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Supporting Information

Tuning the High-Temperature Wetting Behavior of Metals toward Ultrafine Nanoparticles

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Supporting Information

Methods

Preparation of CNF with Al_2O_3 coating.

8% by mass solution of polyacrylonitrile (PAN) (Sigma Aldrich) in dimethylformamide (DMF) was electrospun at a voltage of 10 kV, a spinning distance of 15 cm, and a feeding rate of 1 mL/hour. The as-spinned nanofibers were collected by a rotation drum at a speed of 80 rpm. Then the PAN nanofibers converted into CNFs after stabilizing at 260°C for 2 h in air and carbonizing at 600°C in an argon protected atmosphere. The Al_2O_3 coating was grown on surface of CNFs using ALD that alternated between aluminum and oxygen deposition chemistries to afford layer by-layer control of the thickness.

Fabrication processes of Pt NPs

The Al_2O_3-CNF film was dipped in a 0.025 mmol/mL H_2PtCl_6 solution with vacuum assistance and dried at room temperature. The as-prepared film was then connected to copper electrodes, and the interfaces were glued together with silver paste. Joule heating was performed in an argon-filled glovebox. A Keithley 2400 source meter was used as the external current source. The emitted light was collected by an optical fiber (400 μm diameter), connected to a spectrometer (Ocean Optics Inc). The measurement system was calibrated by a National Institute of Standards and Technology (NIST)-traceable light source. The temperature of lighted CNF is calculated by fitting the emitted light spectra to the gray body radiation equation. So we only get a spectrum line, and calculate the T by ourselves.

$$I_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1}$$

The spectrum was fitted to Planck's law of black-body radiation: where $I_\lambda(\lambda, T)$ is the measured intensity; h, c, k_B, and T are the Planck constant, speed of light in a vacuum, Boltzmann constant, wavelength, and absolute temperature, respectively. The measured spectrum fits well with the Planck's law.

Materials characterization.

The low-magnification morphology of the NPs on Al_2O_3 coated CNFs was examined by a field-emission SEM. Brightfield TEM was performed at an accelerating voltage of 200 kV to characterize the nanoparticle morphology at higher resolution. Z-contrast atomic resolution HAADF-STEM images as well as the EDX maps and spectra were also obtained at 200 kV. Raman characterization was done at a laser wavelength at 532 nm. XPS analysis was performed on a multitechnique photoelectron spectrometer with a standard dual (Mg/Al) anode and monochromatic (Al) X-ray sources for XPS analysis and imaging.

Modeling.

The first-principles computations are performed based on density functional theory and implemented in the Vienna *Ab-initio* Simulation Package (VASP) code. The projector augmented wave potential by the generalized gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE) are used to treat with the exchange correlation interaction. The kinetic energy cutoff for plane wave expansion is set at 600 eV, which is enough for the material system we select. A vacuum of 2 nm is used along the direction perpendicular to the surface to avoid slab's interaction with their periodic images. To obtain the optimized structures, the forces on all atoms were minimized to be smaller than 0.1eV/nm. We computed three different kinds of energies for various Pt_n clusters: average adsorption energy $E_A = (E_{sub}+E_{Ptn}-E_{tot\text{-}Ptn})/n$, average surface formation energy $E_S = (E_{tot\text{-}Ptn}-E_{sub}-n*(E_{tot\text{-}Pt1}-E_{sub}))/n$, and average free formation energy $E_F = (E_{Ptn}-n*E_{Pt1})/n$. Here, E_{sub} represents the energy of substrate, E_{Ptn} represents the energy of Pt_n cluster, and $E_{tot\text{-}Ptn}$ represents the total energy when Pt_n adsorbs on substrate.

Results and Discussion

The exceptional temperature control via Joule heating can be illustrated by an ultrafast 50 ms thermal pulse duration. The materials response was monitored with a specially designed sub-millisecond diagnostics. The temperature versus power relation was shown in Figure S1. This repeatable temperature-power relation can be used to precisely control the temperature of the Joule heating technique for future experiments. A sub-millisecond resolution spectrometer was used to monitor the thermal shock pulse (Figure S1c). The temperature evolution curve extracted from Figure S1c illustrates the heating and cooling process.

