Supporting information

A Generic Wet Impregnation Method for Preparing Substrate-Supported Platinum Group Metal and Alloy Nanoparticles with Controlled Particle Morphology

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Experimental Methods

Materials

Platinum acetylacetonate ($Pt(acac)_2$, 97%), rhodium acetylacetonate ($Rh(acac)_3$, 97%), palladium acetylacetonate ($Pd(acac)_2$, 99%), cobalt acetylacetonate ($Co(acac)_2$, 97%), nickel acetylacetonate ($Ni(acac)_2$, 95%) and copper acetylacetonate ($Cu(acac)_2$, 99.99%) were purchased from Sigma-Aldrich. Carbon support (C, Vulcan® XC-72R) was purchased from Cabot. Aluminum oxide (Al_2O_3, 98%), Titanium oxide (TiO_2, anatase, 99.7%), Cerium oxide (<25 nm nanopowder), Silicon oxide (10-20 nm nanopowder, 99.5%) were also purchased from Sigma-Aldrich. Acetone (C_3H_6O, 99.8%), chloroform ($CHCl_3$, 99.9%) and anhydrous ethanol (EtOH, 95.3%) were from Fisher Scientific. Hydrogen (H_2, 99.999%), carbon monoxide (CO, 99.999%) and nitrogen (N_2, 99.999%) gases were obtained from Praxair.

Synthesis of Cubic Platinum (Pt) Nanocrystals

The carbon-supported cubic platinum nanocrystals (Pt/C) were prepared using a solid-state chemistry method, which involved impregnation of metal precursor on a C support and reducing them in CO and H_2 gas mixture. In a typical experiment for preparing the cubic platinum nanocrystals on carbon substrate (Pt/C) (10 wt.% Pt), C was thermally treated at 300 °C in air overnight for removing moisture prior to use. $Pt(acac)_2$ (20.0 mg or 0.05 mmol) was first dissolved in chloroform (3 mL), and then added drop wisely onto the pretreated C support (90 mg) under vigorous stirring. After the impregnation, the mixture was immediately transferred to a furnace which was then purged by N_2 flow for 30 minutes. The mixtures were reduced by being heated at a ramping rate of 5 °C/min to 200 °C and maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Tetrahedral Palladium (Pd) Nanocrystals

The carbon-supported tetrahedral palladium nanocrystals (Pd/C) were prepared using a similar method applied for preparation of cubic Pt/C. In which, C was thermally treated at 300 ^oC in air overnight for removing moisture prior to use. $Pd(acac)_2$ (28.6 mg or 0.05 mmol) was first dissolved in chloroform (3 mL), and then added drop wisely onto the pretreated C support (90 mg) under vigorous stirring. After the impregnation, the mixture was immediately transferred to a furnace which was then purged by N_2 flow for 30 minutes. The mixtures were reduced by being heated at a ramping rate of 5 °C/min to 100 °C and maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Octahedral Rhodium (Rh) Nanocrystals

$Rh(acac)_3$ (38.9 mg or 0.05 mmol) was first dissolved in chloroform (3 mL), and then added drop wisely onto the pretreated C support (90 mg) under vigorous stirring. After the impregnation, the solid mixture were immediately transferred into a ceramic boat and then into the horizontal furnace, which has been purged by N_2 flow since 30 minutes before following by H_2/CO (5/150 cm^3/min) for another 30 minutes. After that, the mixture-loaded ceramic boat was covered by an alumina foil under continuous H_2/CO flow and reduced by being heated at a ramping rate of 5 °C/min to 200 °C and

maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Octahedral Pt_3Ni/C Alloy Nanocrystals

$Pt(acac)_2$ (40 mg or 0.1 mmol) and $Ni(acac)_2$ (8.6 mg or 0.033 mmol) were first dissolved in chloroform (4 mL), and then added drop wisely onto the pretreated C support (80 mg) under vigorous stirring. After the impregnation, the mixture was immediately transferred to a furnace which was then purged by N_2 flow for 30 minutes. The mixtures were reduced by being heated at a ramping rate of 5 °C/min to 200 °C and maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Octahedral Pt_3Co/C Alloy Nanocrystals

