What could be the low-temperature limit of atomic layer deposition of platinum using $MeCpPtMe_3$ and oxygen?

Hao Van Bui,[a,*] Anh Phan Nguyen,[a] Manh Duc Dang,[a] Truong Duc Dinh,[a] Patricia J. Kooyman,[b] J.Ruud van Ommen[c]

[a.] Faculty of Materials Science and Engineering, Phenikaa University, Yen Nghia, Ha Dong District, Hanoi 12116, Vietnam.

[b.] Catalysis Institute, Department of Chemical Engineering, University of Cape Town, 7701, South Africa.

[c.] Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, Delft, 2629 HZ, The Netherlands.

[*] Corresponding author: hao.buivan@phenikaa-uni.edu.vn

SUPPLEMENTARY INFORMATION

1. Experimental procedures

1.1. ALD of Pt on TiO_2 nanoparticles

The deposition of Pt on TiO_2 nanoparticles was conducted using a home-built fluidized bed reactor (FBR) operating at atmospheric pressure, as described elsewhere.[1,2] Briefly, the system consists of a glass column (internal diameter of 26 mm and height of 500 mm), which is placed on top of a single motor Paja PTL 40/40-24 vertical vibration table to assist the fluidization.[3] Trimethyl(methylcyclopentadienyl)platinum(IV) ($MeCpPtMe_3$, >99% purity, Strem Chemicals) was used as the Pt precursor, which was contained in a stainless steel bubbler and maintained at 70 °C. The stainless steel tubes connecting the bubbler and the reactor were maintained at 80 °C to avoid precursor condensation. Degussa P25 TiO_2 (99.5% purity, Evonik) with an average particle size of 21 nm and surface area of 54 $m^2\ g^{-1}$ was used as the substrate. Synthetic air (20 wt.% oxygen) was used as the oxidizer and nitrogen (99.999 vol.%) was used as the carrier gas. For each experiment, 1.5 g of powder was used. The powder was fluidized by an N_2 gas flow of 0.5 L min^{-1}. An ALD cycle consisted of alternating exposures of the TiO_2 powder to $MeCpPtMe_3$ (5 min), followed by an N_2 purging step (5 min), O_2 (5 min), and finally an N_2 purging of 10 min. For the deposition at room temperature, the O_2 exposure time was increased to 30 min.

To investigate the thermal stability of the room-temperature deposited Pt/TiO_2, the materials were annealed in ambient air at 400 °C for 3 and 6 h, which was carried out using a horizontal quartz-tube furnace. This annealing temperature was clearly higher, and the annealing time was considerably longer than the temperature and the deposition time for the Pt ALD process at 250 °C.

1.2. Materials characterization and analysis

Transmission electron microscopy (TEM) images of the samples were taken using a JEOL JEM1400 transmission electron microscope operated at 120 kV. The Pt sub-nanometer clusters deposited at room temperature were investiagated using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) on a JEOL JEM-ARM200F double Cs-corrected TEM equipped with a FEG, a STEM unit, and an HAADF detector, operated at 200 kV.

The number-based particle size distributions of the Pt NPs were obtained by measuring the projected diameter of the NPs manually using Gatan Digital Micrograph software (Version 2.31.734.0).

X-ray photoelectron spectroscopy (XPS) was employed to investigate the elemental composition and chemical state of the deposited materials. The measurements were performed using a PHI 5000 VersaProbe ll XPS system equipped with a

monochromatic Al X-ray source. Survey scans were acquired in the binding energy range of 0 – 1350 eV with steps of 1.0 eV using the CEA mode and pass energy of 100 eV. The high-resolution spectra of the core levels of each element were acquired with fine steps of 0.1 eV and pass energy of 50 eV.

