Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Hydrogen absorption in 1 nm Pd clusters confined in MIL-101(Cr)

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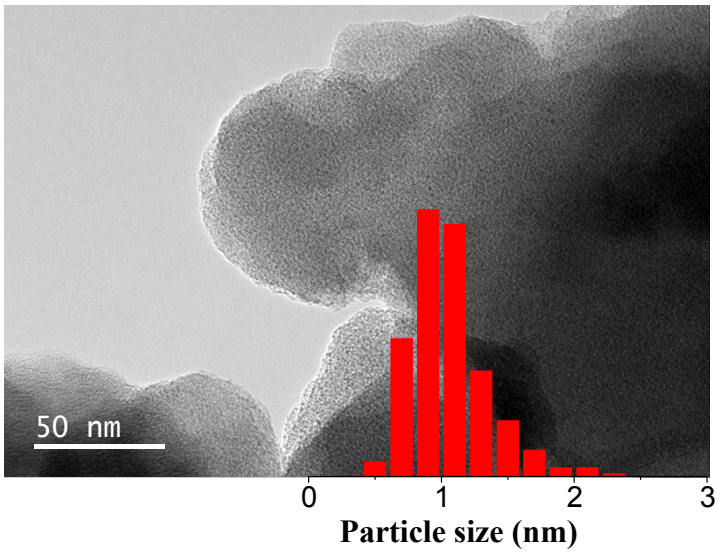
Table SI-1. Chemical analysis of *x*-Pd@MIL-101 (*x* = 5, 10, 15 and 20).

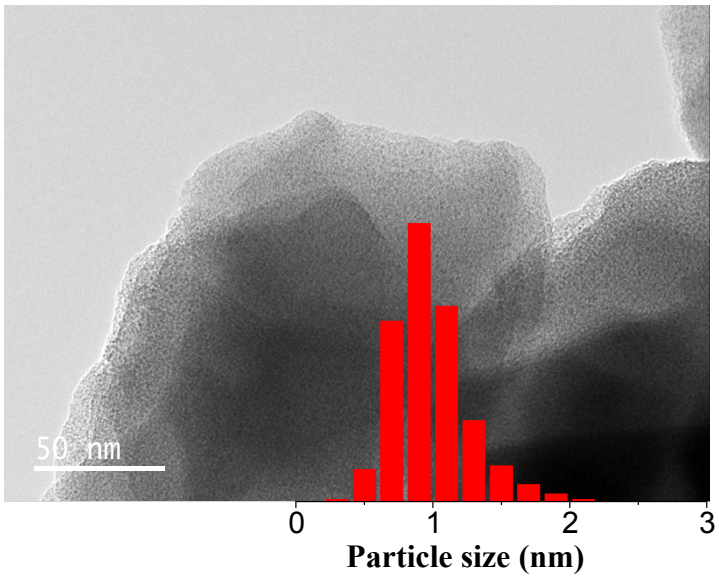
Sample	**Pd content (wt%) ICP-MS**
5-Pd@MIL-101	4.8 (±0.2)
10-Pd@MIL-101	8.3 (±0.4)
15-Pd@MIL-101	13.3 (±0.7)
20-Pd@MIL-101	19.8 (±0.9)

The palladium content in all composites was determined quantitatively by inductively coupled plasma mass spectrometry (ICP-MS) using an ELAN DRC-e Perkin Elmer, after calibration with a 10 μg/ml Pd in HNO_3 standard solution (Multi-element Calibration Standard 3) and digesting the samples by standard protocols in HNO_3/HF/H_2O.

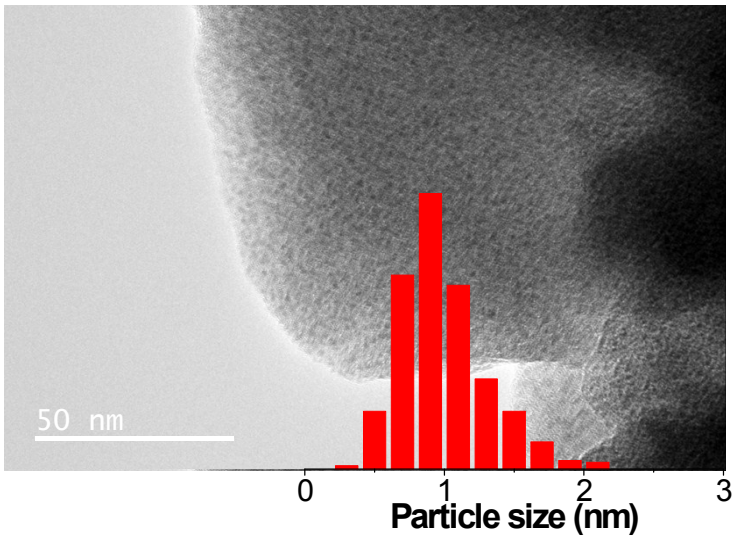
Figure SI-1. TEM images and related particle size histograms for *x*-Pd@MIL-101 (*x* = 5, 10, 15 and 20).



