Supporting Information

Is There a Negative Thermal Expansion in Supported Metal Nanoparticles?: An in Situ X-ray Absorption Study Coupled with Neural Network Analysis

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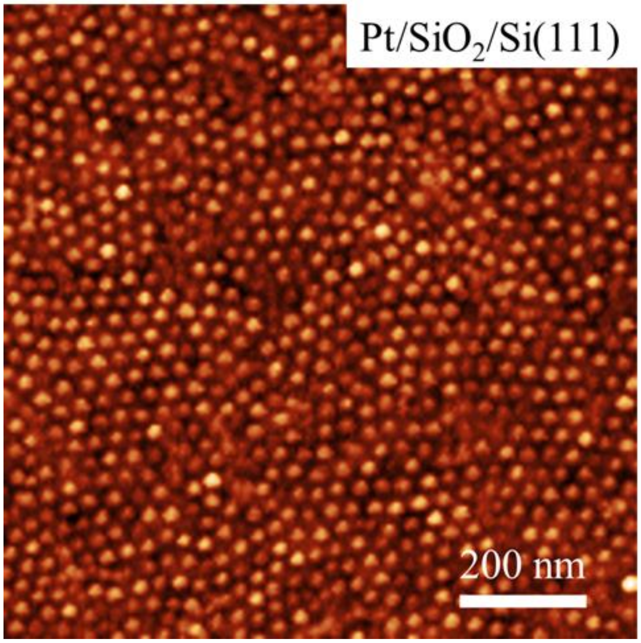

Figure S1. 1 × 1 μm AFM image of the as-prepared Pt nanoparticles (NPs) supported on SiO_2/Si(111). Additional AFM images are available in Ref.[64].

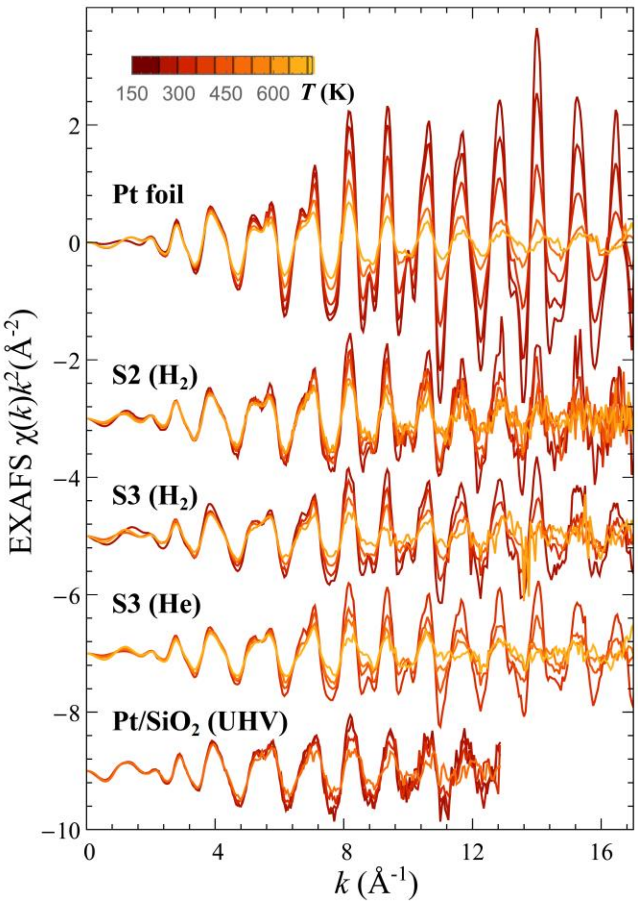

Figure S2. Experimental temperature-dependent Pt L_3-edge EXAFS spectra for a Pt foil, Pt NPs supported on Al_2O_3 (samples S2 and S3) and measured in H_2 and He atmospheres, and for Pt NPs deposited on SiO_2/Si(111) and measured in UHV. Spectra are shifted vertically for clarity.

