Electronic Supporting Information:

Facile Synthesis of Ultra-Small Rhenium Nanoparticles

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Experimental

General and Materials

All operations were carried out using Standard Schlenk tube and Fischer-Porter bottle techniques or in a glove-box under argon. All solvents were purified and degassed by freeze-pumping before using. Anisole was distilled over sodium. Pentane, toluene and dichloromethane were dehydrated through filtration on a column in a purification system (Braun). Hexadecylamine (HDA) was purchased from Sigma-Aldrich and used as received. Polyvinylpyrolidine 40000 (PVP) was purchased from Sigma-Aldrich and dried over P_2O_5 before usage. ^{12}CO, O_2 and H_2 were purchased from Air Liquid.

Dirheniumtetraallyl $[Re_2(C_3H_5)_4]$ was synthesized according to a slightly modified literature procedure[1].

Characterization

Re NPs were characterized by TEM and HAADF-STEM after deposition of a drop of colloidal solutions, prepared by dissolving purified solid nanoparticles into toluene or dichloromethane for Re/HDA and Re/PVP NPs respectively, over a covered holey copper grid inside the glove-box. TEM Analysis was performed at "*Service Commun de Microscopie Electronique de l'Université Paul Sabatier*" (TEMSCAN-UPS) by using JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 Å. The approximation of the particle mean size was made through a manual analysis of enlarged micrographs by measuring at least 250 particles on a given grid. HAADF-STEM analysis was performed at TEMSCAN-UPS with JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.5 Å.

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[1] A. F. Masters, K. Mertis, J. F. Gibson, G. Wilkinson, *New. J. Chem.*, 1977, **1**, 389-395

Wide-Angle X-Ray Scattering (WAXS) was performed at CEMES-CNRS. Purified samples of Re/HDA and Re/PVP NPs were sealed in 2.5 and 1.5 mm diameter Lindemann glass capillaries respectively. The samples were irradiated with graphite-monochromatized Mo K_α (0.071069) radiation and the X-ray intensity scattered measurements were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained by Fourier Transformation of the reduced intensity functions.

Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer GX2000 spectrometer in the range 4000-400 cm^{-1}. All samples were prepared as KBr pellets under argon atmosphere inside a glove-box.

ICP analyses were performed at "*Institut des Sciences Analytiques, Departement Service Central d´Analyse*" (CNRS) in Lyon.

Synthesis

Re/PVP NPs: In a typical experiment, the organometallic precursor $[Re_2(C_3H_5)_4]$ (40 mg, 0.074 mmol) and PVP (249 mg) were introduced into a Fischer-Porter reactor and dissolved in 26 ml anisole, previously degassed by freeze-pump cycles. The resulting orange solution was pressurized to 3 bar of H_2 at room temperature (RT). Then the Fischer-Porter reactor was immersed into oil-bath that was pre-heated to desired temperature. The homogeneous solution was kept stirring either at 120°C for 2 days or at 100°C for 3 days. During this time, the color of the reaction solution changed gradually from orange to dark brown. At the end of the reaction, the solution was cooled down to RT and the excess hydrogen was eliminated under vacuum. The solvent was removed by vacuum and the resultant dark brown solid was washed with pentane several times at RT. Then the residue was dried overnight under vacuum at RT.

Elemental Analysis (EA) data: Re 7.53% for Re/PVP NPs prepared at 120°C for 2 days.

Re 7.75% for Re/PVP NPs prepared at 100°C for 3 days.

FT-IR data: The bands at *v:* 2874-2953, 1681, 1270-1285 and 1370-1490 cm^{-1} are attributed to C-H, C=O, C-N stretching and C-H bending respectively. (See Figure S1, bottom)

Re/HDA NPs: In a typical experiment, the organometallic precursor $[Re_2(C_3H_5)_4]$ (75mg, 0.14 mmol) and HDA (68 mg, 0.28 mmol) were introduced into a Fischer-Porter reactor and dissolved in 48 ml anisole, previously degassed by freeze-pump cycles. The resulting orange solution was pressurized to 3 bar of H_2 at RT. Then the Fischer-Porter reactor was immersed into oil-bath that was pre-heated to desired temperature. The homogeneous solution was kept stirring at either 120°C for 2 days or 100°C for 3 days. During this time, the color of the reaction solution changed gradually from orange to dark brown. At the end of the reaction, the solution was cooled down to RT and the excess hydrogen was eliminated under vacuum. The volume of the solvent was concentrated to 5 ml under vacuum and cold pentane was added. The nanoparticles were washed several times with cold pentane, allowed to precipitate and the supernatant was removed by cannula under Ar atmosphere. The resultant dark brown residue was dried overnight under vacuum at RT. At the end, dark-brown, wet and sticky sample was obtained and used as it is.

EA data: Re 37.0% for Re/HDA NPs prepared at 120°C for 2 days.

Re 35.4% for Re/HDA NPs prepared at 100°C for 3 days.

