Electronic Supplementary Information

Isomerizations of a Pt_4 Cluster Revealed by Spatiotemporal Microscopic Analysis

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Experimental

1. Material

Graphene nanoplatelets (2.5 g) purchased from Aldrich were washed with HCl aqueous solution (300 mL, 3 mol L^{-1}) and ultrapure water (MeOH) to remove the metallic impurities. All the solvent used in this study were purchased from Kanto Chemical Co., Inc.

2. Preparation of Pt clusters on graphene nanoplatelets

Platinum clusters on graphene nanoplatelets were prepared by a vacuum deposition method using a pulsed arc plasma source (Advance Riko, APS-1) equipped with a platinum cylinder target. Graphene nanoplates dispersed in methanol were cast on commercially available thin holey carbon film coated Cu grid for TEM observation. The arc pulse with a period of 0.2 ms and current amplitude of 2 kA was generated with a frequency of 1 Hz. One pulse of the plasma from the cathode was directly irradiated to the graphene nanoplatelets modified on a TEM grid. The sample preparations in present study were performed using the following parameters: C = 360, 720 or 1080 μF and V = 100 V where C is electric capacity and V is applied discharge voltage.

3. Observation of Pt clusters

Time-lapse sequences of HAADF-STEM (High-Angle Annular-Dark-Field Scanning Transmission Electron Microscopy) images were acquired every 0.2 seconds at room temperature using a 80 kV

cold-FEG TEM (JEOL, JEM-ARM200F) with spherical aberration corrected probe (CEOS, ASCOR) at a convergence angle of 31.8 mrad. The inner and outer collection angles used in recording the HAADF images were 68 and 280 mrad, respectively. In order to equalize the electron dose, the probe current was fixed at 26 pA while the beam scanned across a field of view (3.5 × 3.5 nm). The pixel size and the pixel time are 30 pixel/nm and 8μs/pixel, respectively.

4. Image data processing

The time-lapse STEM images were analyzed on ImageJ software[1]. Four peaks in every images were obtained by "Find Maxima" function. The X-Y coordinates were calculated from the pixel address using the calibration (1 nm = 30 pixels).

Based on the X-Y coordinates, spatiotemporal and statistical analyses were carried out. The square radius of gyration (S^2) of each Pt_4 cluster was calculated by the following equation,

$$S^2 = \frac{S_1^2 + S_2^2 + S_3^2 + S_4^2}{4}$$

where S_i is the distance from the center of mass to each atom(i).

5. Computational analysis

To search all possible structures of Pt_4 in a first-principles manner, global optimizations were carried out employing the basin-hopping algorithm[2]. The neutal, monoanionic, and monocationic species of Pt_4 were globally optimized with 300 local optimizations, respectively. In each step, spin-polarized density functional theory (DFT) calculations were performed with the pseudopotential of Pt.pz-nd-rrkjus.UPF. The cutoff energy of plane waves was set to be 25 Ry and the Gauss-type smearing of 0.01 Ry was employed. Only the Γ point was sampled with the supercell of a hexagonal lattice with a = 14.8 Å and c = 12.0 Å. All the DFT calculations were performed using the Quantum ESPRESSO program package[3], in which the basin-hopping algorithm was implemented by our in-house code.

[1] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2012.

[2] D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A*, 1997, **101**, 5111–5116.

[3] P. Giannozzi *et al.*, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.

Results

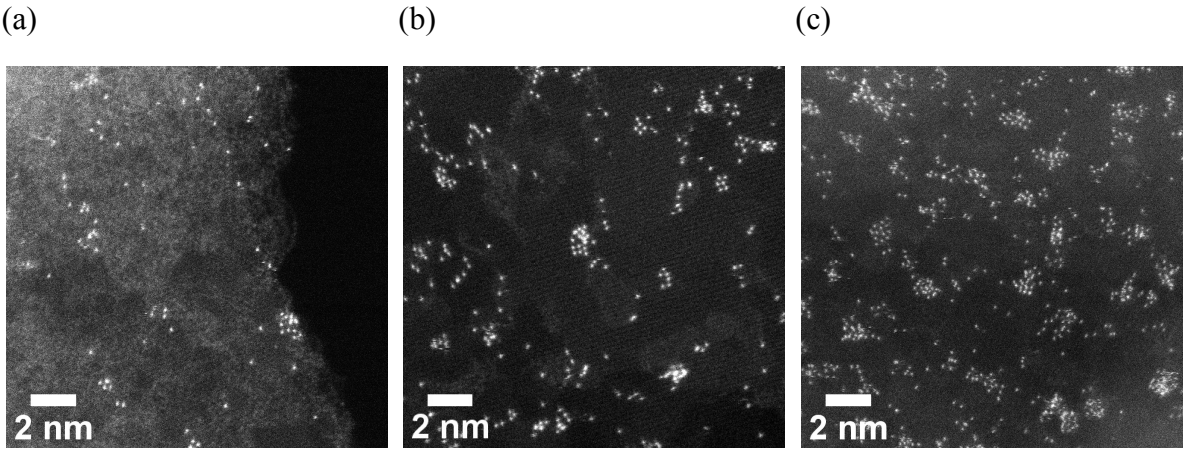

Fig. S1 HAADF-STEM images (80 kV) of platinum clusters and atoms on graphene sheet prepared by arc-plasma deposition method operated with (a) 360 μF, (b) 720 μF and (c) 1080 μF condenser capacitance.

