

Electronic Supplementary Information

PtRu Nano-Dandelions on Thiolated Carbon Nanotubes: a New Synthetic Strategy for Supported Bimetallic Core-Shell Clusters on Atomic Scale

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Experimental Details

MWNT prepared by a conventional CVD method were purchased from Helix Material Solutions. Raw soot containing MWNT was heated for 2 h at 400 °C in static air and subsequently treated with 6M hydrochloric acid at 70 °C for 12 h. Thiolation of the MWNT was conducted by a method based on the formation of amide bonds. Purified MWNT were stirred in a concentrated H₂SO₄/HNO₃ (3:1, 98% and 70% purity respectively, Kanto Chemical) mixture for 15 min to prepare carboxylated MWNT, and then chlorinated by refluxing for 12 h with SOCl₂ (Wako) at 70 °C. After evaporating off the any remaining SOCl₂, thiolated MWNT (S-MWNT) were subsequently obtained via a reaction with NH₂(CH₂)₂SH (Wako) in dehydrated toluene (Aldrich) for 24 h at 70 °C. A suspension of 20 mg of S-MWNT, 5.25 mg of H₂PtCl₆ (Aldrich) and 5.13 mg of RuCl₃ (Aldrich) equivalent to 20 % weight ratio of Pt (10% w/w) and Ru (10% w/w) to carbon was prepared by sonication in 40 ml of deionized water. Subsequently, this Pt and Ru precursor was simultaneously reduced and supported on the carbon supports using NaBH₄ (Kanto chemical) and then washed with deionized water and ethanol several times. After evaporation and drying, we could obtain 20 % PtRu supported on S-MWNT, which are referred to as PtRu-S-MWNT. Heat treatment of PtRu-S-MWNT was performed for 60 min at 473 K, 498 K and 523 K in a H₂ gas flow of 100 sccm. The samples obtained by heat treatment followed by slow quenching of Pt-S-MWNT are denoted by PtRu_{h-q}/MWNT (T_h).

The transmission electron microscopy (TEM, H-9000NAR, Hitachi) images were obtained with accelerating voltages of 300 kV. X-ray absorption near edge structure (XANES) and extended X-ray analysis of fine structure (EXAFS) data for Pt L_{III} and Ru K absorption edges were obtained in transmission mode, using the synchrotron radiation of BL01B1, SPring-8, at room temperature. X-ray was monochromated with two Si (111) plane gratings and detected by two ion chambers, which were continuously purged with a gas mixture of 15 % Ar and 85 % N₂ in I₀ and 100 % Ar gas in I₁. Data reduction was carried out using the computer software, Athena and Artemis. The XANES spectrum was normalized by the Victoreen function and the RDF of EXAFS was obtained by a Fourier transform, in the range from 3 Å⁻¹ to 14 Å⁻¹ in k space, on k³-weighted EXAFS oscillations. FEFF8 was used to obtain theoretical model for the data fitting. X-ray photoelectron spectroscopy (XPS, PHI 5600, ULVAC-PHI) was used to confirm the electronic state of Pt clusters and for elemental analysis. The X-ray source used was an Al Kα with energy 1486.6 eV operating at 15 kV, 300 W and the obtained binding energies were referred to the C 1s (284.5 eV) of the carbon supports.