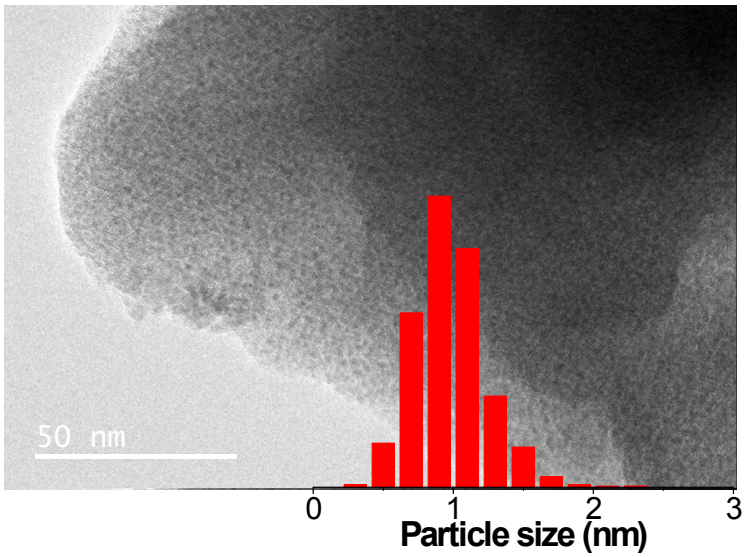
5-Pd@MIL-101



10-Pd@MIL-101

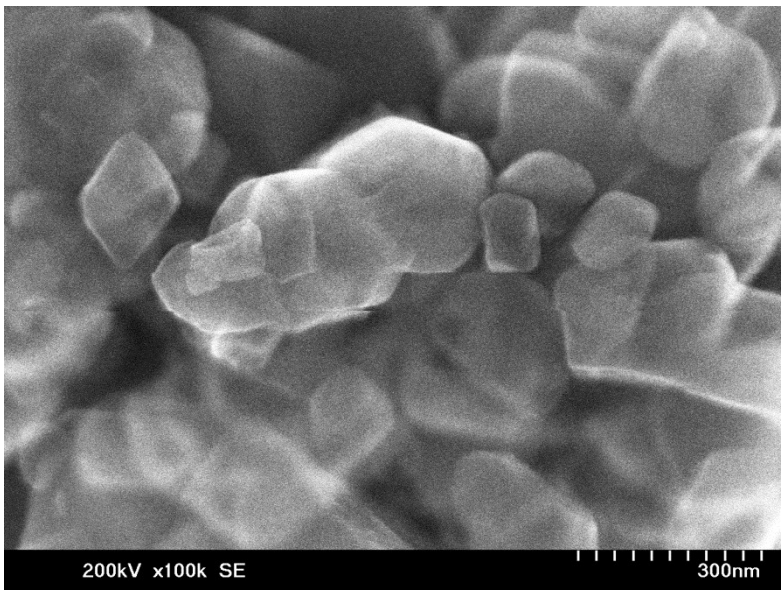


15-Pd@MIL-101

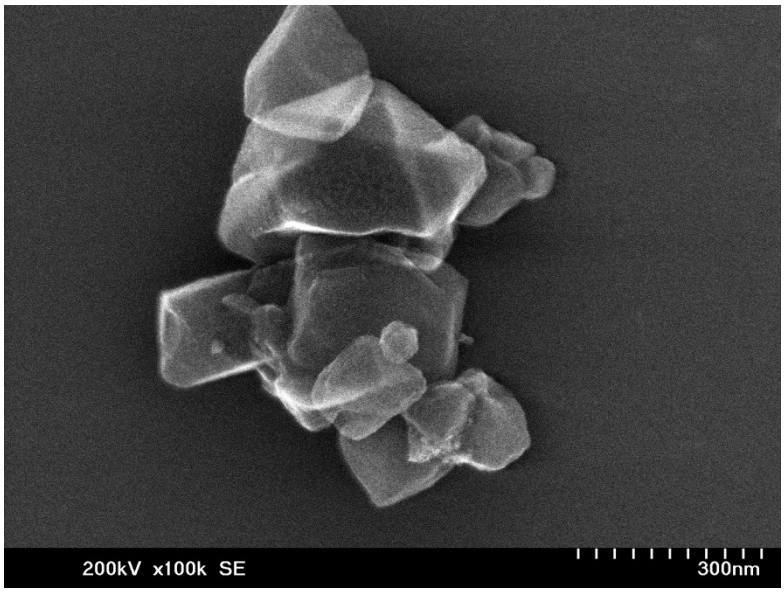


20-Pd@MIL-101

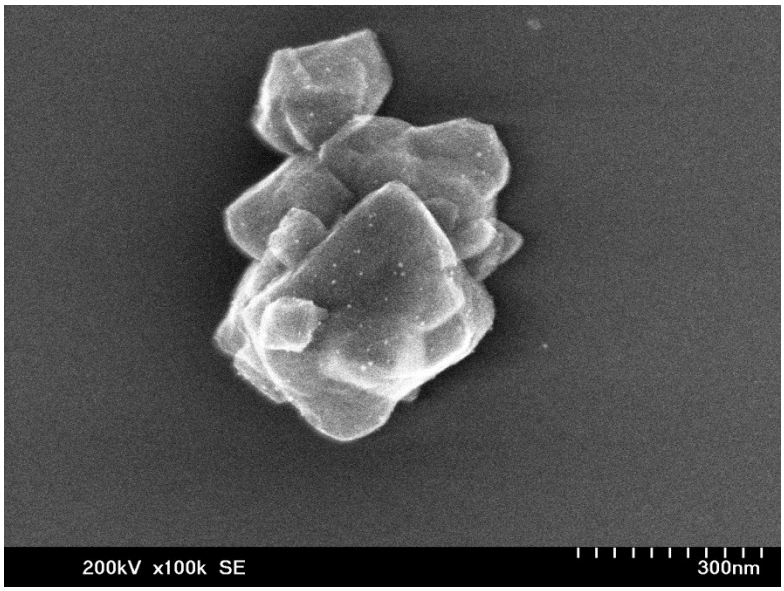