*Use Adobe Acrobat or Acrobat Reader to watch the video.

Fig. S2 A real-time video clips of the fluctuation of a Pt_4 cluster under the HAADF-STEM observation. (a) A typical 2-dimensional cluster analyzed in this study. (b) Another Pt_4 cluster under the typical fluctuation behavior. (c) A cluster with preferential upright stacking of atoms. It is considered that this cluster is locating at a point defect of the graphene support because two stacking atoms are pinned on a specific position of the support.

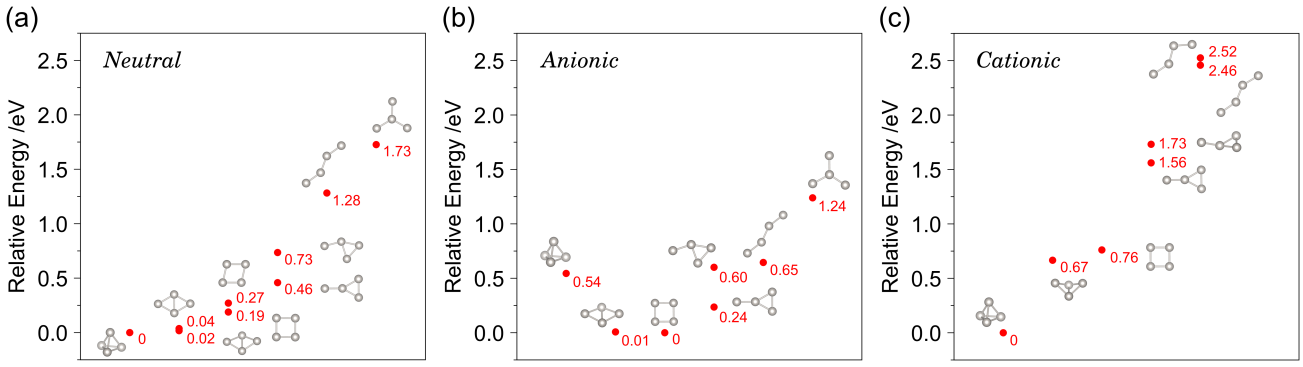

Fig. S3 The stable structures of Pt_4 obtained by DFT-based global optimizations for (a) neutral (b) monoanionic, and (c) monocationic species, respectively.

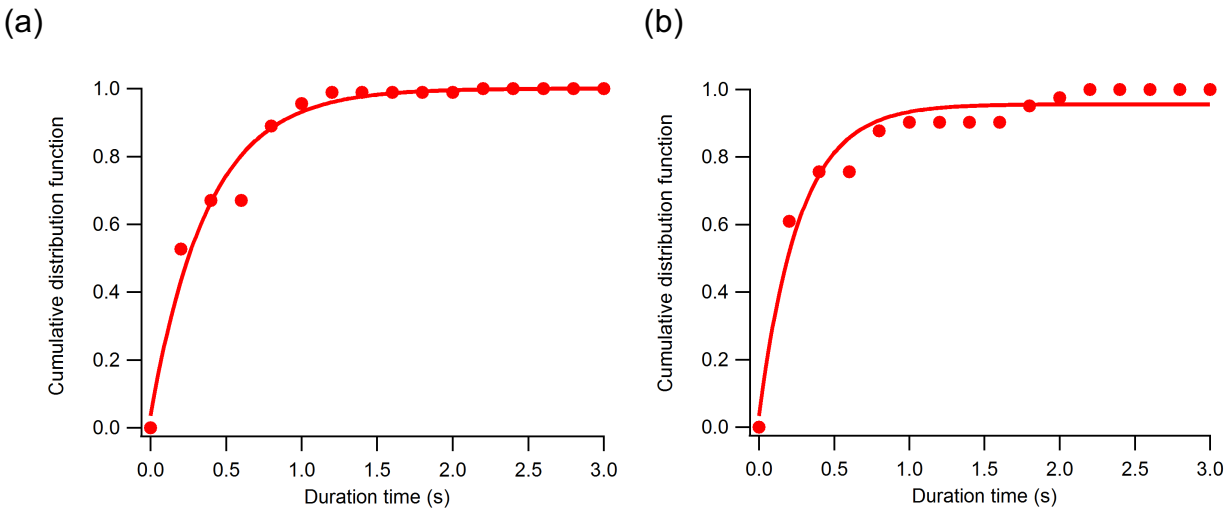

Fig. S4 The cumulative probability distribution of the lifetime similar to that of Fig. 4 in the main text. The data (a) and (b) are based on the clusters shown in Figs. S2b and S2c.