2. Results

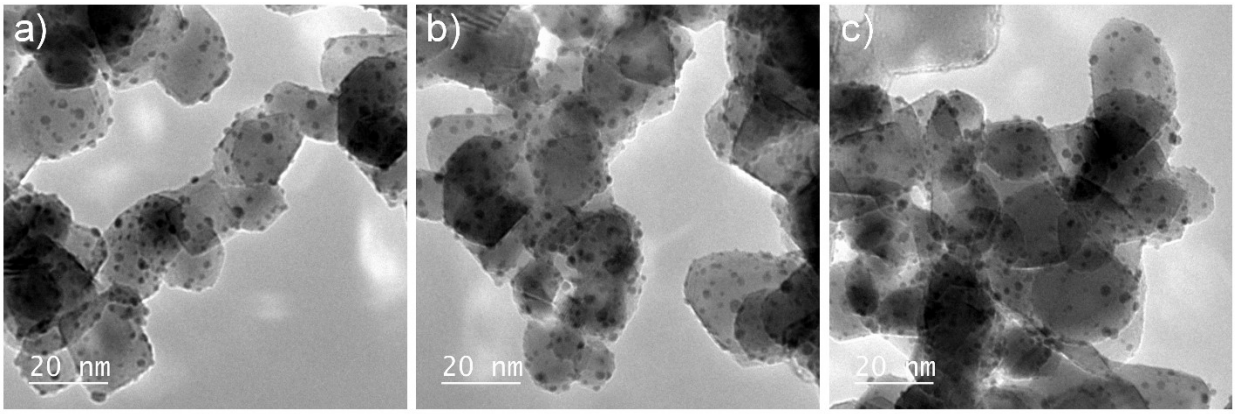

Fig. S1. TEM images of Pt NPs deposited on P25 TiO_2 surface at 250 °C after 5 ALD cycles taken at different locations.

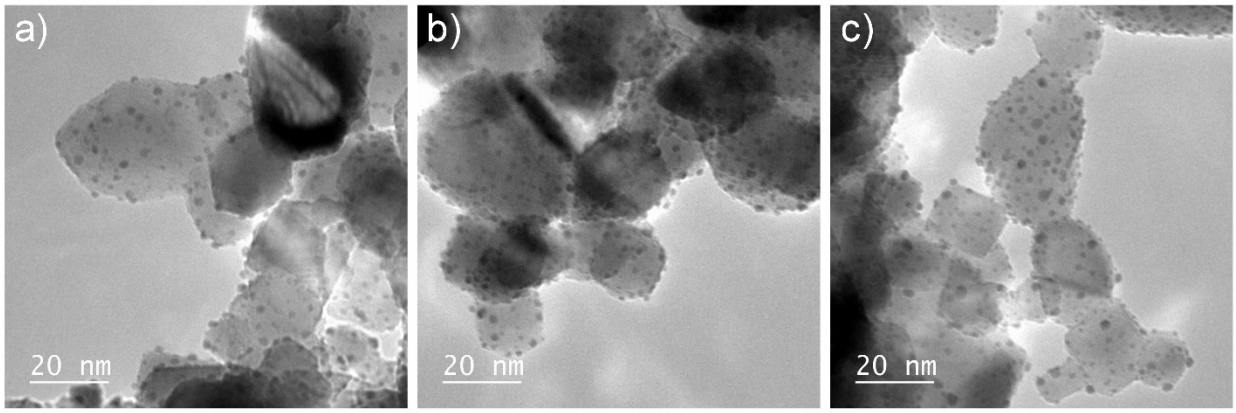

Fig. S2. TEM images of Pt NPs deposited on P25 TiO_2 surface at 150 °C after 5 cycles taken at different locations.