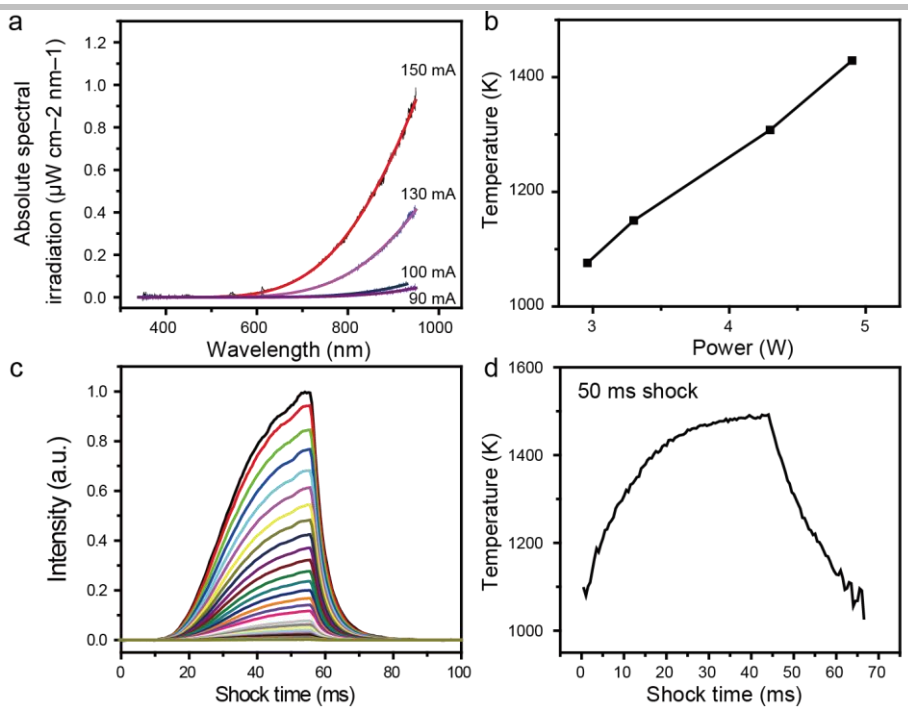

Figure S1. Characterization of the Joule heating process. (a) Light emission spectra at high temperatures fitted to gray body radiation for temperature measurements at different current densities. (b) Temperature as a function of input power for Joule heated CNF. (c) The temporal evolution of temperature for the 50 ms thermal shock. (d) Light emission spectra at different times from 0 to 100 ms, covering both the heating and cooling of 50 ms thermal shock..

To evaluate the variation of nanoparticle size and distribution on the Joule heating time, 1 s treatment process was carried out. The average nanoparticle increased to 7.6 nm when extending the duration time. The Pt mapping coincides with the nanoparticles on the surface, which confirms the chemical composition of the synthesized nanoparticles. The Al mapping clearly shows that Al_2O_3 layer uniformly coats the CNF even after 1 s Joule heating.