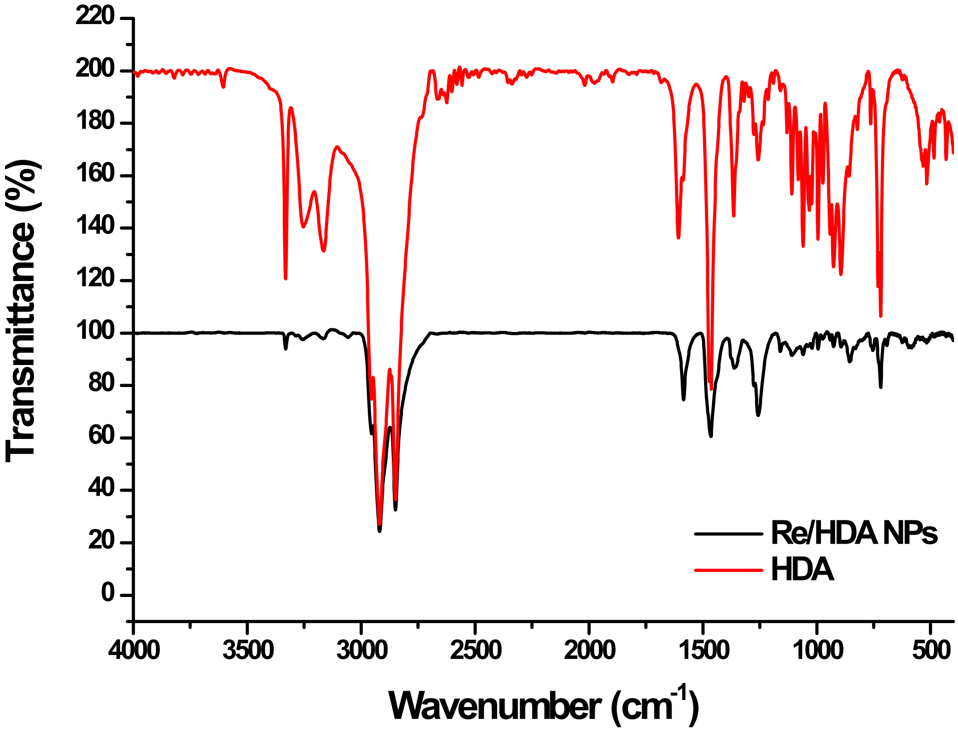
FT-IR data: The peaks at 3331 and 2849-2954 cm^{-1} are attributed to N-H and C-H stretching bands respectively. Bands at 1584, 1256-1362, 1465 cm^{-1} correspond to N-H, C-N and C-H bendings (See Figure S1, top). The decrease in the intensity of N-H stretching and a shift in N-H bending bands could be due to σ-coordination of HDA on the surface of the nanoparticles through amine side and the resulting constrain of the molecular motion.

Hydride Quantification

A solution of freshly prepared Re NPs was submitted to 5 cycles of 1 min vacuum/ 1 min argon in order to eliminate any hydrogen dissolved in anisole. Then 5 molar equiv. of 2-norbornene was added and reaction solution was heated to 80°C to overcome the high dissociation energy of Re-H bond. The conversion of 2-norbornene to norbornane was monitored by GC until having stable norbornane amount. It was found ca. 1.1 and 0.7 hydrides per surface Re atom for Re/PVP and Re/HDA NPs respectively.

Surface Oxidation:

The surface oxidation of Re NPs was performed in solid state. Re NPs were exposed to 3 bar of O_2 in different reaction conditions as given in the main text and the changes were followed by TEM, WAXS and FT-IR techniques.



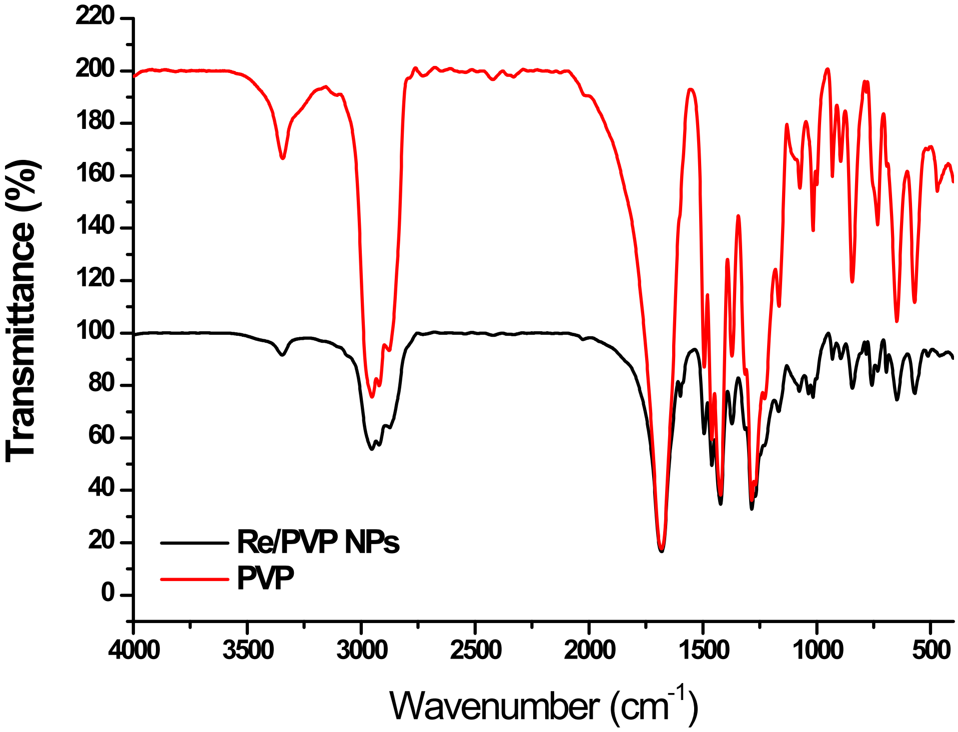


Figure S1. Top: FT-IR spectra of free HDA (red) and Re/HDA NPs (black) prepared at 120°C in 2 days with 1 molar equiv. of HDA, Bottom: FT-IR Spectra of free PVP (red) and Re/ PVP NPs (black) prepared at 120°C in 2 days with 10 wt.% Re content.