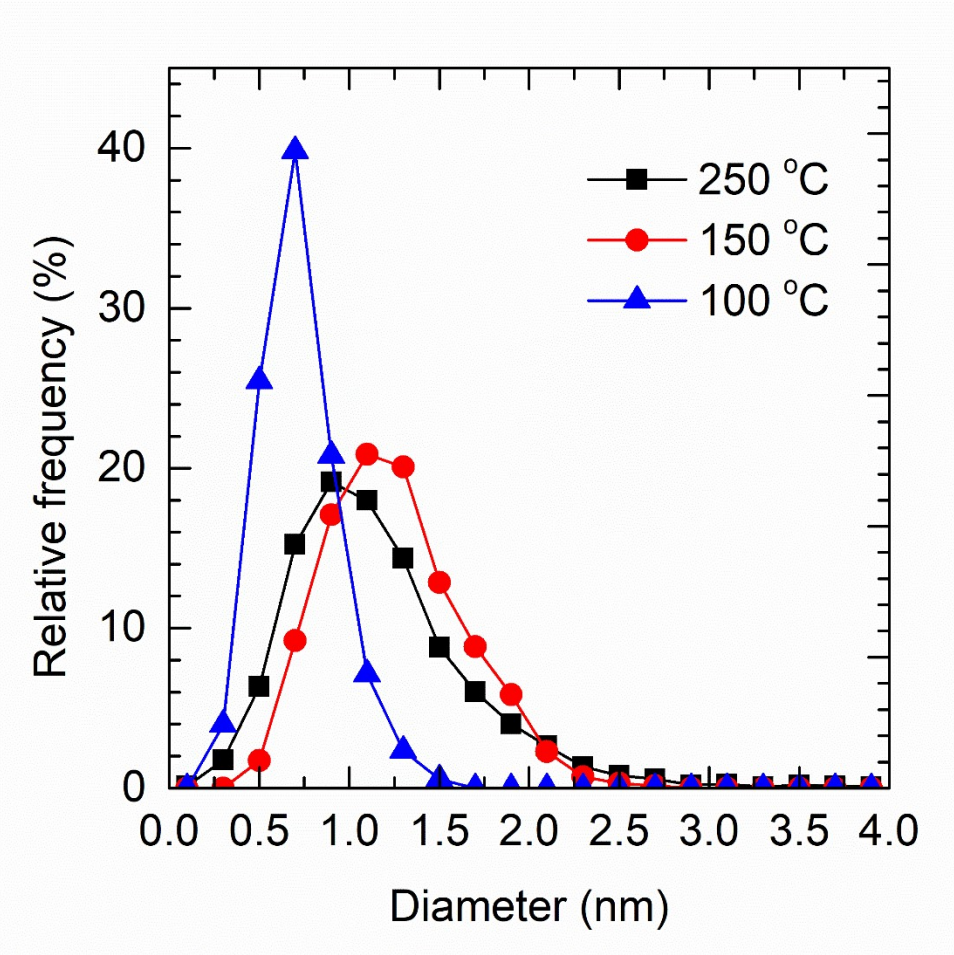

Fig. S3. Particle size distributions of Pt NPs deposited at 250 °C (■), 150 °C (●) and 100 °C (□) after 5 cycles. The distributions are obtained by analysing from 800 - 1500 particles on different TEM images. The bin size of the histograms is 0.2 nm.

