Supplementary information for:

Solvent dispersible nanoplatinum-carbon nanotube hybrids for application in homogeneous catalysis

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Materials and instrumentations:

Multi-walled carbon nanotubes (MWNTs) were purchased from Cheap Tubes Inc. (CAS# 7782-42-5, 95 %). The original MWNTs had diameter in the range of 20-50 nm and the length was about 50 μm. All other chemicals were purchased from Sigma Aldrich Inc. The preparation of dispersible nanoplatinum coated MWNTs (NP-MWNTs) were carried out in a microwave accelerated reaction system (CEM Mars) fitted with internal temperature and pressure controls. The 100 mL reaction chamber was lined with Teflon PFA® (perfluoroalkoxy) with an operating range of 0~200 °C and 0~200 psi. The scanning electron microscopy (SEM, LEO 1530 VP) and transmission electron microscopy (TEM, LEO 922 200 kV ultrahigh- resolution microscope) were used for studying the morphology of the samples. Energy dispersive X-ray spectrometer (EDS) was performed on the EDAX new silicon drift detector (SDD) with superior capabilities for surface mapping. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer 15-255GAR spectrometer with dual anode X-ray source. For the survey scan, the pass energy of 100 eV was used by Al anode. Thermo gravimetric analysis (TGA) was performed using a Pyris 1 TGA from PerkinElmer Inc. to quantify nanoplatinum concentration.

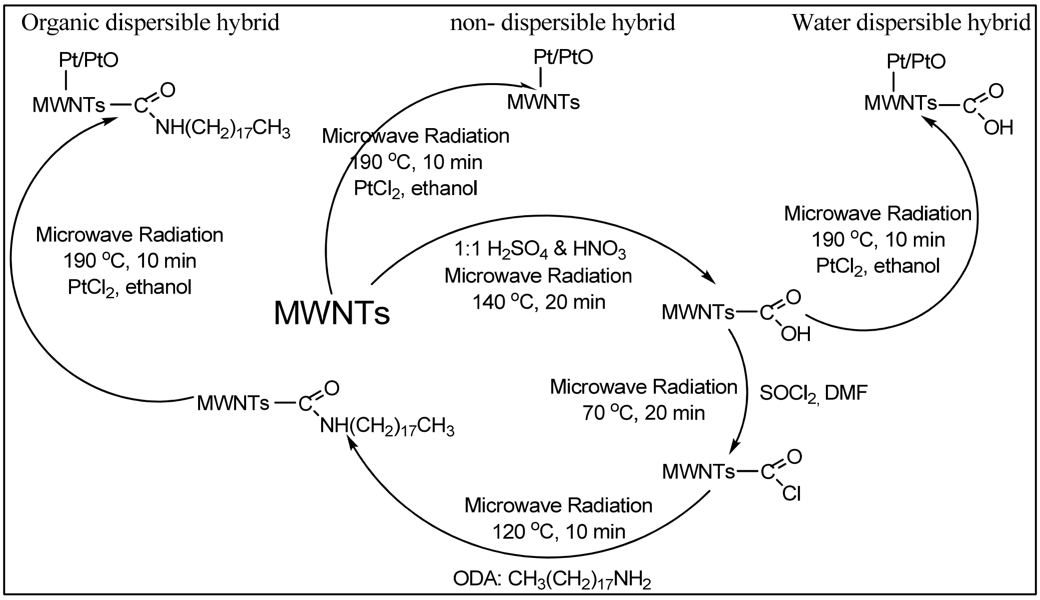
Microwave synthesis of dispersible NP-MWNT hybrids:

The microwave synthesis of polar (p-MWNTs) and nonpolar organic dispersible MWNTs (o-MWNTs) were carried out as per procedures described before[15,16]. In a typical reaction, 300 mg of the MWNTs were added to 25 mL 1:1 concentrated H_2SO_4 and HNO_3. The reaction vessels were subjected to the microwave radiation with temperature set at 140 ^{o}C for 20 min. After the reaction, the reactants were transferred into a beaker with deionized (DI) water and cooled down to room temperature. The product was filtered under vacuum using a Teflon membrane with pore size of 0.45 μm. The resulting solids were thoroughly washed with DI water until a neutral pH was reached. The solids were stored in the vacuum oven for drying at 70 ^{o}C for 12 h to yield a dry product.