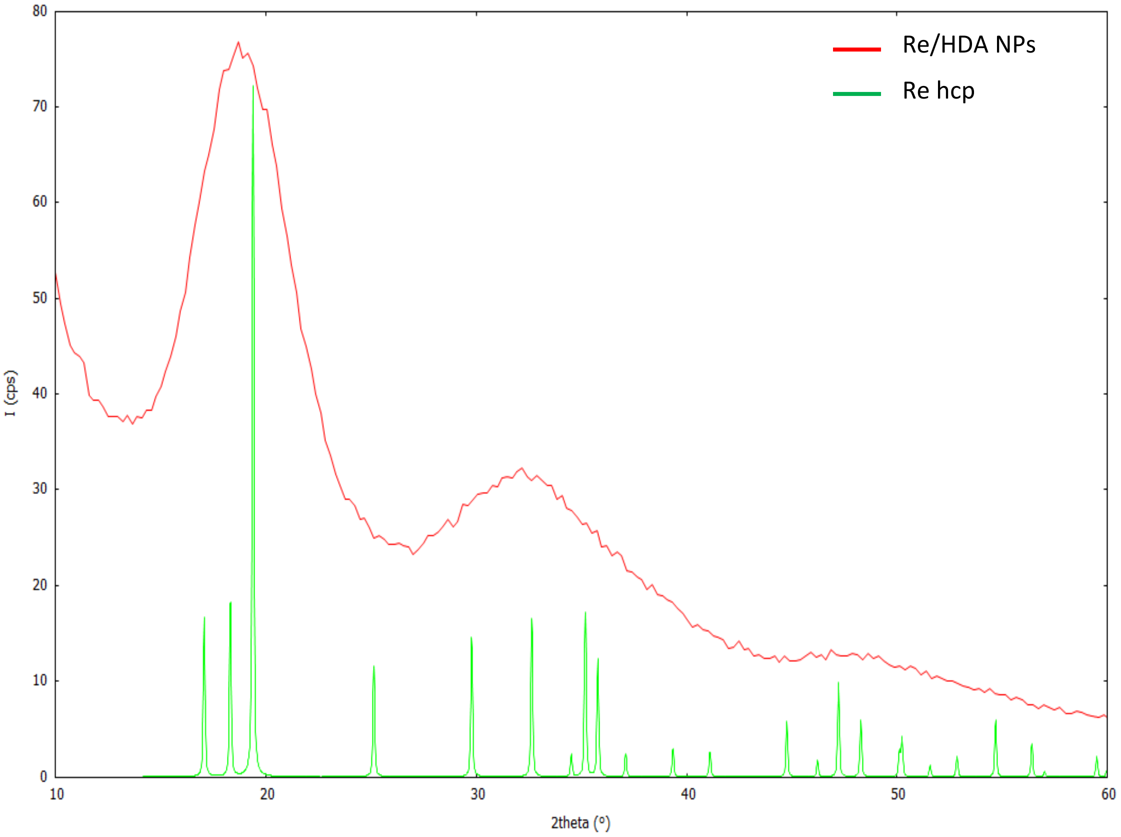


Figure S2. Comparison of low-angle part diffractogram of Re/HDA NPs, prepared at 120^{o}C in 2 days with 1 molar equiv. of HDA, with the powder pattern computed for hcp Re.