Figure SI-2. SEM images for *x*-Pd@MIL-101 (*x* = 5, 10, 15 and 20).



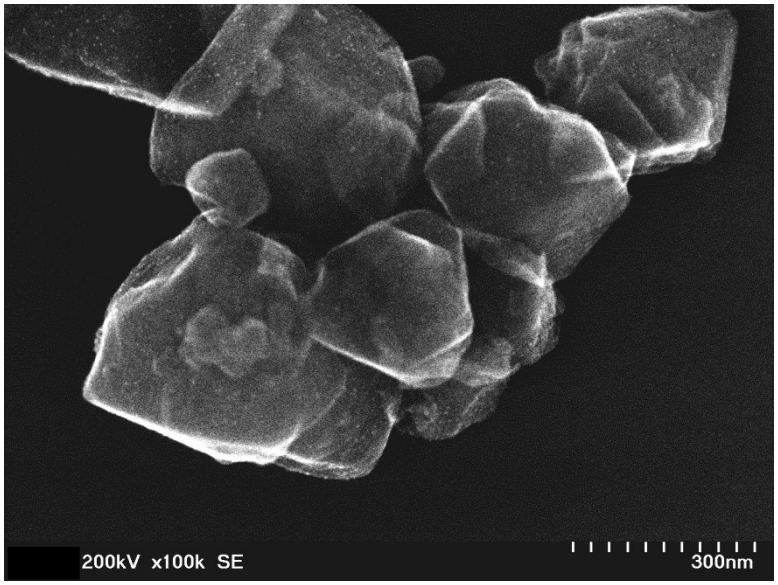
5-Pd@MIL-101



10-Pd@MIL-101



15-Pd@MIL-101



20-Pd@MIL-101

Figure SI-3. Experimental and simulated XRD patterns of MIL-101.