The p-MWNTs were used as the starting material to synthesize organic dispersible MWNTs. In a typical reaction, 1000 mg of p-MWNTs was added to a reaction vessel together with 50 mL thionyl chloride ($SOCl_2$) and 2 mL dimethylformamide (DMF). The reaction vessels were subjected to microwave radiation around 70 ^{o}C for 20 min. The microwave method shortened this procedure from 24 h to just 20 min. The final suspension was filtered and washed with tetrahydrofuran (THF) till there was no brown color in the solution. These solids were dried in a vacuum oven at room temperature for 12 h to obtain MWNTs with –COCl functionality (efficiency of 93.3 %). After modification, a 1:10 mixture of the MWNTs-COCl and octadecylamine (ODA) were loaded in the vessel and heated under the microwave radiation at 120 ^{o}C for 10 min. After cooling to room temperature, the excess ODA was first removed by thoroughly washing with hot ethanol. The remaining solids were filtered through a membrane with the pore diameter of 0.45 μm. The solid residues were washed with dichloromethane to remove unreacted ODA. The resultant black solid was dried at room temperature under vacuum to obtain final product (o-MWNTs). The weight percentage of ODA in MWNTs was about 10.5 %. The o-MWNTs were highly dispersible in organic solvents such as o-dichlorobenzene (ODCB), xylene and THF.

The original MWNTs, p-MWNTs and o-MWNTs were used as the starting materials for synthesizing NP-CNTs. In the typical set of reactions, 100 mg of the selected CNTs was added to a reaction chamber together with 30 mL of 12.5 mM platinum dichloride ($PtCl_2$) ethanol mixture, and the reaction vessel was subjected to microwave radiation. The microwave power was set to 80 % of a total of 1600 watts, and the temperature was set at 190 °C. The reaction was carried out for 10 min. Once cooled, the mixture was filtered, washed with 0.5 N hydrochloric acid (HCl) solutions and DI water separately. The product was dried at room temperature in the vacuum oven for 12 h. The samples in powder form were weighed for further analysis. The NP coated unfunctionalized MWNTs, p-MWNTs and o-MWNTs are referred to as NP-MWNTs, p-NP-MWNTs and o-NP-MWNTs respectively.

The different steps in the process are described in Scheme S1. The whole process is rapidly under microwave induced conditions, leading to the development of fast and scalable methodology.



Scheme S1. Reaction schemes for microwave synthesis dispersible NP coated MWNTs.

Energy dispersive X-ray spectroscopy measurements:

EDS data provided the elemental analysis for the different NP-CNT hybrids (Figures are showed in S1). The original MWNTs showed mainly the presence of C, O and residual Co (2.0 %), which originated from the residual catalyst. After microwave acid treatment, most metals were removed. However, after hybrid formation, large amounts of platinum existed on the tube wall. The lack of chloride on the tube surface confirmed that all the platinum dichloride had been decomposed completely.