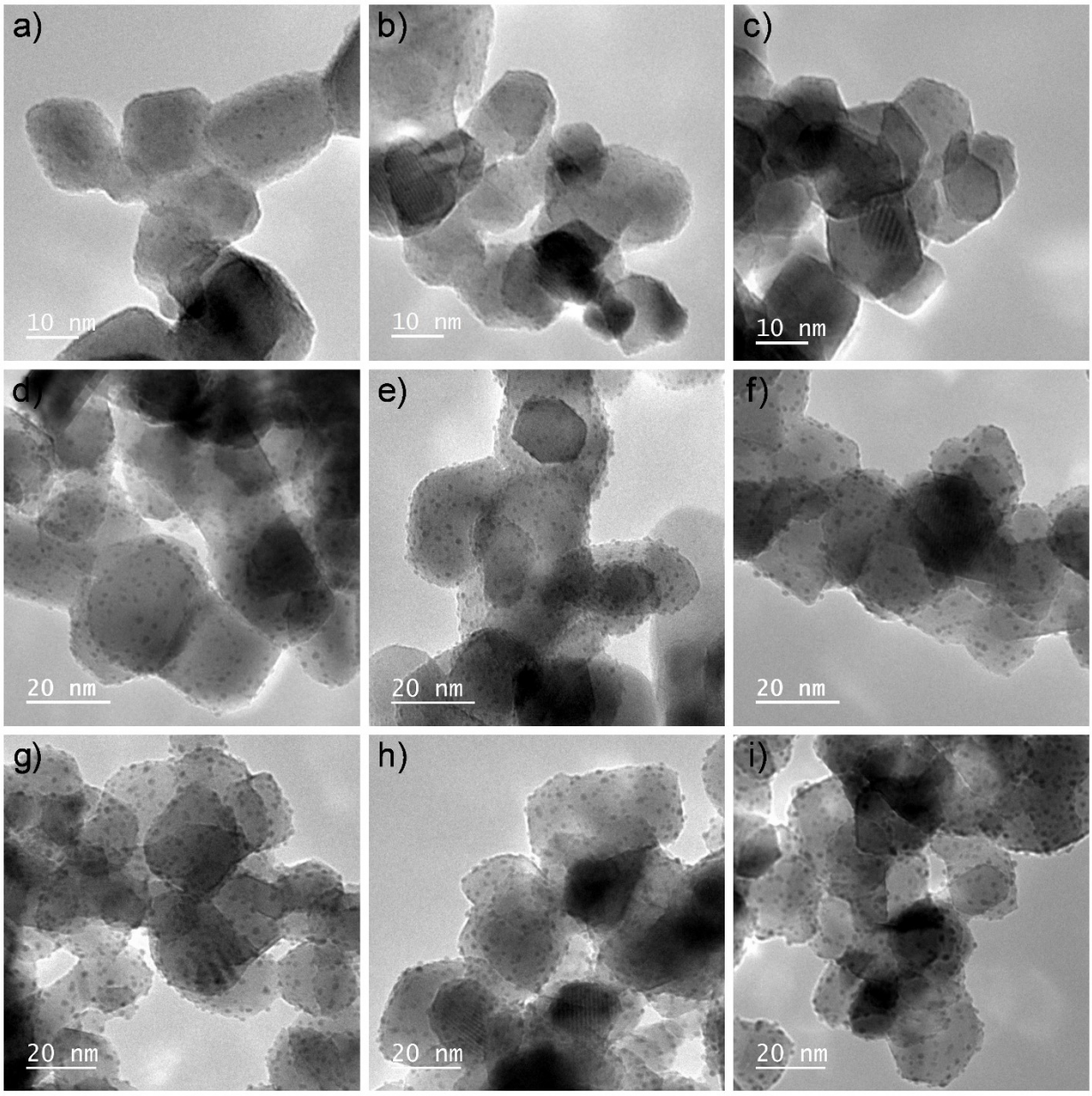

Fig. S4. TEM images taken at different locations of Pt NPs deposited on P25 TiO_2 surface at 100 °C after 1 cycle (a – c), 5 cycles (d – f), and 10 cycles (g – i).