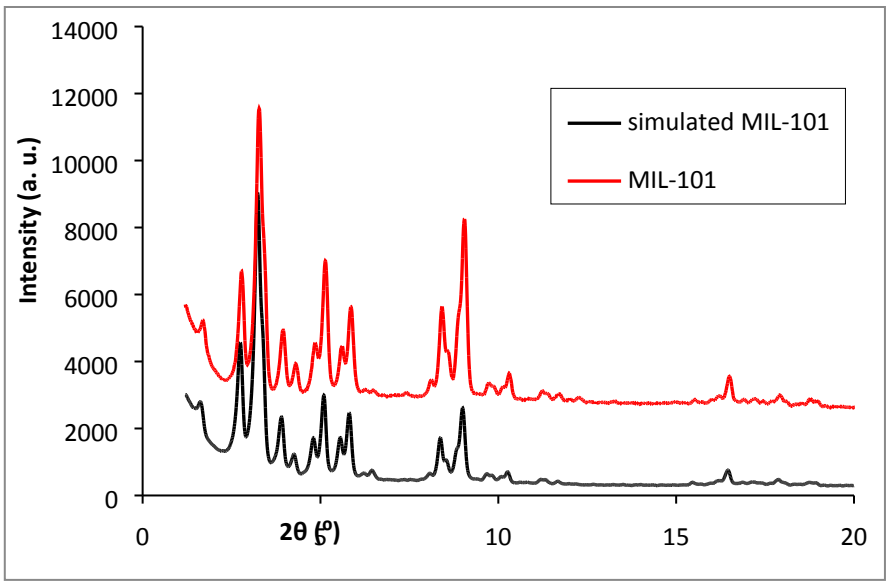


Figure SI-4. Thermogravimetric analysis under air (100 ml·min^{-1}) with heating rate of 10 °C·min^{-1}.

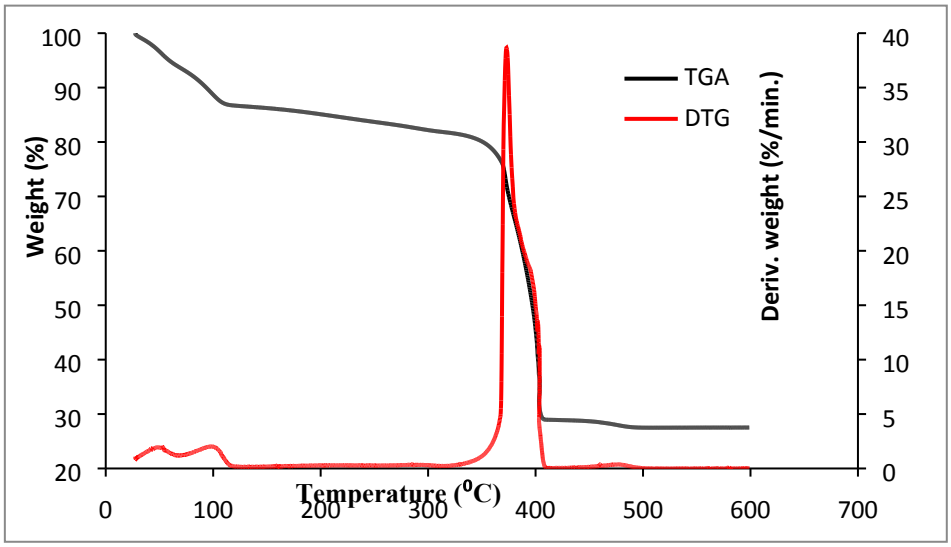
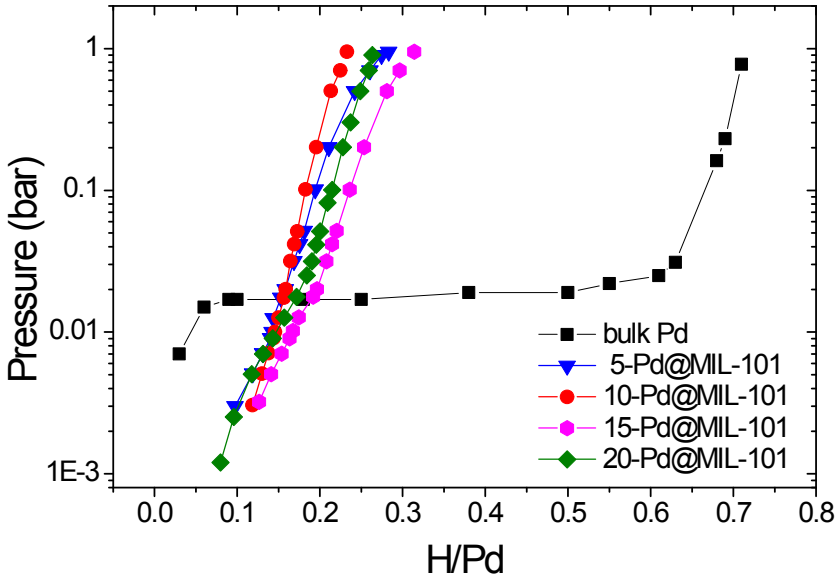


Figure SI-5. Hydrogen absorption PCI curves at room temperature for all composites and bulk Pd expressed as equilibrium pressure *vs*. capacity (H/Pd).