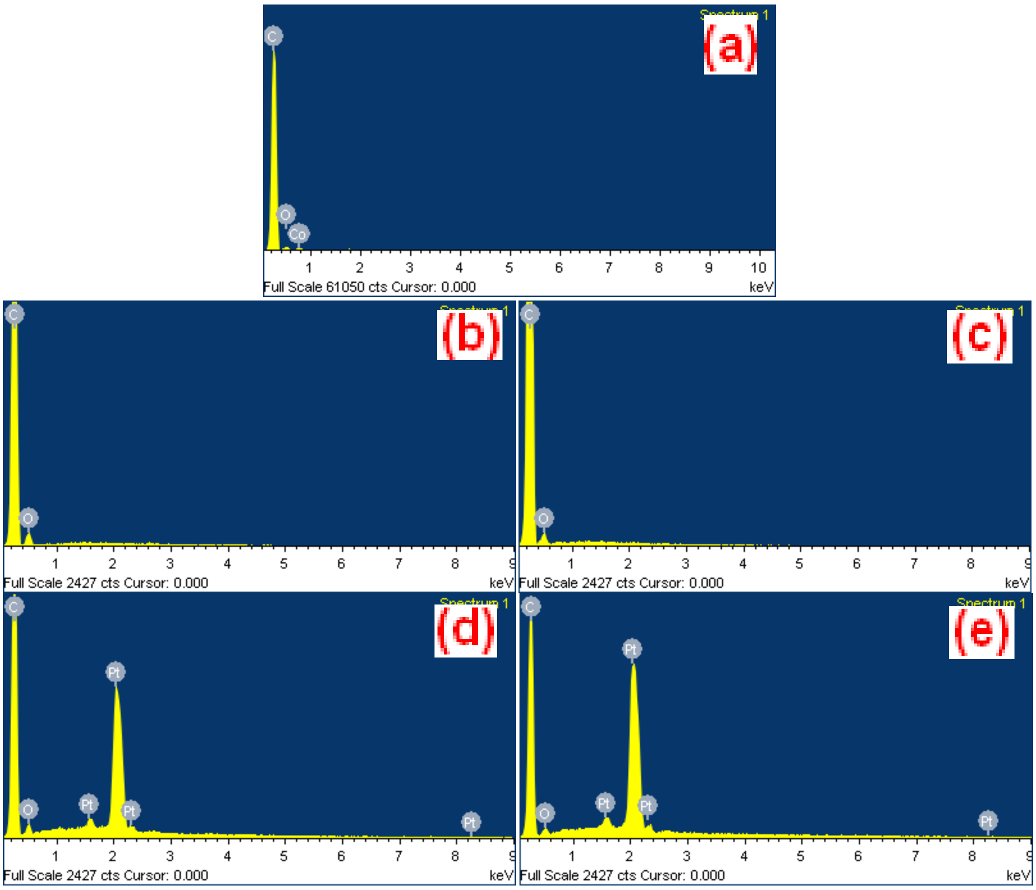


Figure S1. EDS spectra of (a) original MWNTs; (b) p-MWNTs; (c) o-MWNTs; (d) p-NP-MWNTs and (e) o-NP-MWNTs.

The novel silicon drift detector has fast data acquisition and high count rates which enabled it to collect full X-ray maps within a couple of minutes. Figure S2 are the spatial distribution of the different dispersible NP-hybrids under the magnification of 500 X. The color of red or blue represents the respective element of carbon and platinum. It is evident that the distribution of Pt on the p-MWNT and o-MWNTs were quite uniform and had high surface density.

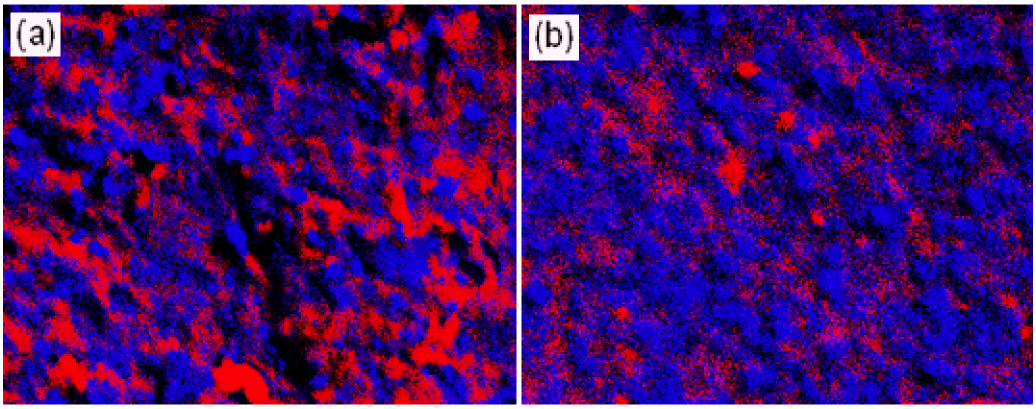


Figure S2. EDS overlay maps of respective elements: C (red color) and Pt (blue color) of: (a) p-NP-MWNTs and (b) o-NP-MWNTs. (Magnification: 500X)

Scanning electron microscopy images:

SEM images of water dispersible and organic dispersible MWNTs were showed in Figure S3 and the nanotubes did not lose their structures.