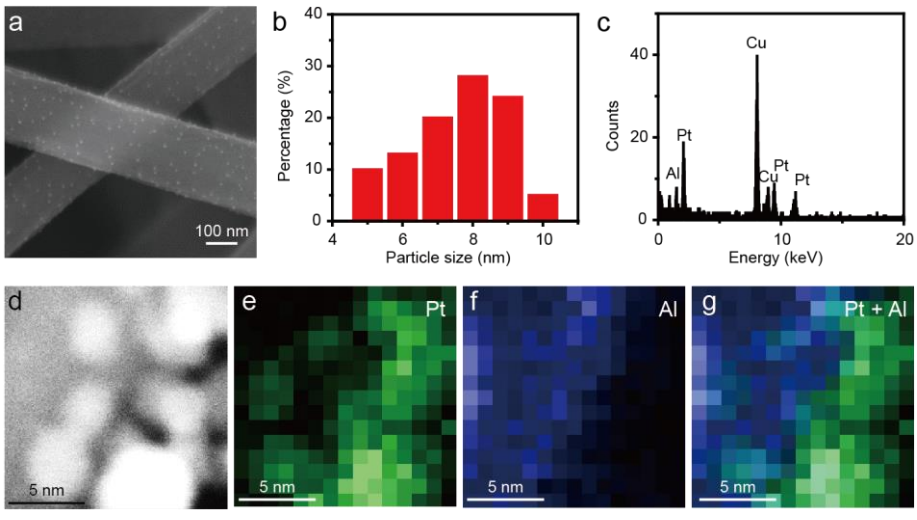

Figure S2. (a) SEM image of Pt nanoparticles formed on Al_2O_3 coated CNFs by 1 s Joule heating treatment. The particle size distribution (b) and EDX spectrum (c) of the sample in panel (a). (d) High-magnification STEM-HAADF image and (e-g) EDX mapping for the detected elements: Pt, Al, and Pt with Al, respectively.

The microstructure of the *in situ* synthesized Pt nanoparticles on the Al_2O_3/CNF matrix was examined by TEM. The synthesized Pd NPs possess a highly crystalline structure as shown in Figure S2 based on a number of observations.

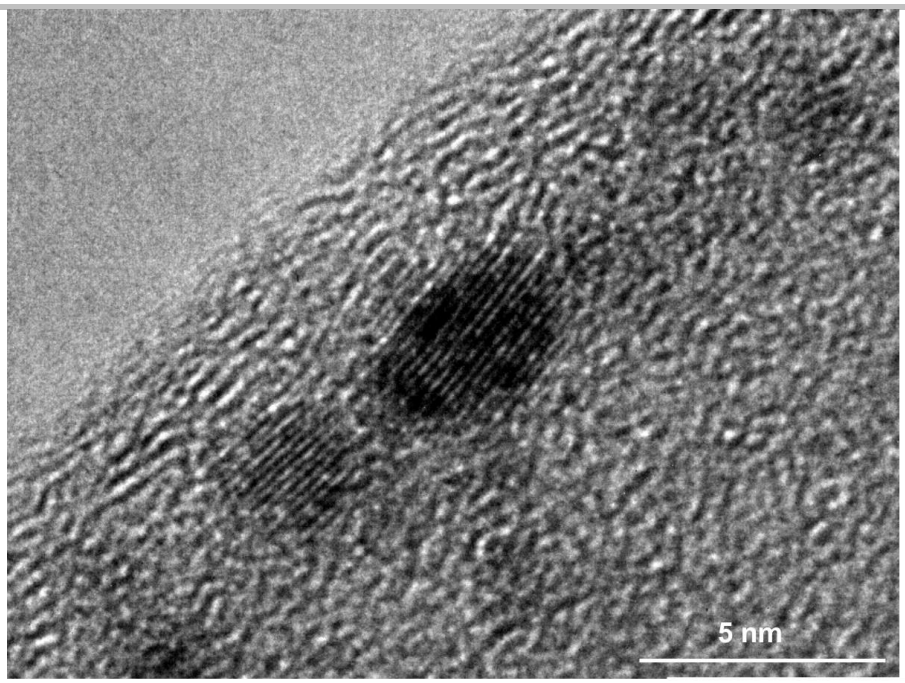

Figure S3. HRTEM image of Pt/Al_2O_3 coated CNF after thermal pulse treatment.

The synthesized Pt nanoparticles on the surfaces of Al_2O_3 coated CNFs were dispersed in ethanol by bath sonication and dropped on Cu grid to evaporate the solvent at 80 ^oC. Then they were characterized by a scanning transmission electron microscope (STEM) equipped with energy dispersive X-ray spectrometer (EDX). The elemental analyses indicate the chemical composition of the synthesized nanoparticles. Since the intensity of the HAADF-STEM image is proportional to the atomic number $Z^{1.7}$ of the sample, the CNF matrix appears dark, however, the Pt nanoparticles can be easily identified.