On the overall, the dispersion among PCI curves for all composites is satisfactory and no plateau pressure could be observed, irrespective of Pd content.

The dispersion of PCI curves is small at low pressures and slightly increases with pressure. This can be understood by mainly two factors: accumulation of errors with rising pressure, typical for volumetric measurements and the large uncertainties in PCI measurements with decreasing the weight of the active material (decreasing the Pd content). Consequently, only the PCI curve for the highest Pd content was discussed in the manuscript.

Figure SI-6. XAS spectra for Pd bulk under air (black) and Pd@MIL-101 under 1 bar He (blue) and H_2 (red) at 300 K.

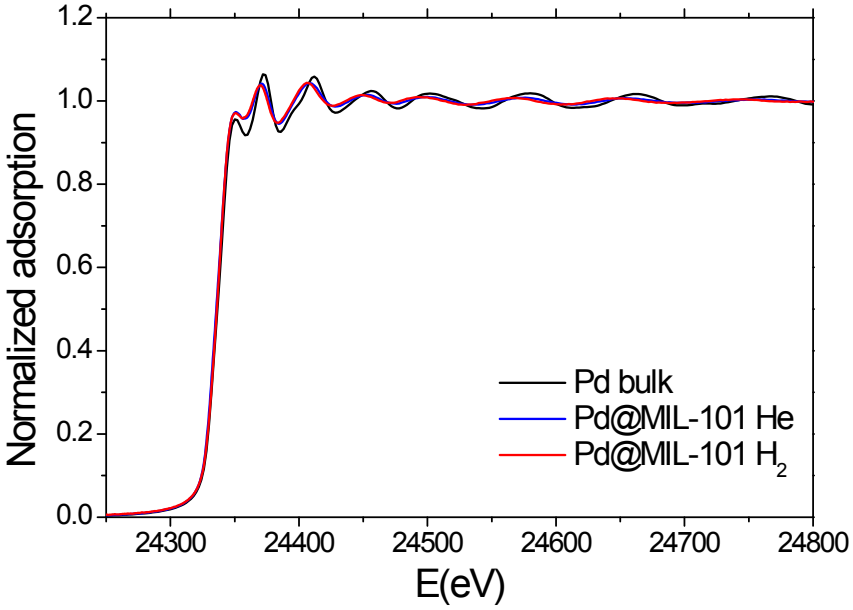
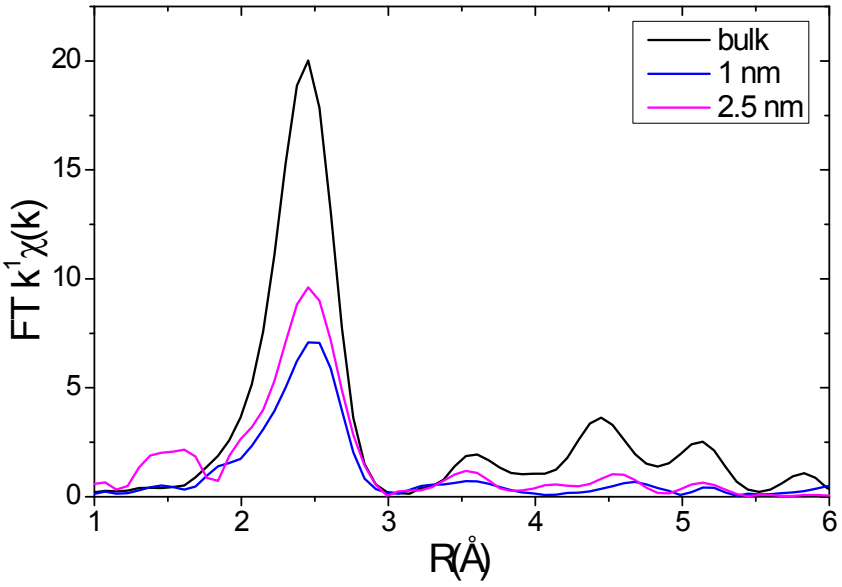


Figure SI-7. Comparison of the module of FT for bulk, 2.5 nm and 1 nm Pd at room temperature.