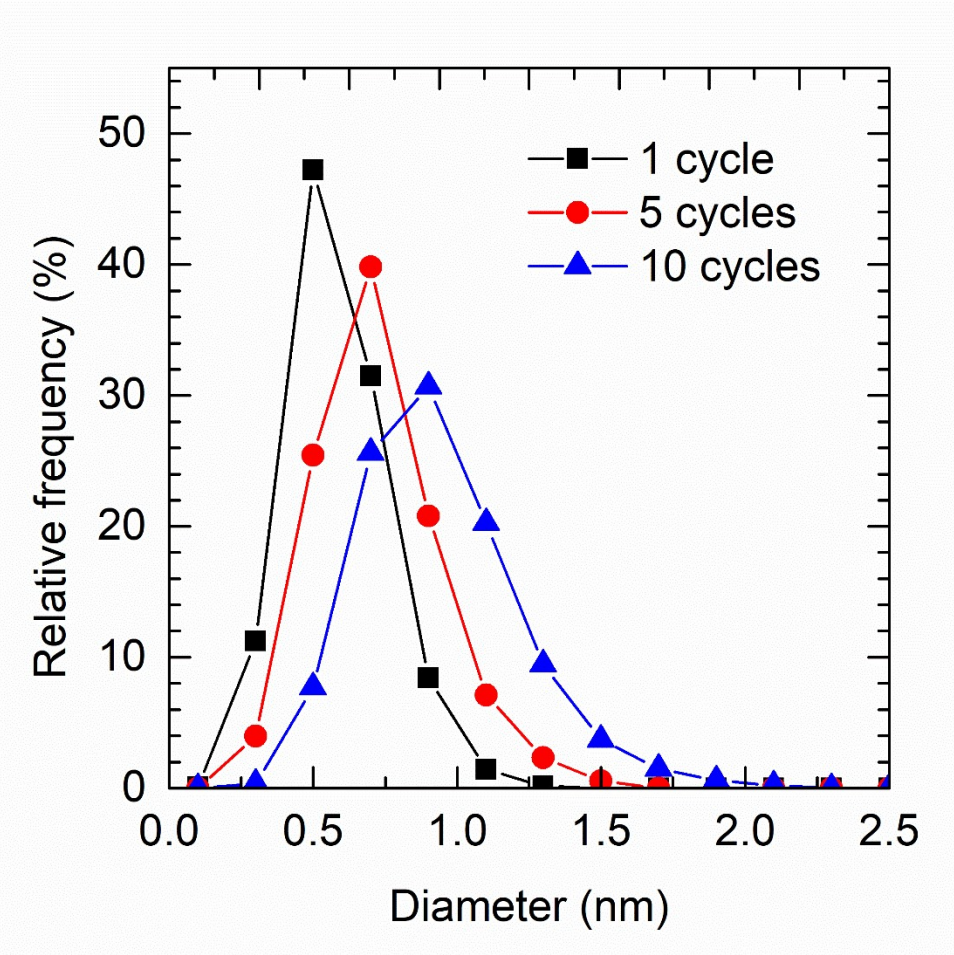

Fig. S5. Particle size distributions of Pt NPs deposited at 100 °C after 1 ALD cycle (■), 5 ALD cycles (●), and 10 ALD cycles (□). The distributions are obtained by analysing from 800 - 1300 particles on different TEM images. The bin size of the histograms is 0.2 nm.