SUPPLEMENTARY NOTE 1

The photoelectron reference energy E_0 value can change from sample to sample due to, e.g., charge transfer between different parts of a multicomponent material, and may change also with temperature. In conventional EXAFS data analysis, a correction to the E_0 value, ΔE_0, is commonly used as a fitting parameter. However, the effect of ΔE_0 on EXAFS spectra correlates with that of changes in the interatomic distances and shapes of the radial distribution function (RDFs). To disentangle the effects of ΔE_0 and the RDF shape in neural network (NN)-based analysis of EXAFS spectra, during the NN training, each of ca. 50000 training EXAFS spectra is artificially shifted by a random ΔE_0 value in the range between +10 and -10 eV. In this way we ensure that the NN does not assign any physical meaning to a small shift of the energy scale in the experimental EXAFS data. To demonstrate the importance and successfulness of this solution, in Figure S3 we compare the RDFs obtained by two different NNs from experimental Pt foil EXAFS data, which were artificially shifted by ΔE_0 value in the range between +10 and -10 eV, Figure S3(a). The first NN (NN with flexible E_0) was trained, as described above. The second NN (NN with fixed E_0) was trained without randomized ΔE_0 during the training. As one can see from Figure S3(b,c), the NN with fixed E_0 is very sensitive to misalignment of the spectra or changes in the E_0 value: amplitudes, shapes and positions of the RDFs obtained vary wildly when ΔE_0 is changed in the range between -10 and +10 eV, Fig. S3(b). More importantly, even small changes in E_0 (between -1.0 and +1.0 eV) result in visible differences in the shape of the RDFs (Figure S3(c)), which can affect the analysis of subtle changes in the RDFs due to thermal expansion. The NN, trained with randomized ΔE_0 values, does not have this problem. Even for large changes in the E_0 values, the positions, shapes and intensities of all RDF peaks remain stable, thus this NN is ideally suited for studies of thermal expansion effects.

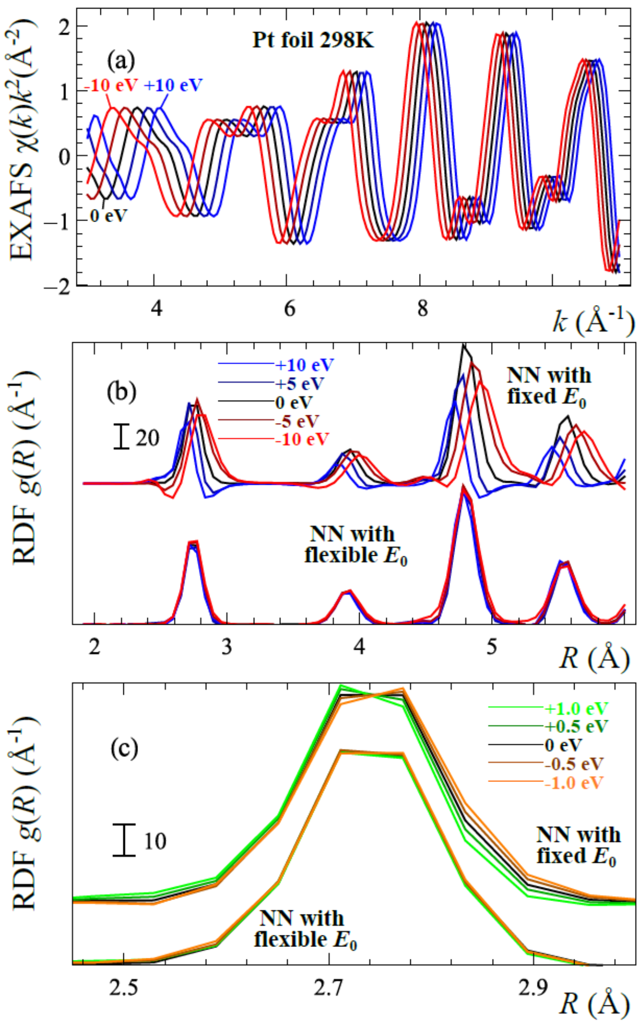

Figure S3. Experimental Pt L_3-edge EXAFS spectra for a Pt foil (room temperature) shifted by ΔE_0 between -10 and +10 eV (a). Corresponding RDFs extracted by a NNs trained on data with fixed and flexible E_0 values (b, c). For clarity, RDFs are shifted vertically in (b,c).