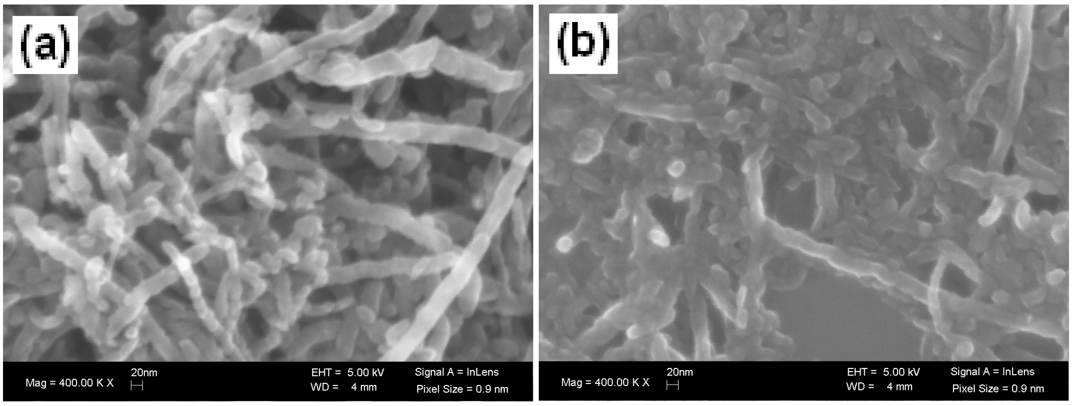


Figure S3. SEM images of: (a) p-MWNTs and (b) o-MWNTs. (Scale bar: 20 nm).

Chemistry under microwave radiation is known to be somewhat different, faster and more efficient. Microwave processing can cause superheating and lower the activation energy. In order to compare the microwave-assisted platinum-salt decomposition with other methods, the same reaction was carried out under reflux at 120 °C for over an hour. SEM images were used to look at the particle size distribution on the CNTs, and these are shown in Figures S4. S4 (a) shows incomplete decomposition with the large clusters of Pt salt, where as Figure S4 (b) shows complete decomposition and the formation of nano particles.

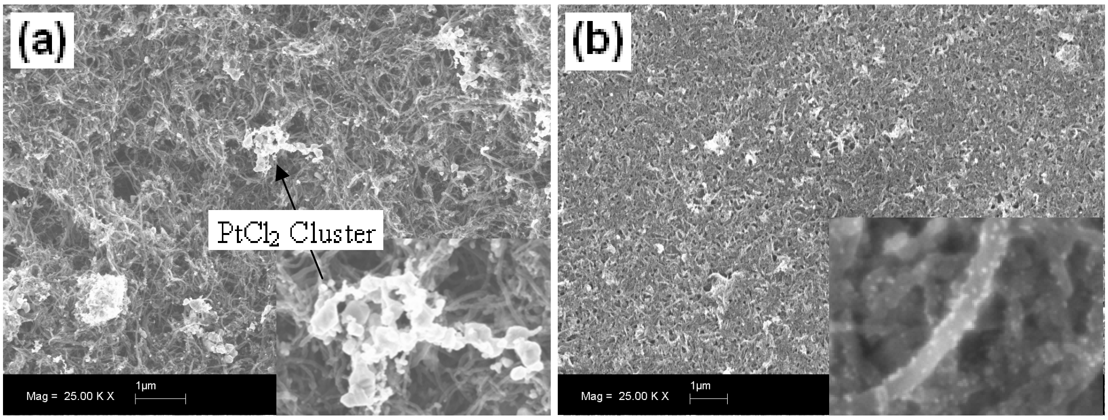


Figure S4. SEM images of $PtCl_2$ decomposition: (a) under the refluxing procedure and (b) under the microwave radiation. (Scale bar: 1 μm).