$Pt(acac)_2$ (40 mg or 0.1 mmol) and $Co(acac)_2$ (8.6 mg or 0.033 mmol) were first dissolved in chloroform (4 mL), and then added drop wisely onto the pretreated C support (80 mg) under vigorous stirring. After the impregnation, the mixture was immediately transferred to a furnace which was then purged by N_2 flow for 30 minutes. The mixtures were reduced by being heated at a ramping rate of 5 °C/min to 200 °C and maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Octahedral PtRh/C Alloy Nanocrystals

$Pt(acac)_2$ (40 mg or 0.1 mmol) and $Rh(acac)_3$ (40 mg or 0.1 mmol) were first dissolved in chloroform (6 mL), and then added drop wisely onto the pretreated C support (80 mg) under vigorous stirring. After the impregnation, a stainless-steel vessel and the solid mixture were immediately transferred to a furnace which was then purged by N_2 flow for 30 minutes following by H_2/CO (5/150 cm^3/min) for 30mins. After that, the mixture was sealed into the stainless-steel vessel under the continuous H_2/CO flow and reduced by being heated at a ramping rate of 5 °C/min to 200 °C and maintaining at the temperature for 1 hour. The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Cubic Pt_4Cu/C Alloy Nanocrystals

$Pt(acac)_2$ (40 mg or 0.1 mmol) and $Cu(acac)_2$ (6.7 mg or 0.025 mmol) were first dissolved in chloroform (4 mL), and then added drop wisely onto the pretreated C support (80 mg) under vigorous stirring. After the impregnation, the mixture was immediately transferred to a furnace which was then purged by N_2 flow for 20 minutes. The mixtures were reduced by being heated at a ramping rate of 5 °C/min to 200 °C and maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Synthesis of Octahedral Pt_3Ni Alloy Nanocrystals on Al_2O_3, TiO_2, SiO_2 and CeO_2

Prior to use, all the supports were thermally treated at 700 ^oC in air overnight for removing moisture. $Pt(acac)_2$ (40 mg or 0.1 mmol) and $Ni(acac)_2$ (8.6 mg or 0.033 mmol) were first dissolved in chloroform (4 mL), and then added drop wisely onto the 180 mg of the pretreated Al_2O_3, TiO_2, SiO_2 and CeO_2 supports under vigorous stirring. After the impregnation, the mixture was immediately transferred to a furnace which was then purged by N_2 flow for 30 minutes. The mixtures were reduced by being heated at a ramping rate of 5 °C/min to 200 °C and maintaining at the temperature for 1 hour in H_2/CO (5/150 cm^3/min). The gas atmosphere was switched back to N_2 and the product was cooled down to room temperature after the reaction was complete. The samples were then collected and stored in N_2 before any characterizations and testing.

Characterization

Transmission electron microscopy (TEM) characterizations of the prepared samples were conducted with a JEOL JEM-1230 microscope operated at 120 KV. High-resolution TEM (HRTEM) images were taken using a FEI Tecnai G2 F20 microscope operated at 200 KV. The X-ray diffraction (XRD) patterns were recorded on a Bruker AXS Dimension D8 X-Ray diffractometer with Cu Kα radiation source. Composition Analyses of the samples were performed using quantitative EDX equipped on a JEOL-7401 field emission scanning electron microscope (FESEM) with an operating voltage at 25 KV. All the samples are measured in three distinct locations. Compositions of PGM alloy nanoparticles are presented as the average values with standard deviations. X-ray photoelectron spectroscopy (XPS) was accomplished using a PHI VersaProbe II Scanning XPS Microprobe with Al-K α line excitation source. In-situ diffuse reflectance infrared Fourier transform (DRIFT) measurements were carried out using a Thermo Scientific Nicolet 6700 spectrometer, which is equipped with a DRIFT system and high temperature/high pressure reaction cell (Praying MantisTM, Harrick Scientific Products, Inc.). FTIR spectra of silica supported fresh Pt-Ni sample before and after exposing to air were also recorded by the DRFITspectrometer.