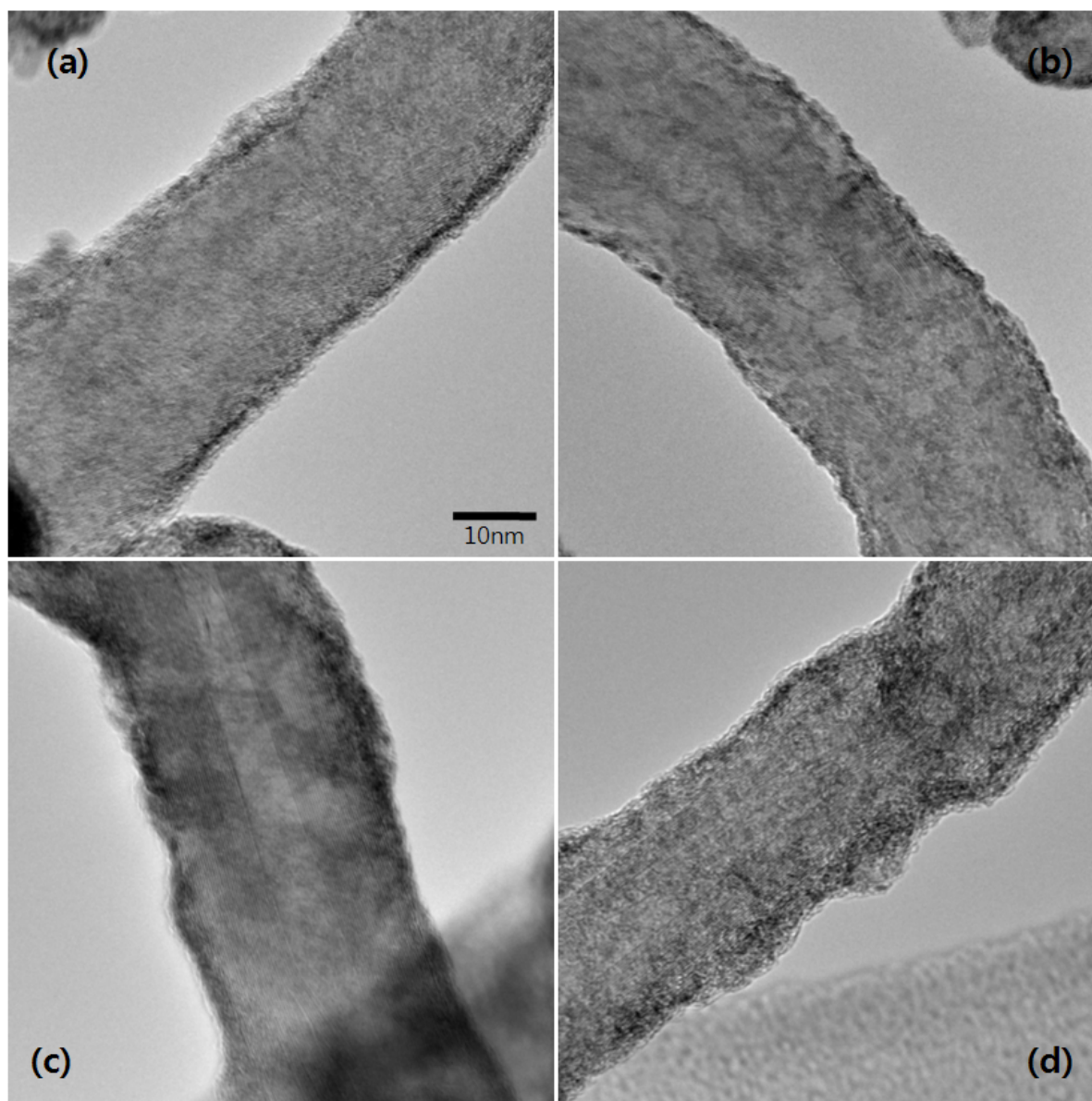


Figure 1 TEM images for (a) PtRu-S-MWNT (b) HT PtRu-S-MWNT($T_h=473K$)
(c) HT PtRu-S-MWNT($T_h=498K$) (d) HT PtRu-S-MWNT($T_h=523K$)