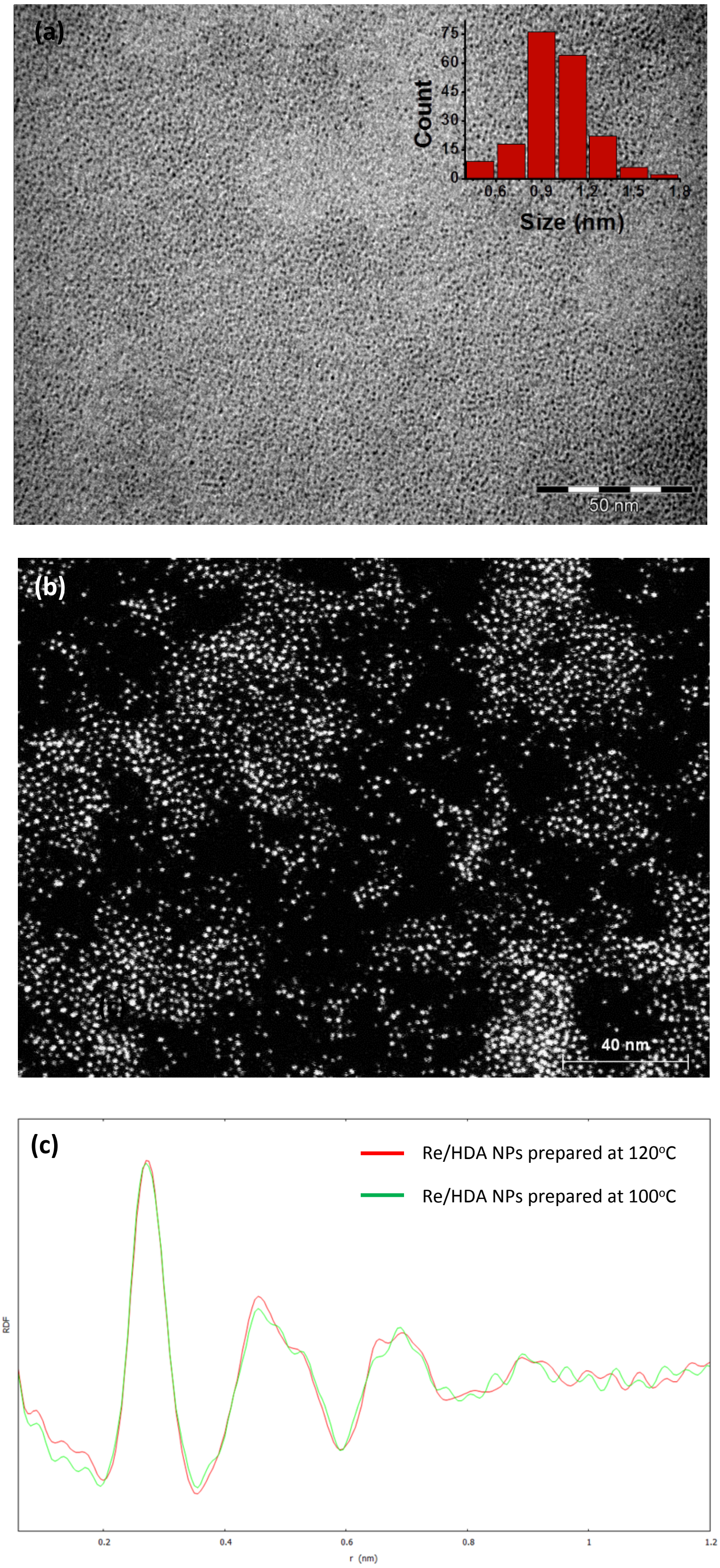


Figure S3. (a) and (b) TEM and HAADF-STEM images of Re/HDA NPs prepared at 100ºC in 3 days with 1 molar equiv. of HDA. The inset is the size histogram of corresponding image. (c) Comparison of WAXS graphs of Re/HDA NPs prepared at 120ºC and 100ºC.