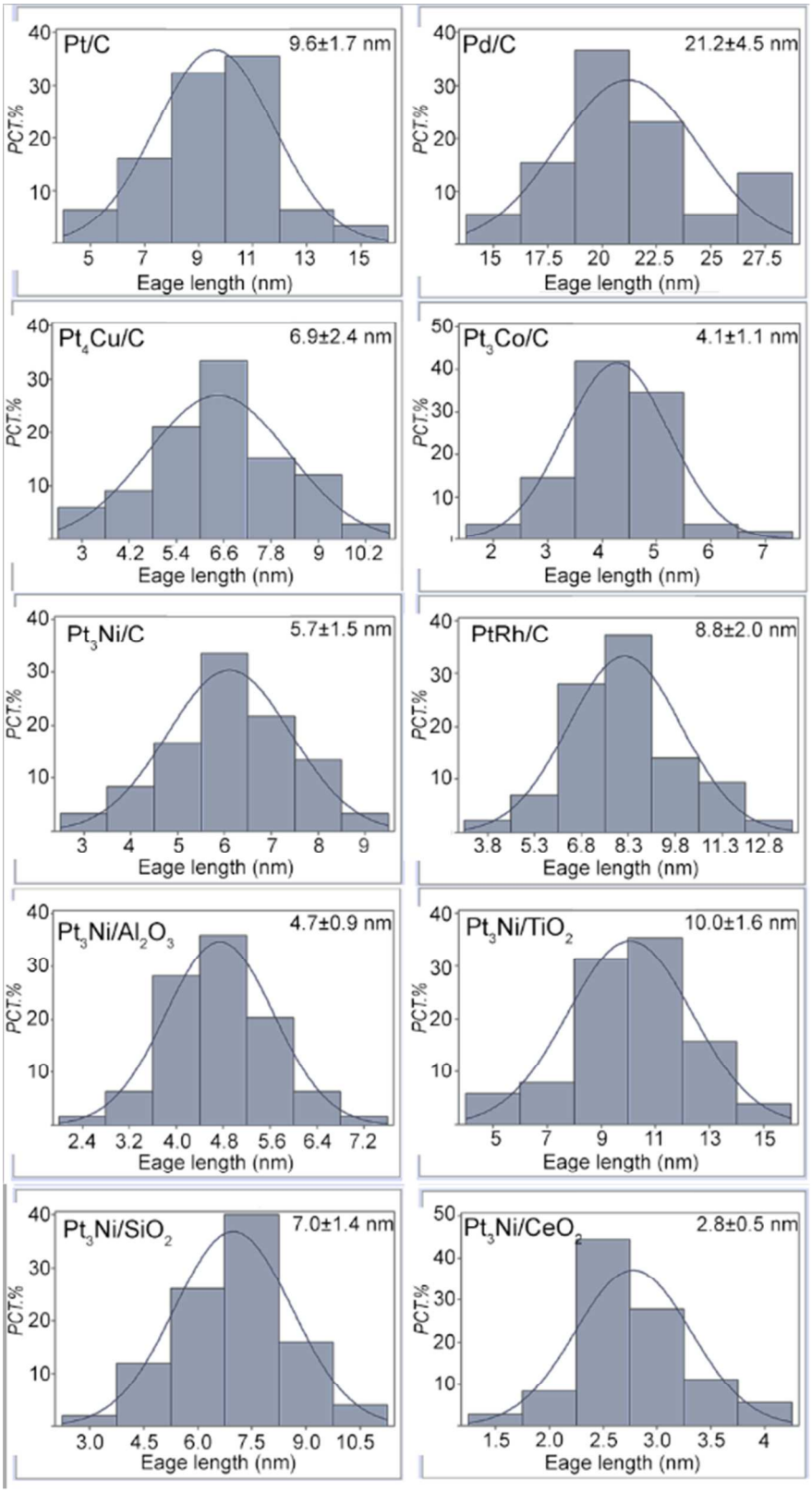

Fig. S1 Size distributions histogram of prepared PGM and alloy particles. The number of particles is over 100 in the statistical measurement.