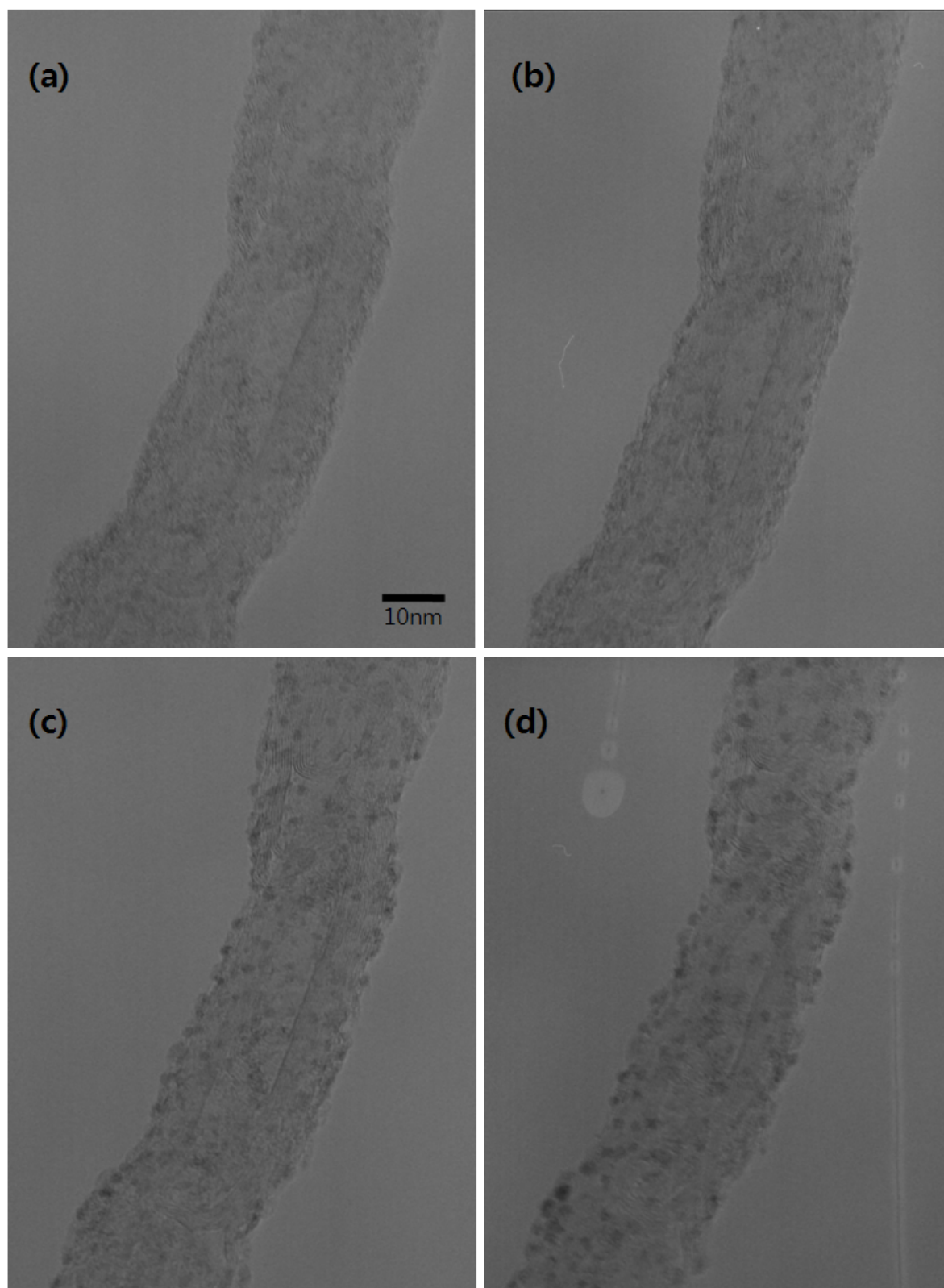


Figure 2 Change of TEM image for HT PtRu-S-MWNT($T_h=523K$) with observation time,
(a) 0 sec. (b) 20 sec. (c) 40 sec. (d) 60 sec..