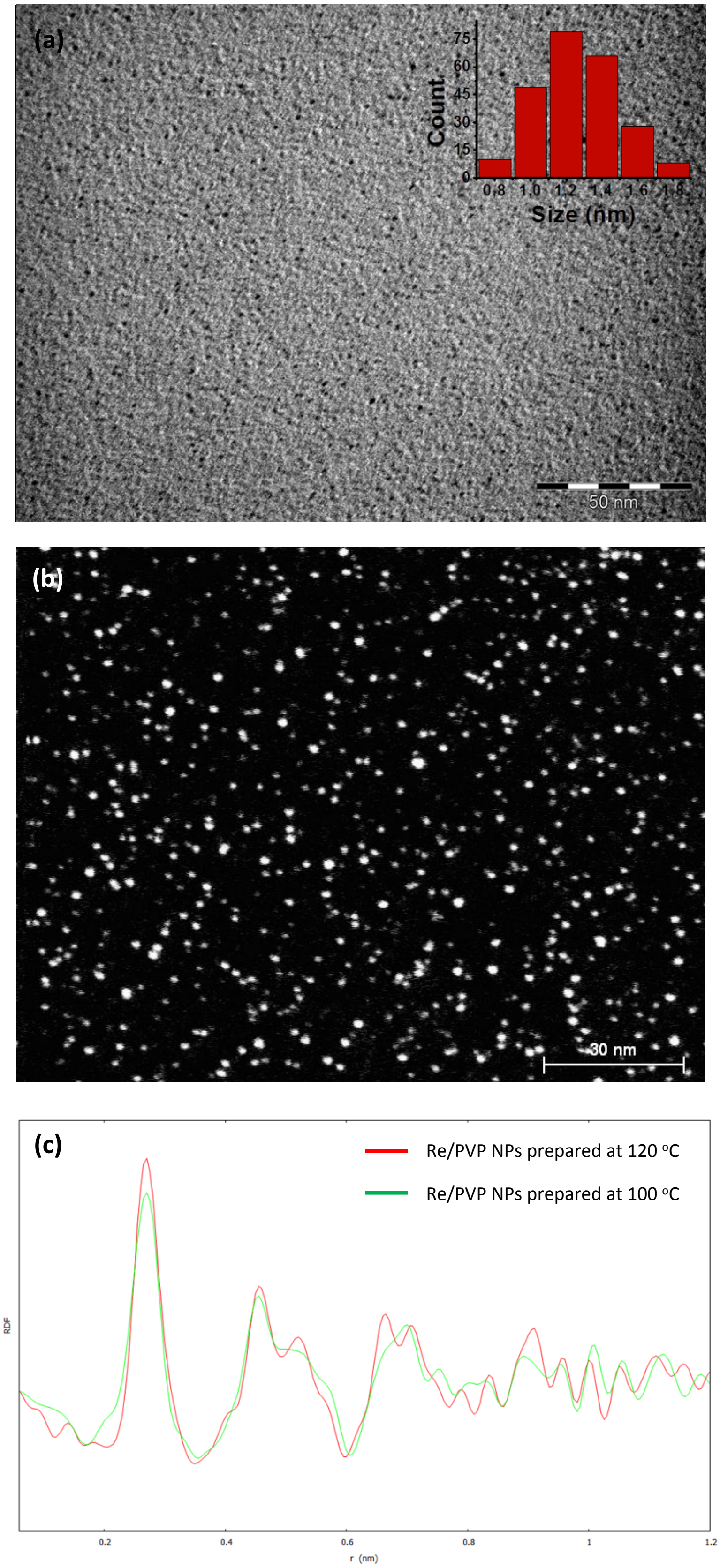


Figure S4. (a) and (b) TEM and HAADF-STEM images of Re/PVP NPs prepared at 100ºC in 3 days with 10 wt.% Re content. The inset is the size histogram of corresponding image. (c) Comparison of WAXS graphs of Re/PVP NPs prepared at 120ºC and 100ºC.

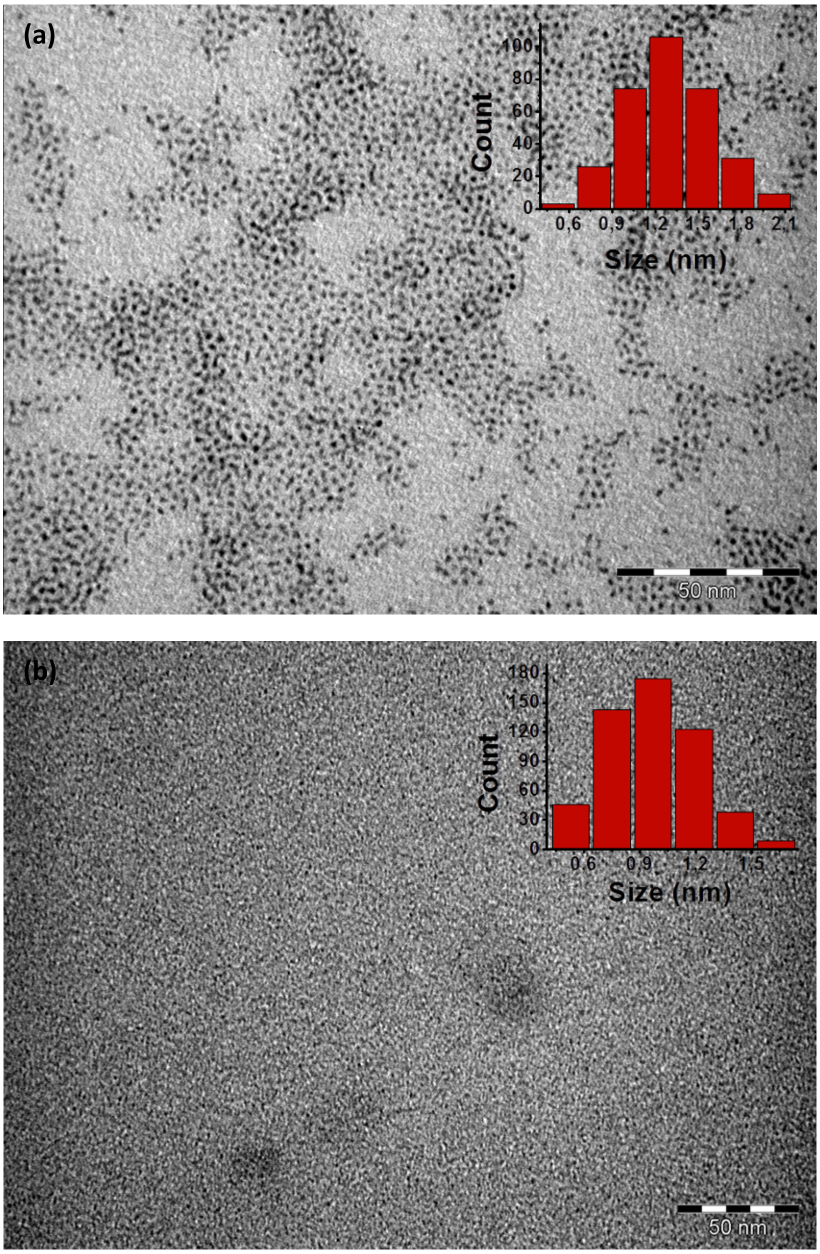


Figure S5. (a) TEM Image of Re/HDA NPs prepared at 120^{o}C in 2 days with 0.5 molar equiv. of HDA (b) TEM Image of Re/PVP NPs prepared at 120^{o}C in 2 days with 5 wt.% Re content.