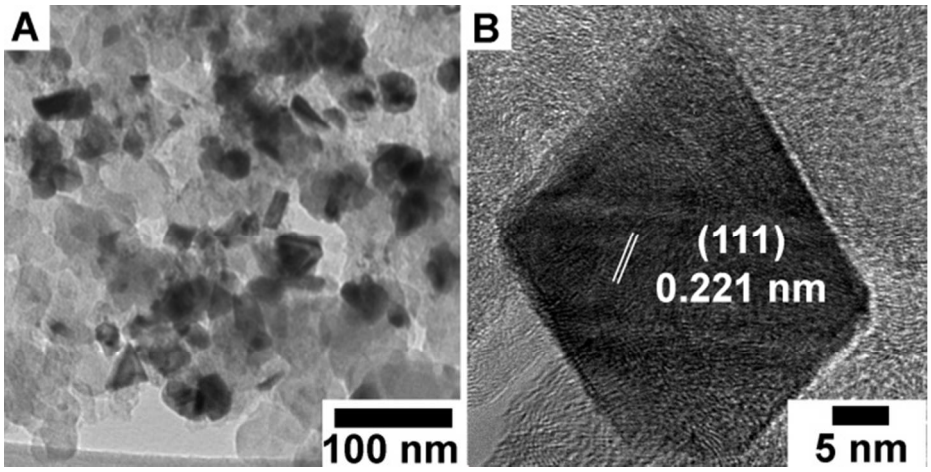

Figure S2. (A) TEM and (B) HRTEM images of as-prepared Rh/C nanoparticles.

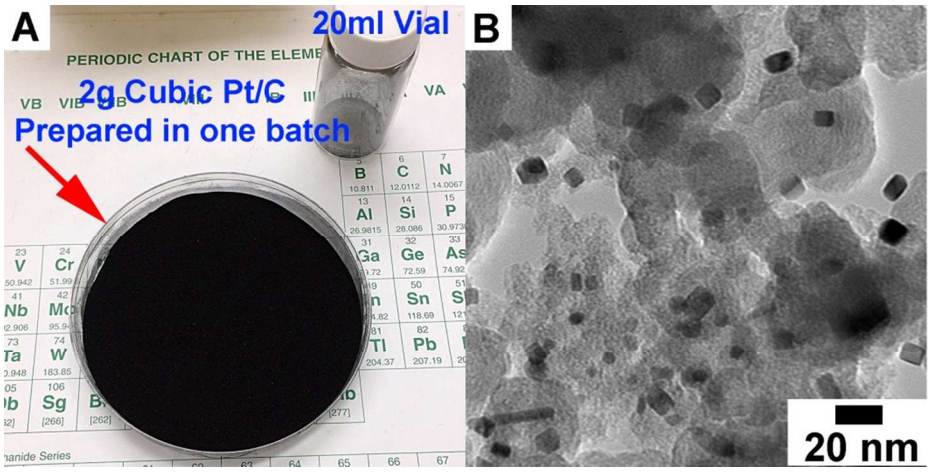

Figure S3. (A) Photo and (B) TEM image of as-prepared cubic Pt/C with a batch size of 2 gram.