The XAS data for 2.5 nm Pd nanoparticles are taken from our previous results reported in J. Am. Chem. Soc., 2010, 132, 7720-7729. Since the XAS data for 2.5 nm Pd nanoparticles are recorded after air exposure without H_2 pre-treatment, these nanoparticles are slightly oxidized, as proven by the small peak at around 1.75 Å typical for Pd-O distance.

Figure SI-8. Comparison between FT experimental (black) and fitted (red) by EXAFS refinements at Pd K edge for bulk Pd.

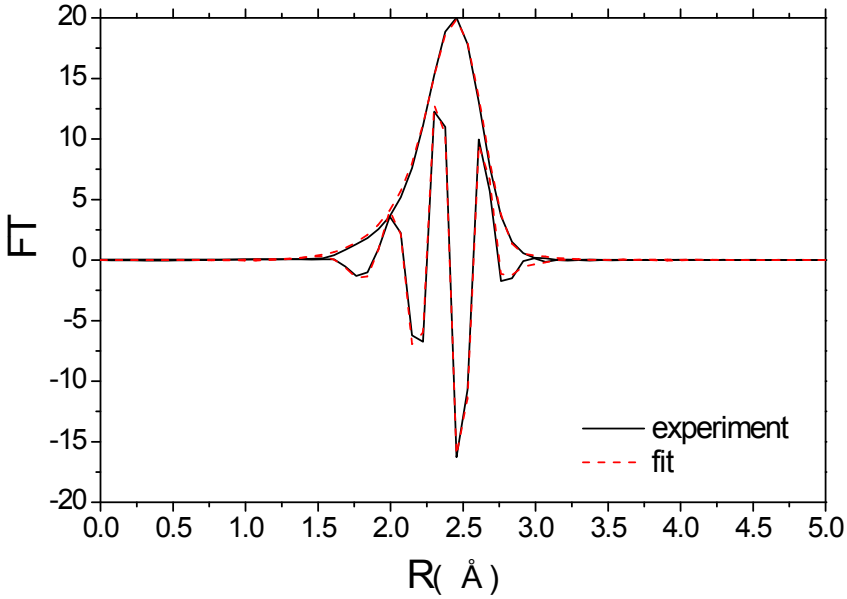


Figure SI-9. Comparison between FT experimental (black) and fitted (red) by EXAFS refinements at Pd K edge for Pd@MIL-101 under He.

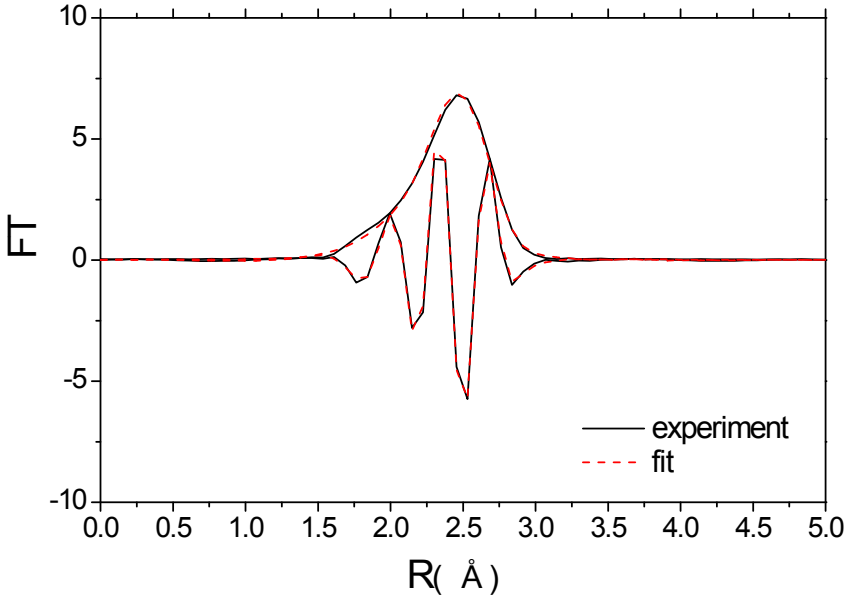


Figure SI-10. Comparison between FT experimental (black) and fitted (red) by EXAFS refinements at Pd K edge for Pd@MIL-101 under H_2.