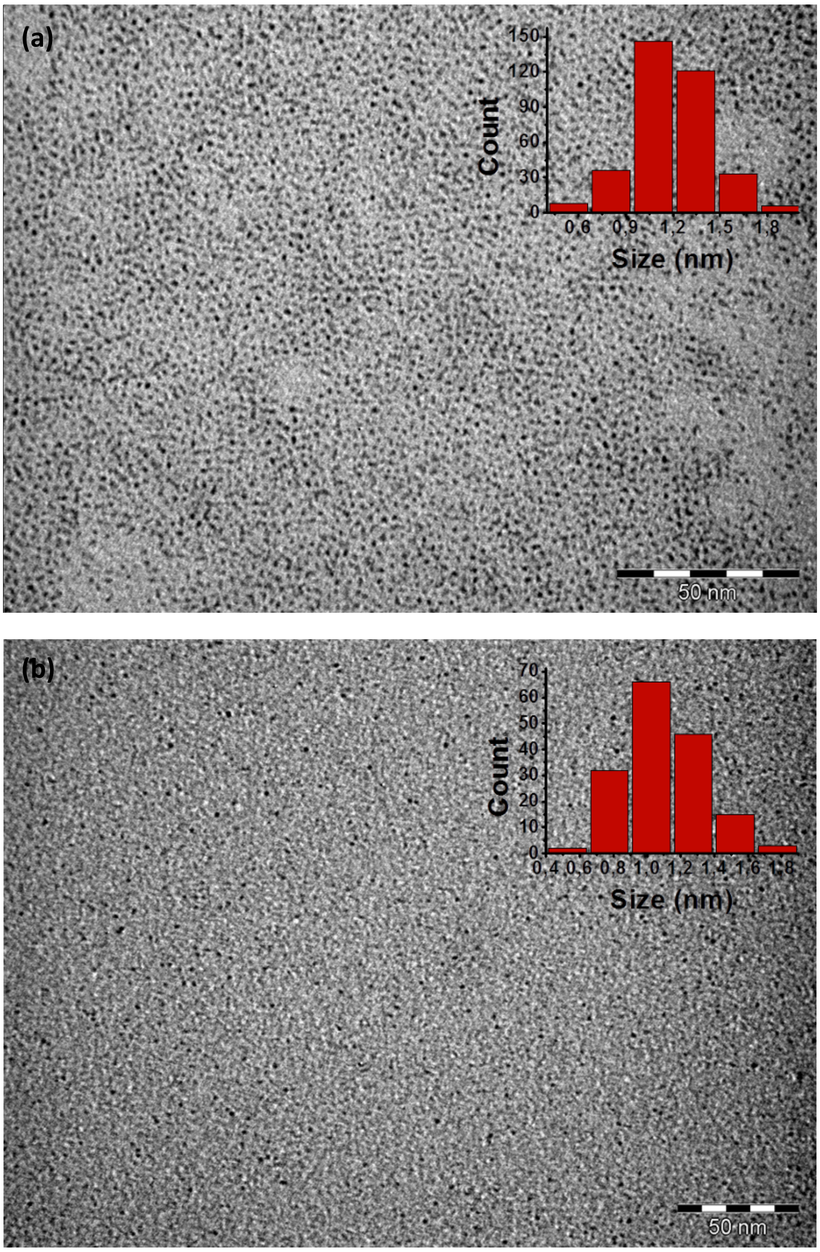


Figure S6. (a) TEM image of Re/HDA NPs prepared at 120°C in 4 days with 1 molar equiv. of HDA (b) TEM image of Re/PVP NPs prepared at 120°C in 4 days with 10 wt.% Re content.