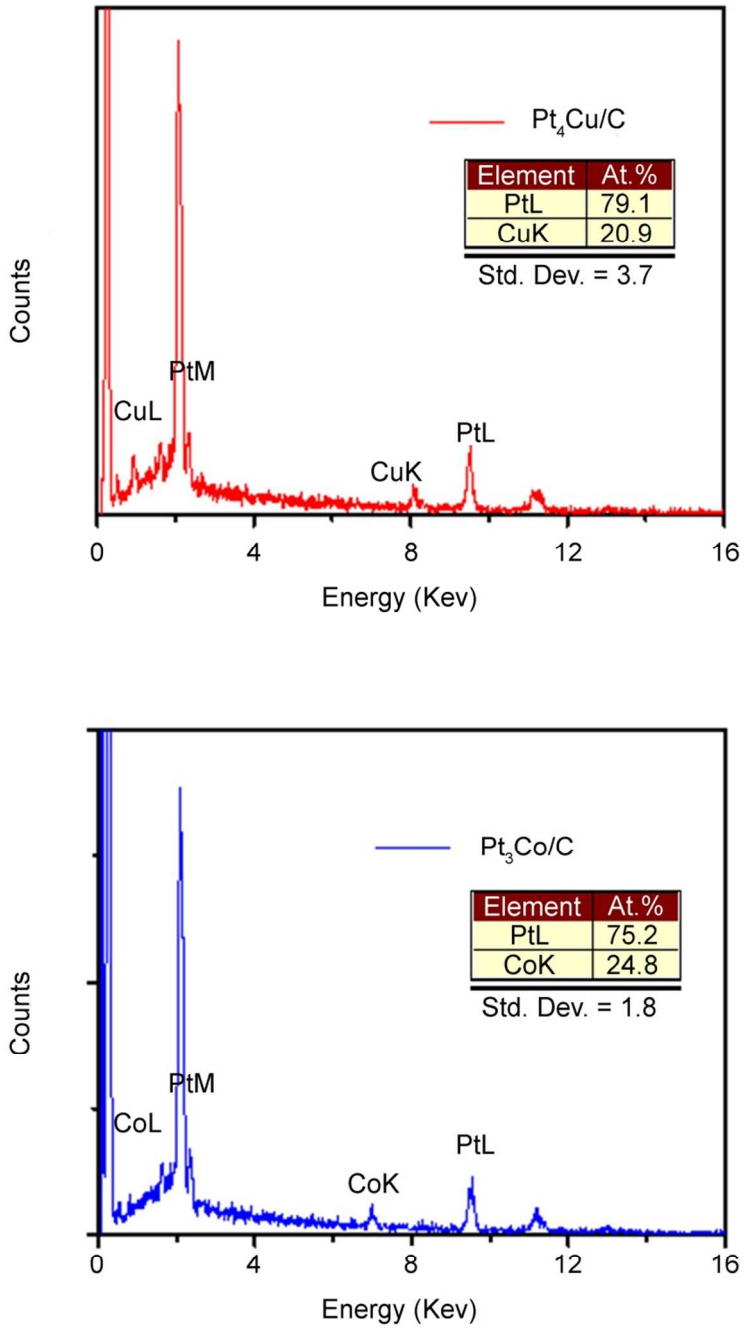

Figure S4. EDX spectra of as-prepared octahedral Pt_4Cu/C and octahedral Pt_3Co/C nanoparticles. Both samples are measured in three distinct locations and composition shows the average values with standard deviation 3.7% and 1.8% respectively.

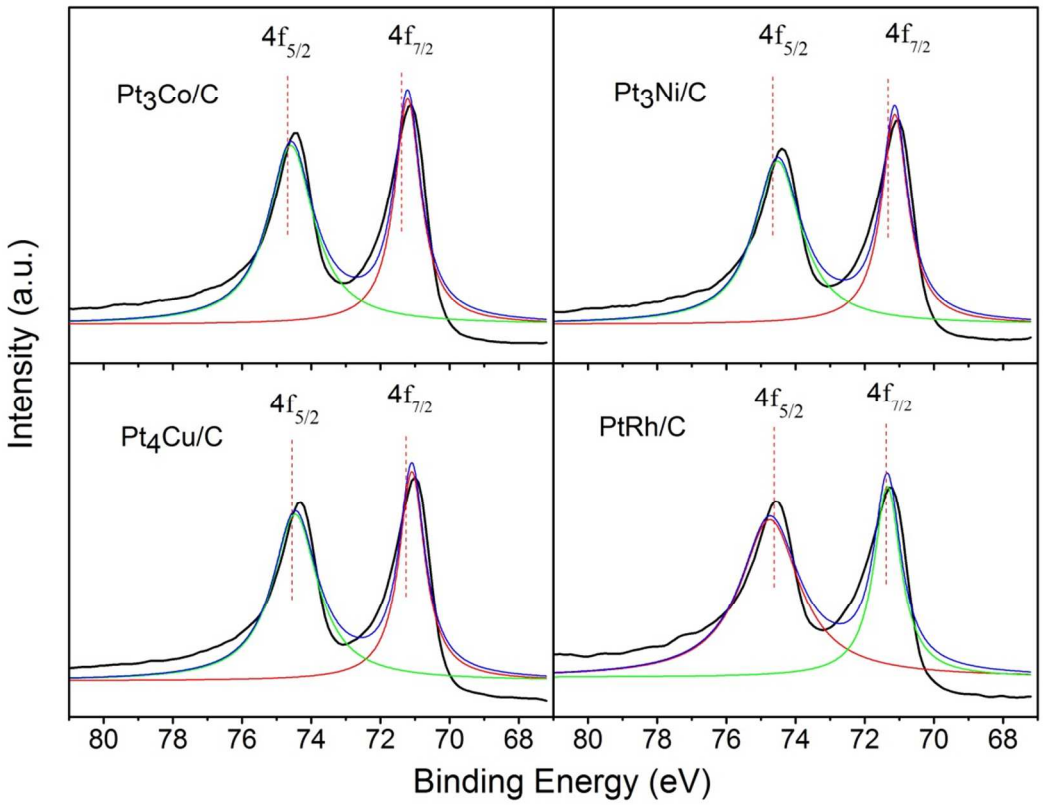

Fig. S5 Pt XPS spectra of Pt3Co/C, Pt3Ni/C, Pt4Cu/C and PtRh/C. The red dot lines represent the characteristic peaks of metallic Pt prepared on the same support. All the states of Pt 4f7/2 and 4f5/2 have been detected shifting to lower binging energy positions.