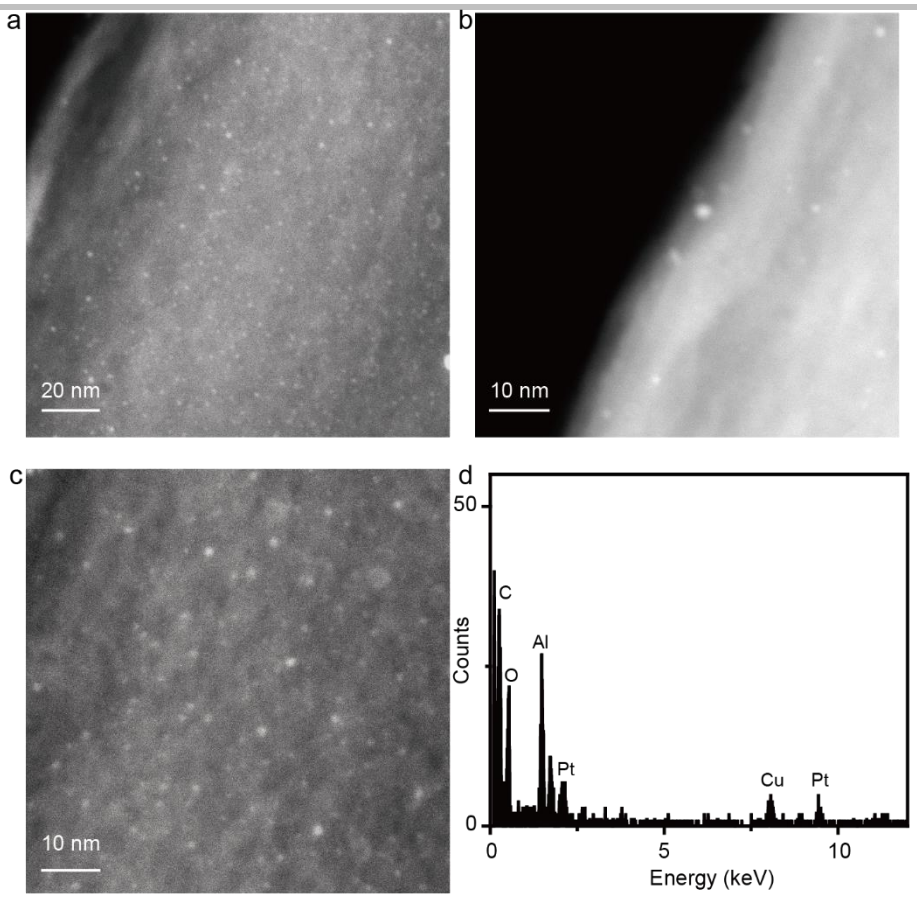

Figure S4. (a) HAADF-STEM image of Pt/Al_2O_3 coated CNF sample. HAADF-STEM image of the edge (b) and center (c) part of an individual fiber in panel (a). (d) Typical EDX spectra for particle constitution. Cu peaks arise from copper TEM grid

Pt is present in the form of islands. It is difficult to clearly map very small (≈1 nm) Pt islands using EDX. However the corresponding pixels are visible in Figure S5b.

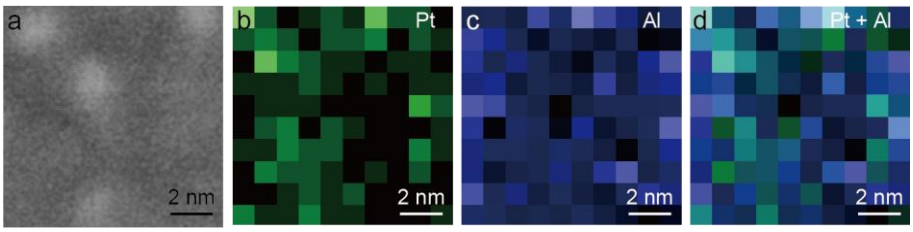

Figure S5. TEM characterization for ≈1 nm Pt nanoparticles. (a) High-magnification STEM-HAADF image of Pt nanoparticles on the Al_2O_3 layer after Joule heating treatment. (b-d) EDX mapping for the detected elements: Pt, Al, and Pt with Al, respectively.