The fast microwave method is also applicable to other metals, including silver, cobalt, zinc sulfide and cadmium sulfide. Some of the preliminary microscopic images are shown in Figure S5.

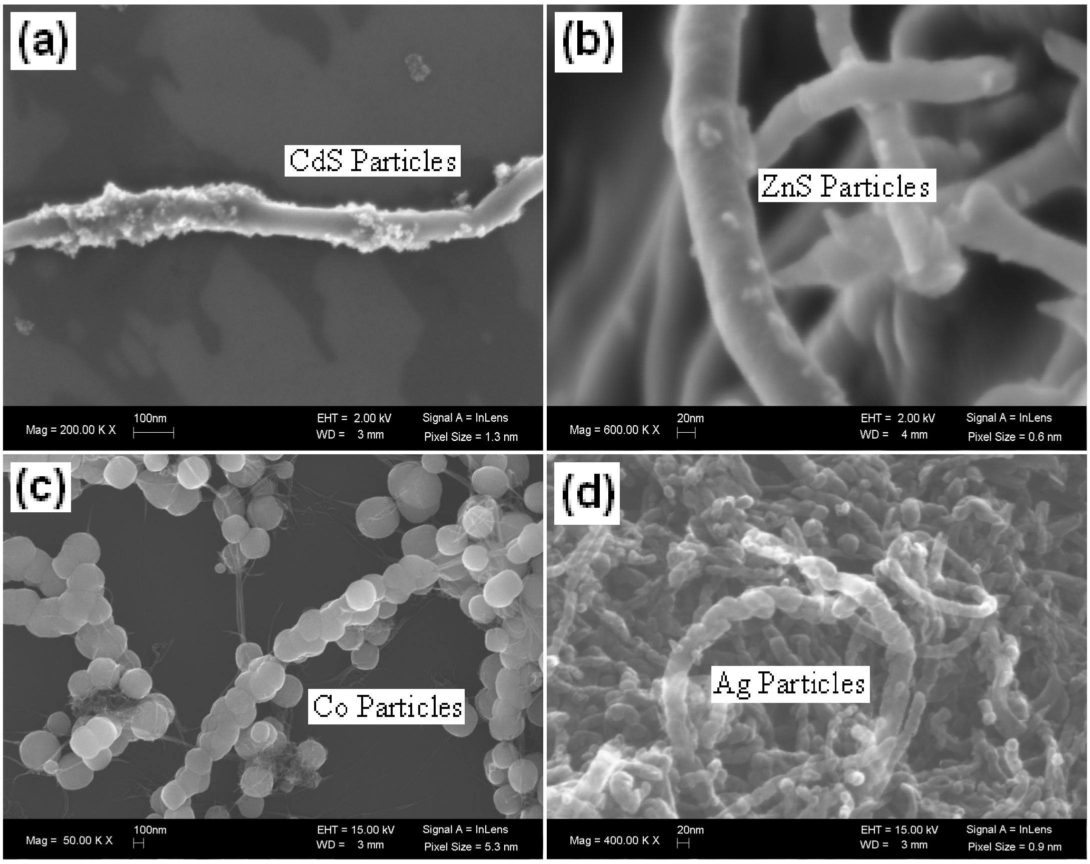


Figure S5. SEM images of nanometal or metal sulfide particles on CNT matrix under the microwave radiation: (a) cadmium sulfide particles; (b) zinc sulfide particles; (c) cobalt particles and (d) silver particles. (Scale bar: (a) and (c) 100 nm; (b) and (d) 20 nm).