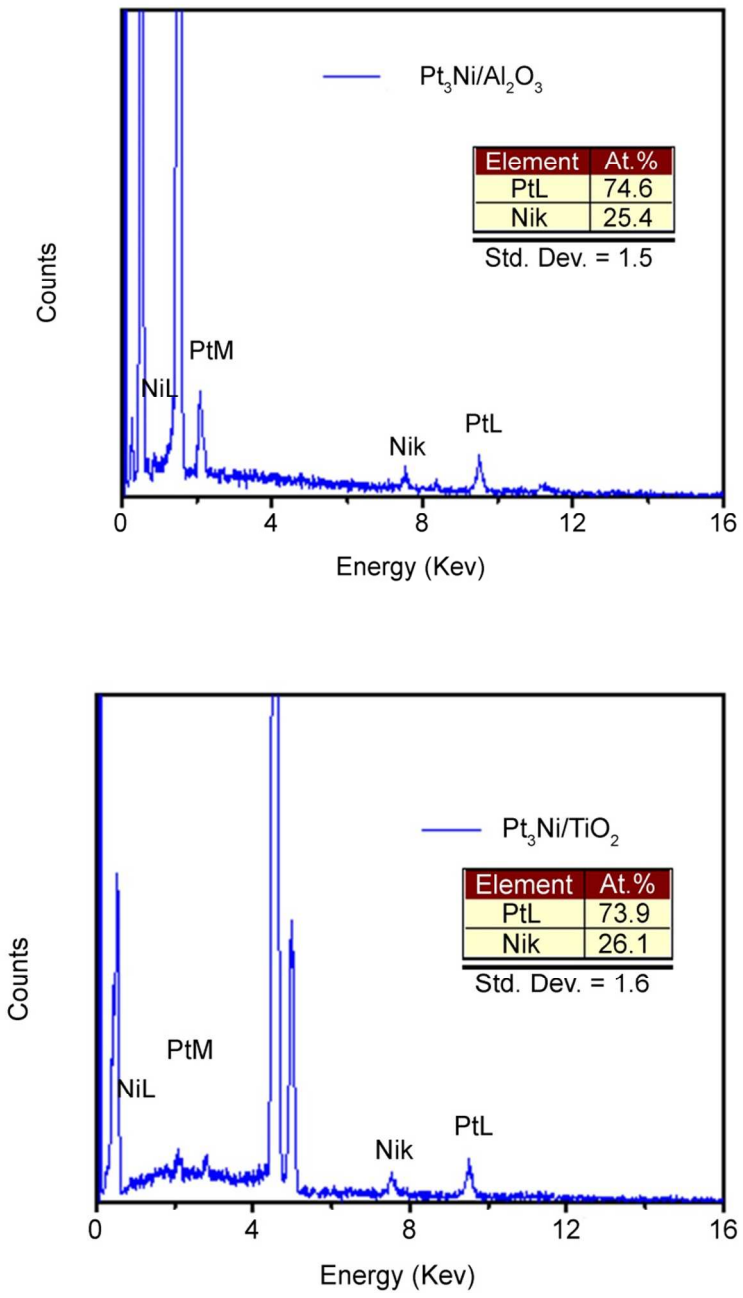

Figure S6. EDX spectra of as-prepared Al_2O_3 and TiO_2-supported octahedral Pt_3Ni nanoparticles. Both samples are measured in three distinct locations and composition shows the average values with standard deviation 1.5% and 1.6% respectively.