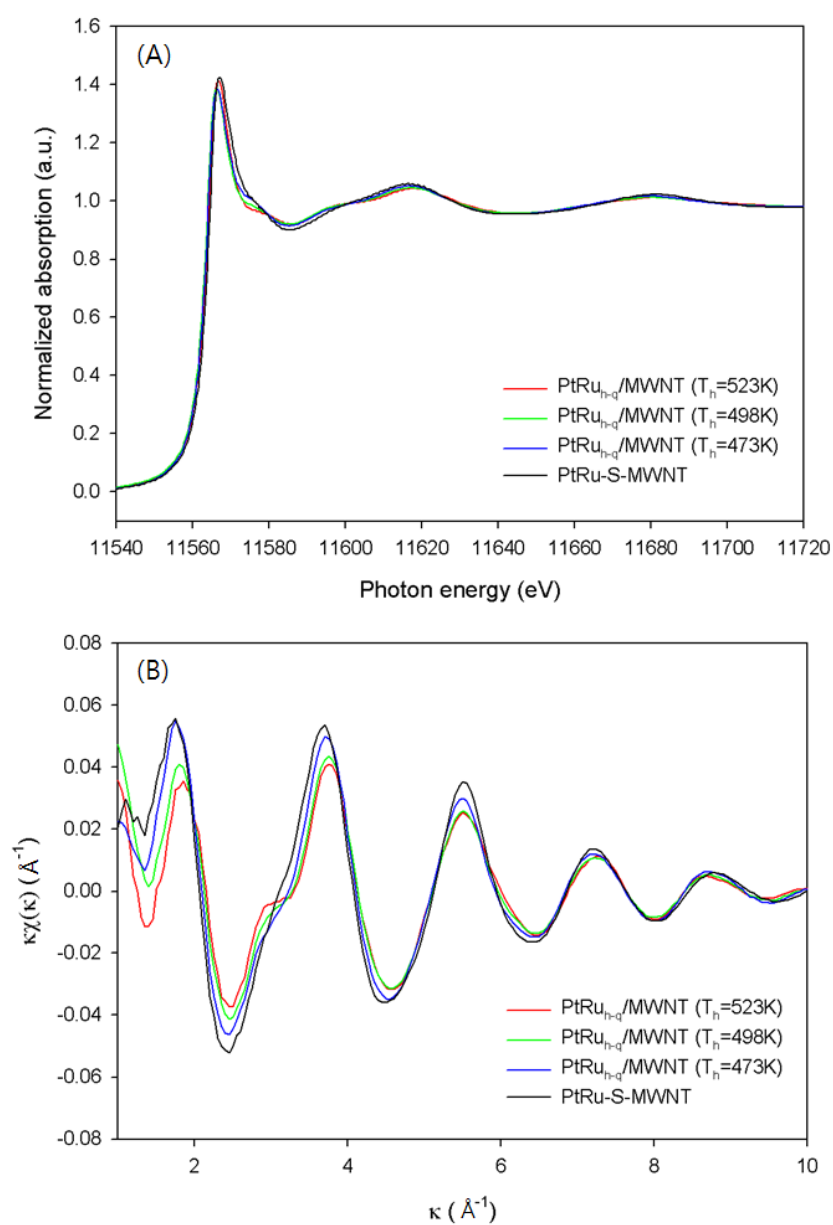


Figure 3 (a) XANES spectra and (b) EXAFS signal in k-space for Pt L₃ absorption edge.

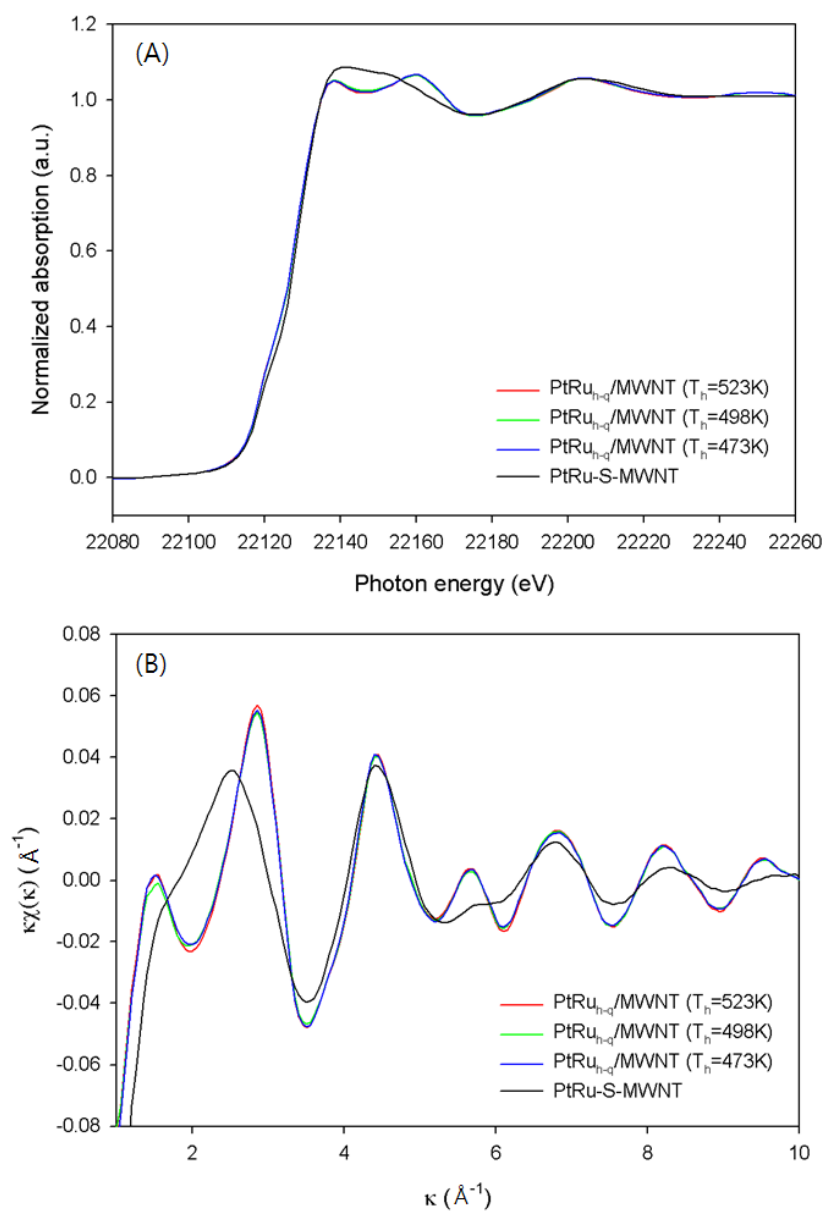


Figure 4 (a) XANES spectra and (b) EXAFS signal in k-space for Ru K absorption edge.