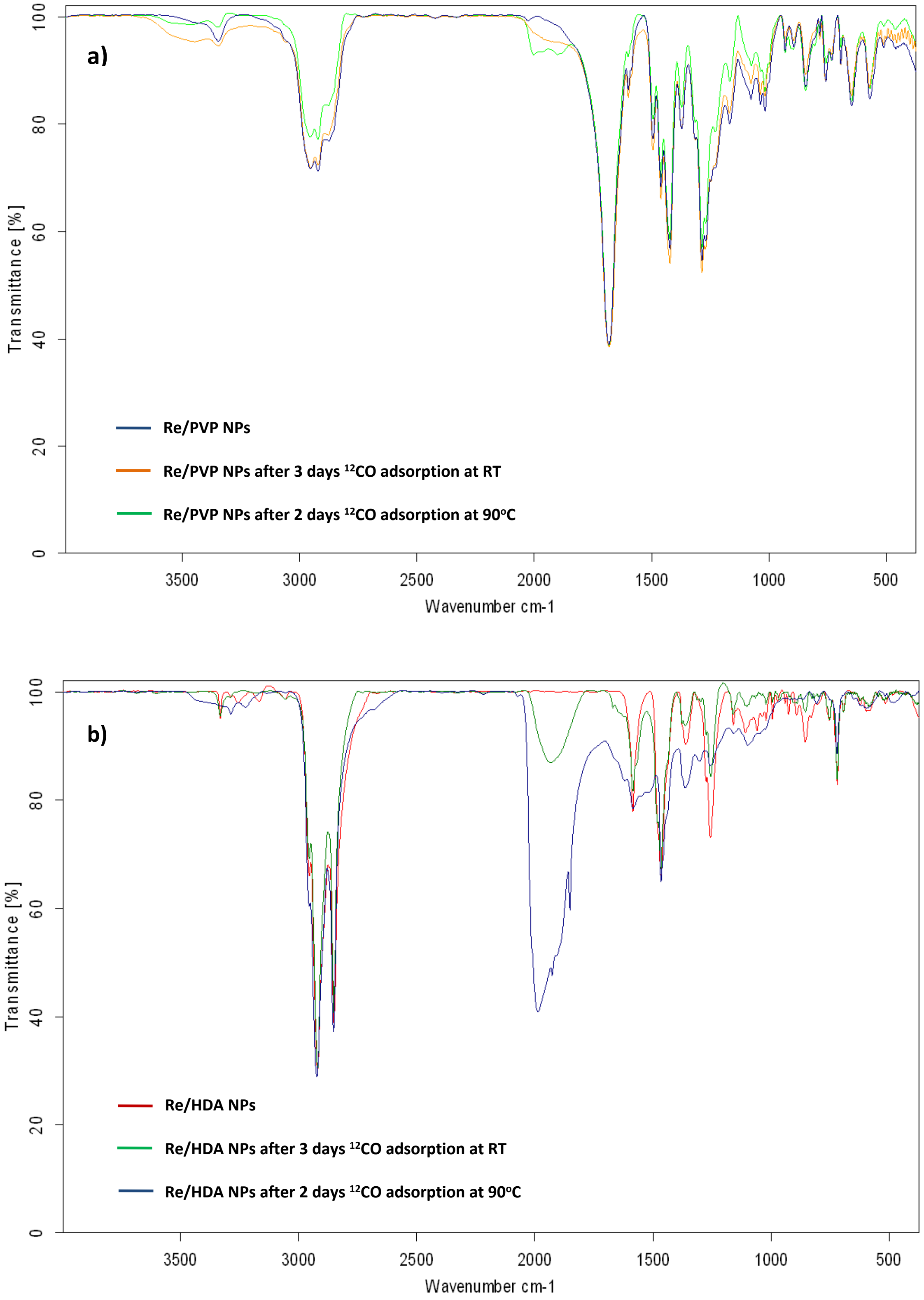
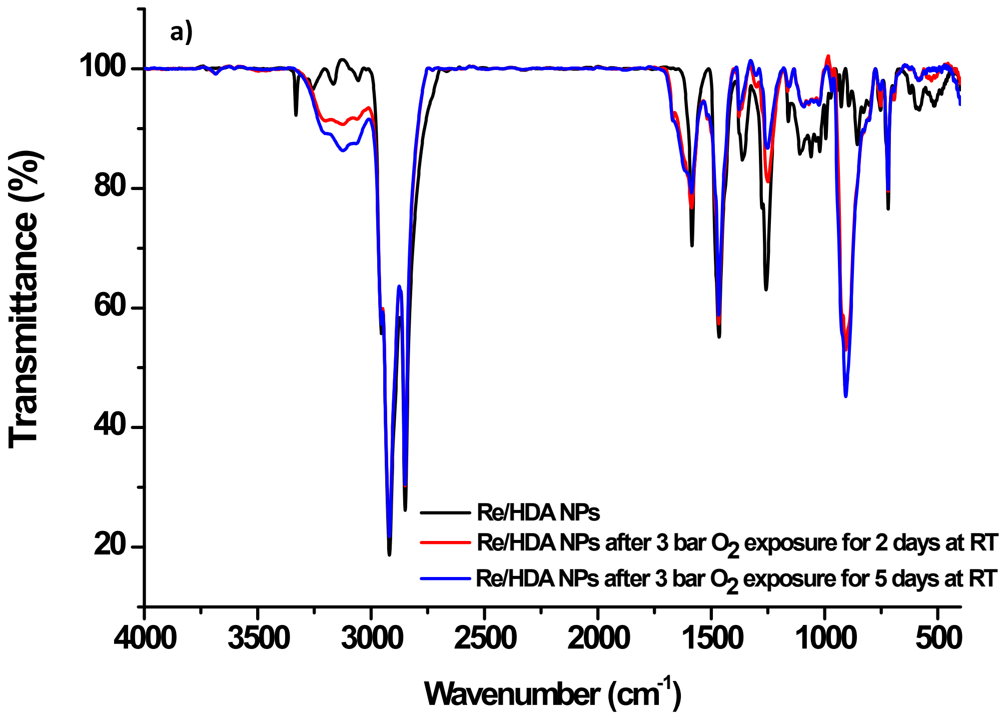


Figure S7. FT-IR spectra of (a) Re/PVP NPs and (b) Re/HDA NPs after exposure of 3 bar ^{12}CO at RT for 2 days and 90^{o}C for 3 days.