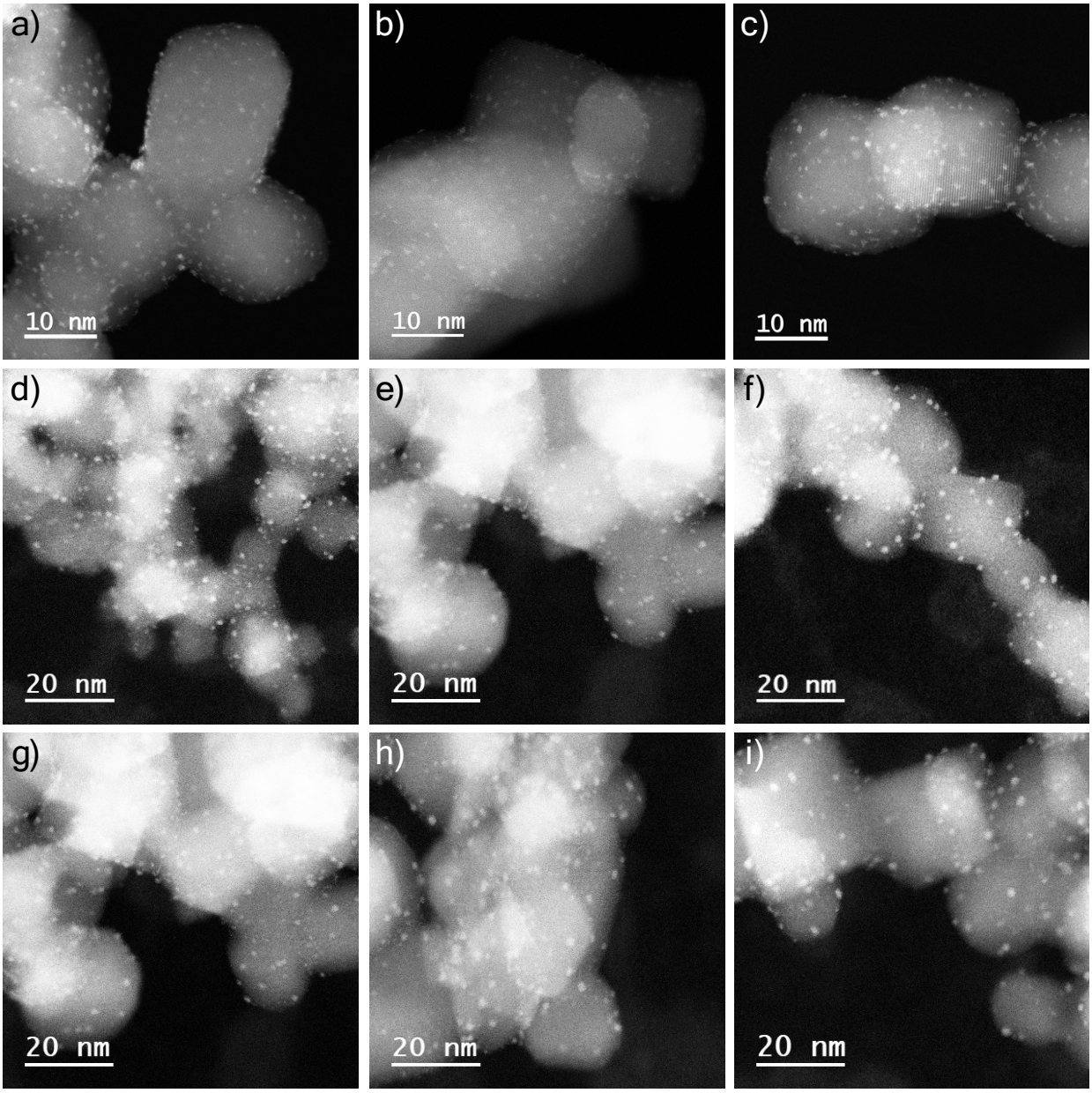

Fig. S6. HAADF-STEM images taken at different locations of Pt NPs deposited on P25 TiO_2 surface at room temperature (i.e., 25 °C) after 5 ALD cycles (a – c), followed by the annealing in ambient air at 400 °C for 3 h (d – f) and 6 h (g – i). The images in (a – c) reveal the irregular shape of the deposited Pt s-NCs due to their ultra-small size. This contrasts to the more regular shape (i.e., spherical shape) of the Pt NPs obtained after the annealing indicated in (d – i) and the Pt NPs deposited at higher temperature shown in Fig. S4.

Fig. S7 shows the XPS spectra of the Pt/TiO_2 deposited at room temperature after 1, 5 and 10 cycles. The survey spectra in Fig. S7a show the O *1s*, Ti *2p*, C *1s*, Pt *4d* and Pt *4f* core levels. The C *1s* spectra are used to calibrate the peak positions by setting this peak to a binding energy of 284.8 eV, as indicated in Fig. R1b. The Pt *4f* spectra are shown in Fig. R1c. For the Pt/TiO_2 obtained after 1 ALD cycle, the intensity of the peaks is very low, which can be explained by the low Pt loading. After 5 and 10 ALD cycles, the two Pt *4f* peaks, i.e., $4f_{5/2}$ and $4f_{7/2}$, are observed at the binding energies of 74.7 and 71.4 eV, respectively. These peaks represent the metallic state of Pt, which is strong evidence of the successful deposition of Pt at room temperature. In addition, a small shift (~0.3 eV) of the peaks is observed, which could arise from the enhanced metal-support interactions as observed by Khalily *et al*.[4] and Li *et al*.[5]