Raman spectroscopy measurements:

The Raman spectra of the original MWNTs and the corresponding dispersible products are shown in Figure S6. All of the MWNTs samples showed similar Raman scattering patterns, demonstrating that microwave treated MWNT hybrids did not affect their graphite structure. The peak around 1330 cm^{-1} was assigned to the disorder induced band (D-Band), and the high peak around 1580 cm^{-1} corresponded to the tangential band (G-Band). However, these spectra showed weak energy shift. The different MWNT species consisted of different chemical bonds, so the excitation light (laser) shifts from the vibrations of chemical bonds within the molecules. The disorder in the water soluble products appeared to be larger compared to the other organic soluble products.

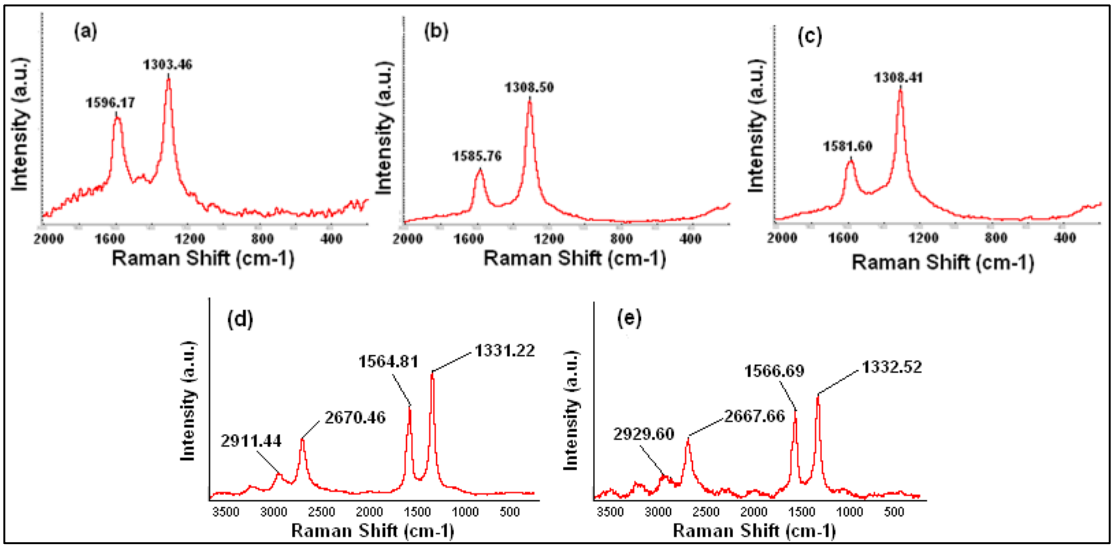


Figure S6. Raman spectra of: (a) original MWNTs; (b) p-MWNTs; (c) o-MWNTs; (d) p-NP-MWNTs and (e) o-NP-MWNTs.

The reaction steps of platinum deposition during the microwave treatment are shown in Scheme S2. During the NP deposition, the $PtCl_2$ grafted to the surface of MWNTs were oxidized to be primarily PtO. However, carbon monoxide (CO), which could be produced under microwave radiation from the original MWNTs or from the COOH functionality served as the agent to reduce PtO to metallic Pt. More metallic particles with characteristic BE (71.2 eV) of Pt (0) were obtained using p-MWNTs than o-MWNTs. In o-MWNTs, all of –COOH groups had been converted to ODA. Without reduction via the COOH, much of the platinum was present as Pt (II) with BE of 74.0 eV. The presence of the metallic Pt changed the surface morphology of the tubes, which is clearly supported from the SEM images. The Pt particles on the wall of p-NP-MWNTs resulted in a more luminescent image (when viewed under the same brightness and contrast) compared to the o-NP-MWNTs.

$$2\ PtCl_2 + O_2 \xrightarrow{ethanol} 2\ PtO + 2HCl + 2\ Cl_2 \quad (1)$$
$$C + (1/2)\ O_2 \longrightarrow CO \quad (2)$$
$$PtO + CO \longrightarrow Pt + CO_2 \quad (3)$$
$$PtO + 2\ \text{-}COOH \longrightarrow Pt + 2\ CO_2 + H_2O \quad (4)$$

Scheme S2. Reaction schemes for microwave process of reduction $PtCl_2$ salt into metallic Pt[5].