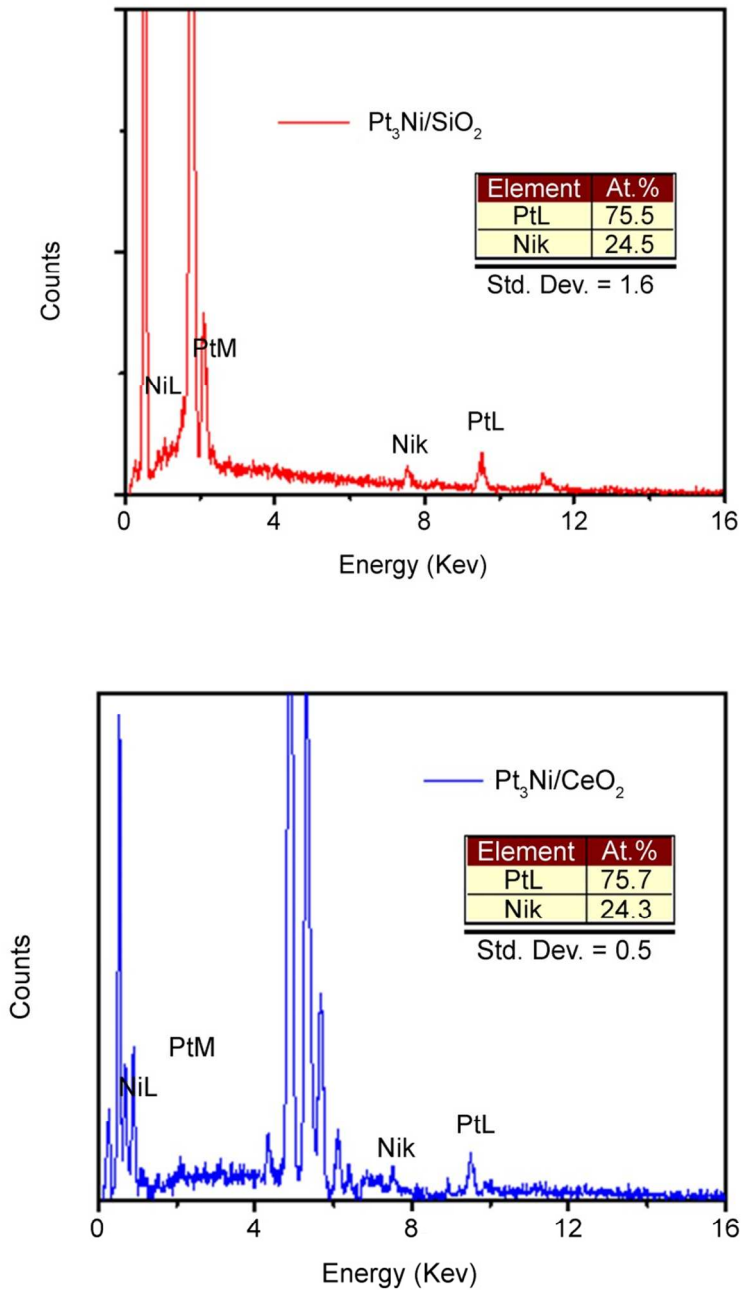

Figure S7. EDX spectra of as-prepared SiO_2 and CeO_2-supported Pt_3Ni nanoparticles. Both samples are measured in three distinct locations and composition shows the average values with standard deviation 1.6% and 0.5% respectively.