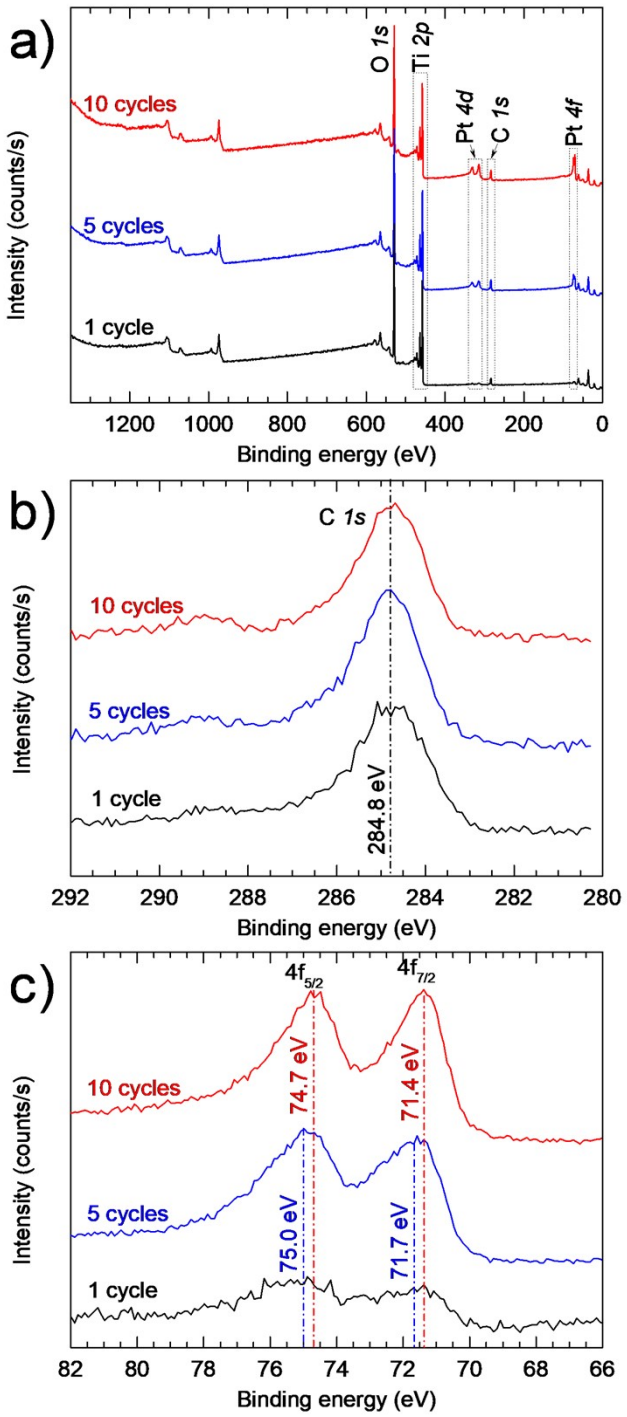

Fig. S7. XPS spectra of Pt/TiO_2 deposited at room temperature for 1, 5 and 10 cycles: (a) survey scan, (b) C *1s* spectra with the peak at 284.8 eV as the reference for calibration to eliminate charging effects, and (c) the Pt *4f* core-level spectra.