<u>Thermal gravimetric analysis:</u>

TGA was used to quantity the different components in the CNTs (shown in Figure S7). The samples were heated at 10 °C/min from room temperature to 900 °C using air at a flow rate of 10 mL/min. The resulting weight above 600 °C was attributed to the weight of residual metal or metal oxide. This particular highly-loaded sample was found to contain as much as 42.5 % (by weight) of Pt in o-NP-MWNTs and 39.6 % (by weight) in p-NP-MWNTs. These imply that approximate atomic ratio between Pt and Carbon was 4:100. The catalytic activity of the NP is evident from the TGA data, where it altered thermal stability of the CNTs. The hybrid degraded at a significantly lower temperature (nearly 200 °C) compared to the CNTs, because the NP catalyzed its oxidation. This is consistent with our previous publication, where it was demonstrated that residual metal catalysts made CNTs more unstable [Brukh, R. & Mitra, S. *J. Mater. Chem.* **2007**, *17*, 619].

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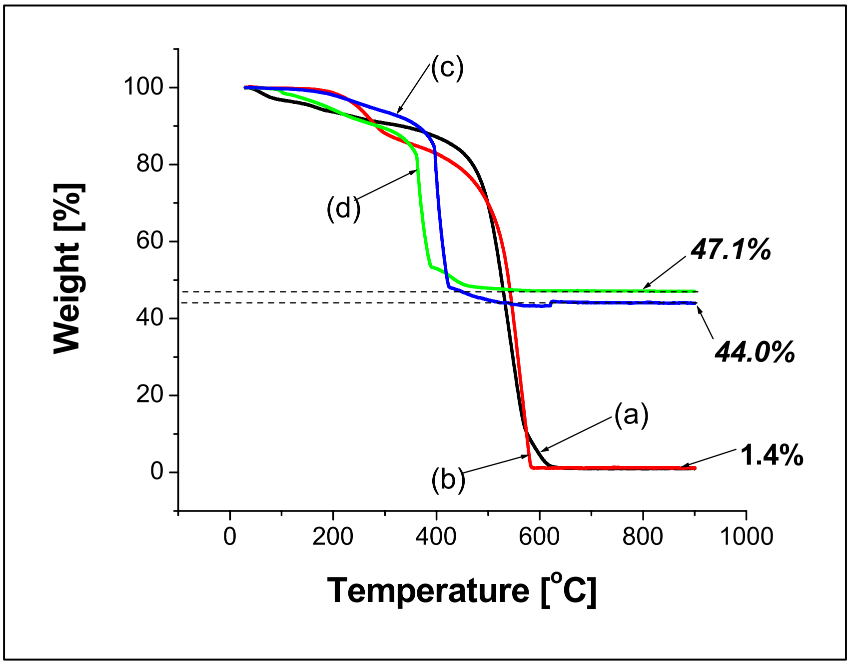

Figure S7. TGA data for: (a) p-MWNTs; (b) o-MWNTs; (c) p-NP-MWNTs and (d) o-NP-MWNTs.

