binary systems have been conducted, *it is the first time that such treatment was introduced to a Pt-Co system in the present study.*

Buffat and Borel developed a thermodynamic model to describe the melting behavior of small particles in pure substances,¹¹ which was further extended to work on the eutectic transition of a binary alloy particle.^{7,12} In this model, the depression of melting temperature of small particles is derived from the phase equilibrium condition between the solid and liquid particles, leading to the following equation:

$$\frac{T}{T_0} = 1 - \frac{2}{r^{\rm S} L \rho^{\rm S}} [\gamma^{\rm S} - \gamma^{\rm L} (\frac{\rho^{\rm S}}{\rho^{\rm L}})^{2/3}]$$

where T and T_0 are the eutectic temperature of small particles and of bulk sample, respectively; γ is the surface tension (the superscript "S" refers to solid phase, and "L"

refers to liquid phase.); r corresponds to the particle radius; ρ is the mass density; and L is the latent heat of the eutectic transition. <u>It is clear that there is a linear</u> *relationship between the eutectic temperature and the inverse radius of the particle.* The density of liquid and solid phases can be calculated as:

$$\rho = (w_{\rm Pt}/\rho_{\rm Pt} + w_{\rm Co}/\rho_{\rm Co})^{-1}$$

For Pt₃Co alloy, the weight fractions are: $w_{Pt} = 0.9085$, $w_{Co} = 0.0915$, so we can calculate the densities of the mixed phase: $\rho^{S} = 19.02$ and $\rho^{L} = 17.31$, and the unit is 10^{3} kg/m³. As the concentration of Co is low, the surface tension of the liquid and solid phases are estimated with pure Pt, i.e. $\gamma^{S} = 2.06$ J/m², and $\gamma^{L} = 1.75$ J/m².

The latent heat L can be calculated with this formula:

$$L = l_{0,\text{Pt}} w_{\text{Pt}} + l_{0,\text{Co}} w_{\text{Co}} + \Delta H_{\text{mix}}$$

The former two values are the latent heat of the two contents ($l_{0,Pt} = 113.7 \times 10^3$ J/kg and $l_{0,Co} = 274.9 \times 10^3$ J/kg), and ΔH_{mix} is the mixing enthalpy at the composition in experiments.

The mixing enthalpy of Co-Pt alloy is taken from ref. 13, and is calculated with spline interpolation method, as $\Delta H_{\text{mix}} = -9290 \text{ J/mol}$, or $-14.42 \times 10^3 \text{ J/kg}$. So $L = 114.0 \times 10^3 \text{ J/kg}$.

With the known physical quantities, we now have:

$$\frac{T}{T_0} = 1 - \frac{1.79 \times 10^{-10}}{r^{\rm S}}$$

Therefore we plot normalized eutectic temperature T/T_0 as a function of the reciprocal of the particle radius (1/nm), and the relationship is disclosed as shown in **Figure S4** with a blue line. In comparison with the experimental result (the red line), it is obvious that the experimental result falls slightly below the calculated one. This is expected since the calculated result was obtained from the equilibrium state where the driving force of the eutectic transition ceases;⁷ namely, the calculated line indeed acts as an upper limit of the practical eutectic measurement. Based on these discussions, our experimental observations are in good accordance with the theoretical results.

S6. Discussion on the potential application of our method

In our study, the amorphous carbon film was pre-coated on the heating E-chip by vacuum evaporation technique to realize the observation of Pt_3Co-C liquid-solid process. In fact, the carbon here can be changed to other amorphous content (such as Si *et al.*) through the same deposition technique, and the Pt_3Co nanoparticles can be replaced by other semiconductor/metallic nanostructures to visualize purposed dynamic liquid-solid processes.

In case of monitoring reactions between crystalline materials with liquid intermediaries, inert polymeric supports can be chosen (such as PVF) so that two (or more) different materials in the form of nanoparticles/nanowires/nanotubes can be mixed and deposited on the polymer support for *in situ* heating and observation. In association with other TEM techniques such as HAADF-STEM (high angle annular dark-field scanning TEM), EDS (energy dispersive spectrum) elemental mapping and three-dimensional tomography, different nanoparticles or even different atoms can be identified in a dynamic process at high resolution.

In summary, our as-developed method is all set to be applied in other liquid-solid processes with atomic precision and more interesting results can be expected from further works.

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