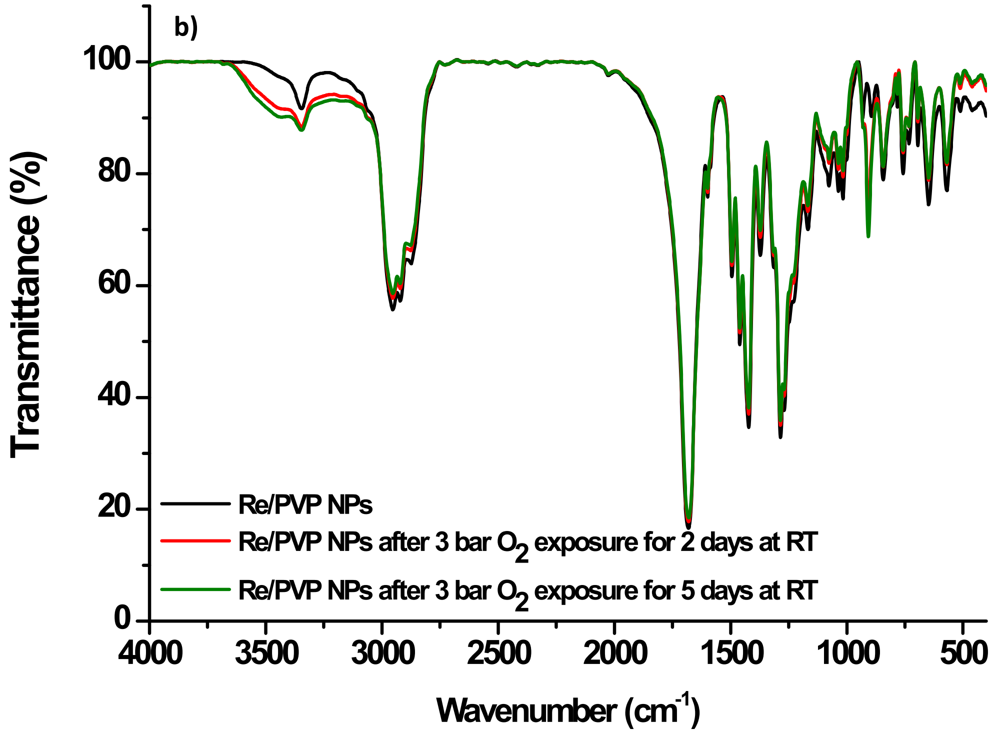


Figure S8. a) FT-IR spectra of oxidized Re/HDA NPs compared to Re/HDA NPs (120°C in 2 days with 1 molar equiv. of HDA) and b) FT-IR Spectra of oxidized Re/PVP NPs compared to Re/PVP NPs (120°C in 2 days with 10 wt.% Re content).

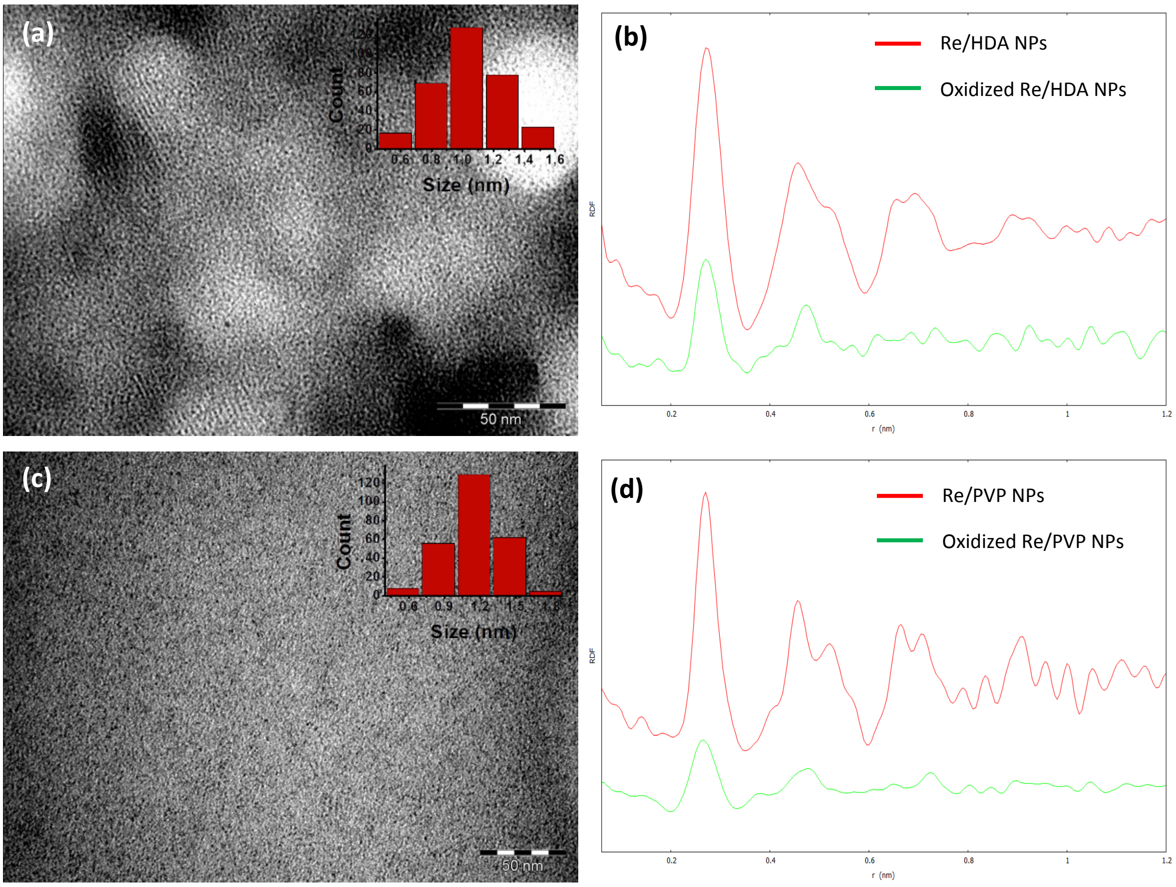


Figure S9. (a) and (c) TEM images of oxidized Re/HDA NPs and Re/PVP NPs respectively, the inset is the size histogram of the corresponding images; (b) and (d) WAXS Analysis of oxidized Re/HDA NPs and Re/PVP NPs respectively and their comparison with pure Re NPs.