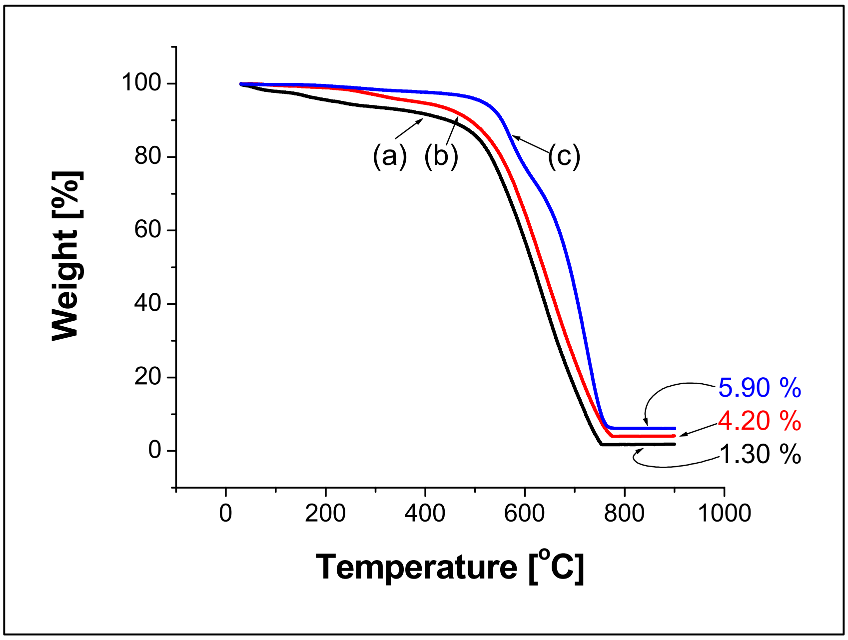

Figure S8 TGA of dispersible NP-CNT hybrids used in catalytic reactions: (a) p-MWNTs; (b) p-NP-MWNTs and (c) o-NP-MWNTs.

Catalytic hydrogenation of m-nitrochlorobenzene to m-chloroaniline:

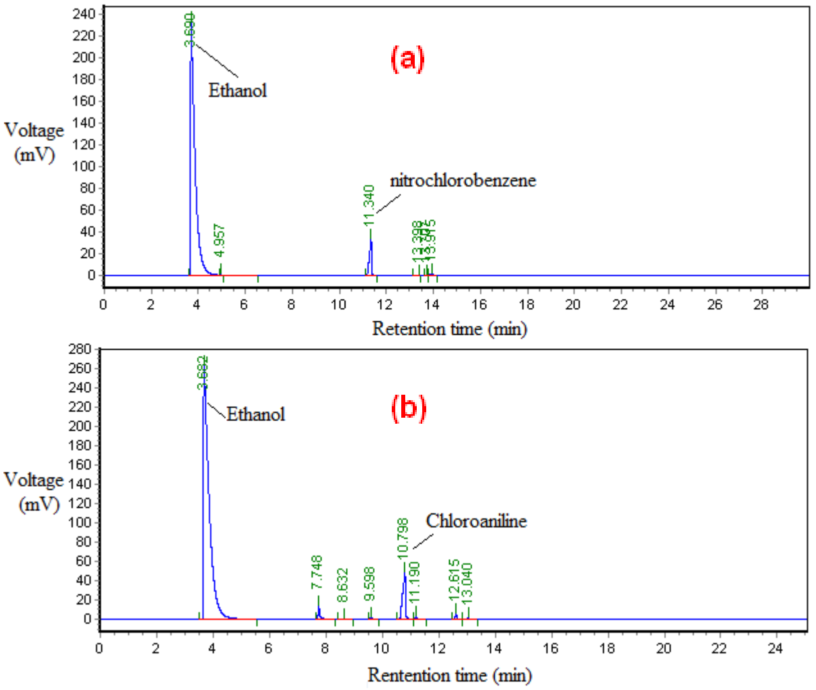

Figure S9 GC data from: (a) reactant and (b) products.

The concentration of starting $PtCl_2$ could be varied to control the final platinum loading on the nanotubes. Both o-NP-MWNT and p-NP-MWNT were tested for the liquid phase hydrogenation of m-nitrochlorobenzene to m-chloroaniline. The o-NP-MWNT was found to have limited dispersibility in the ethanol, which was used as the solvent in this reaction. In the typical catalytic reactions, 20 mL m-nitrochlorobenzene, 1 g of dispersible NP-MWNTs (with 2 weight% platinum loading, show in Figure 8S) and 50 mL ethanol were mixed into 200 mL high-pressure autoclave. The reaction was carried out under a pressure of 1.0 MPa and 100 ^{o}C for eight hours. The products were filtered under vacuum using a Teflon membrane with pore size of 0.45 µm and analyzed by gas chromatography equipped with a flame ionization detector (FID). The yield from p-NP-MWNTs was close to 100 % with negligible quantities of nitrochlorobenzene detected in the reaction product.