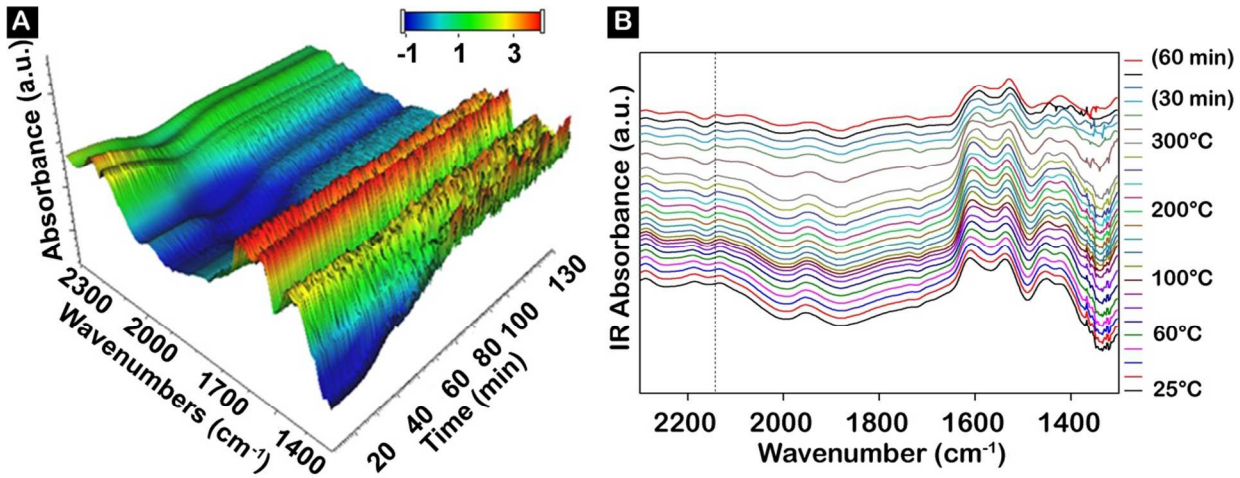

Figure S8. (A) In situ-FTIR spectra and (B) representative spectra in range of wavenumber of interest of $Ni(acac)_2$ on SiO_2 substrate upon heating the mixture at 5 °C min^{-1} to 300 °C and then keeping it at this temperature for 1 h in 150/5 cm^3 min^{-1} CO/H_2.

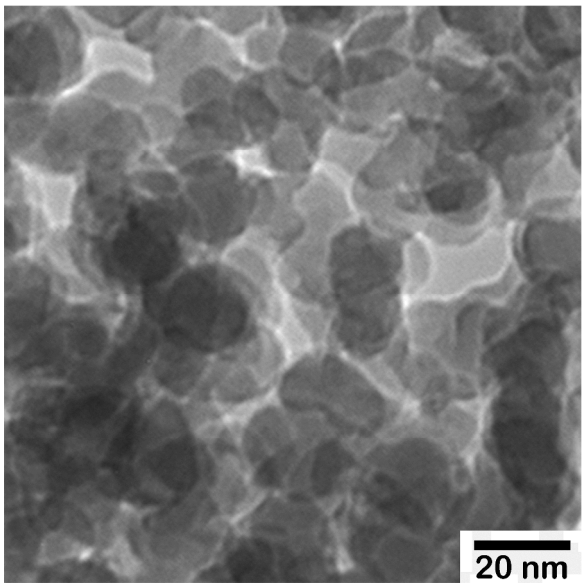

Figure S9. TEM image of SiO_2-supported $Ni(acac)_2$ after being reduced at 300 °C for 1 hour in 150/5 cm^3 min^{-1} CO/H_2.

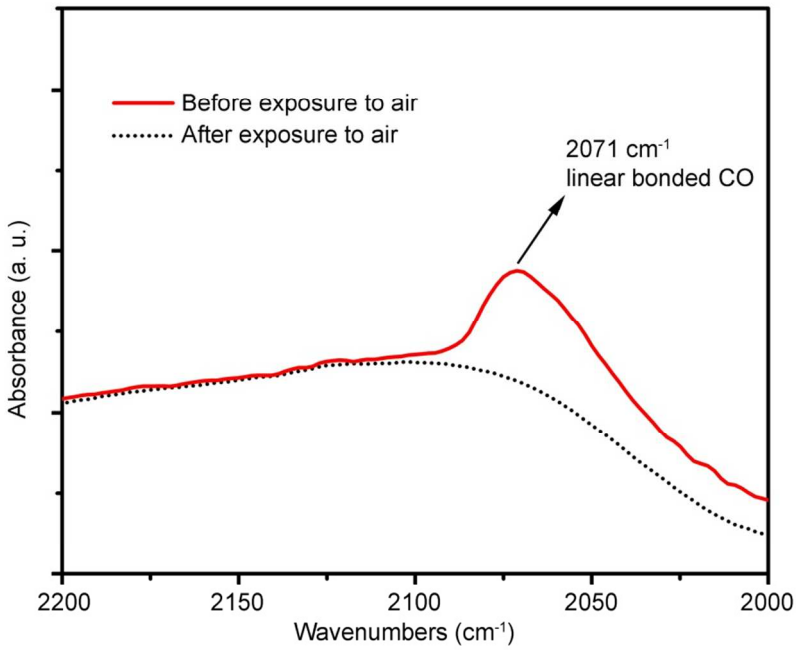

Fig. S10 FTIR CO absorbance spectra of fresh prepared octahedral Pt-Ni nanoparticles before and after exposure to dry air.