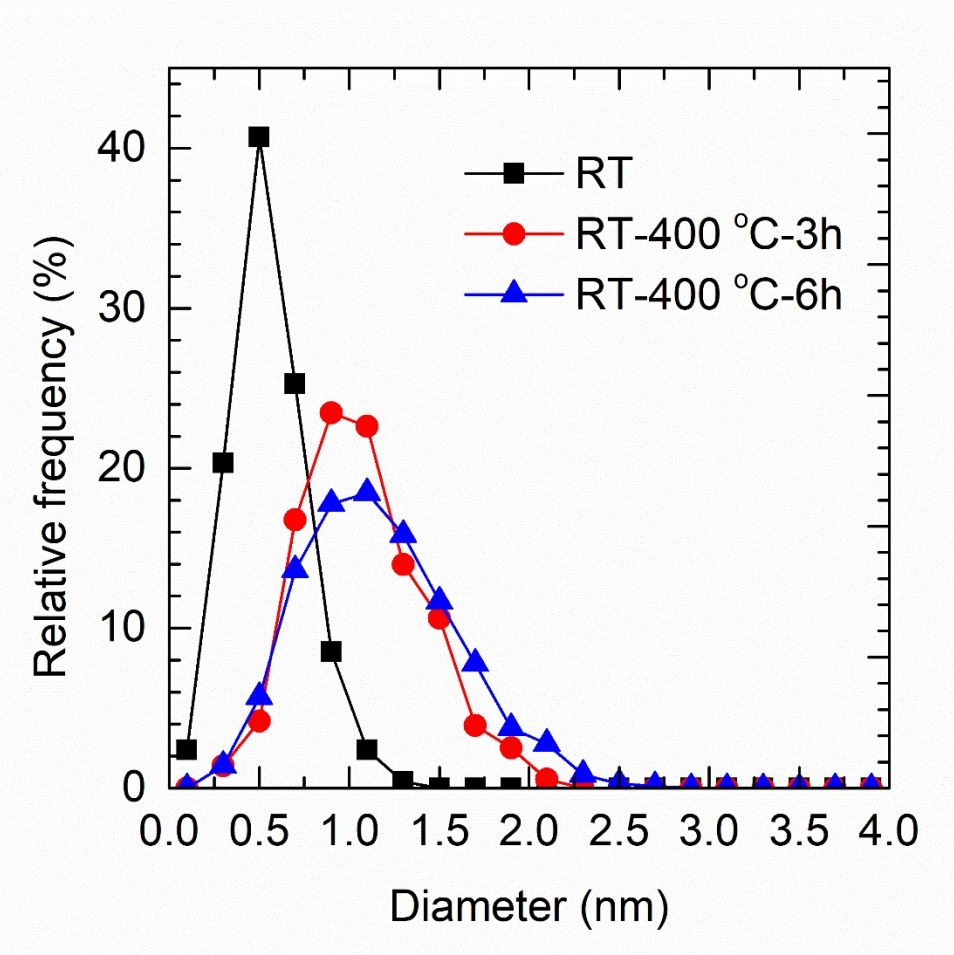

Fig. S8. Particle size distributions of Pt NPs deposited at room temperature after 5 ALD cycles (■), followed by post treatment in ambient air at 400 °C for 3 h (●) and 6 h (□). The distributions are obtained by analysing from 400 - 700 particles on different TEM images. The bin size of the histograms is 0.2 nm.

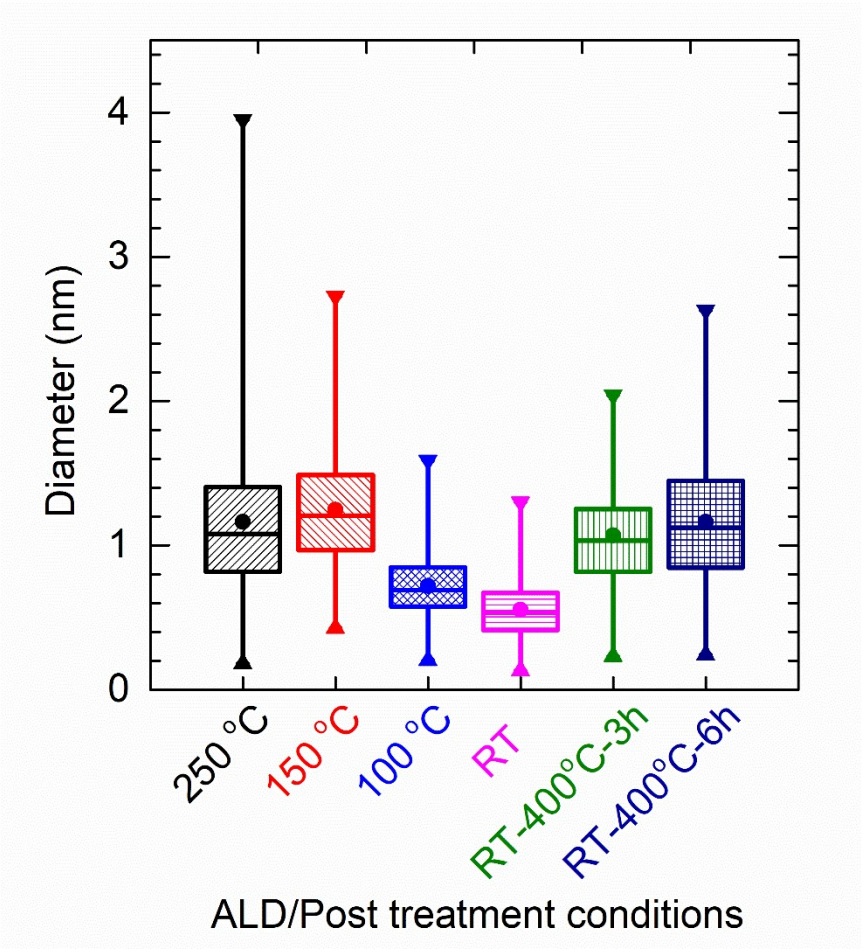

Fig. S9. Box and whisker plot describing the PSDs of Pt NPs obtained after 5 ALD cycles under various deposition and annealing conditions. The boxes indicate the 25th and 75th percentiles of the particles, the whiskers indicate the spans from the minimum (□) to the maximum (❑) particle size, and the filled circles (●) indicate the average size.

References

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