

Synthesis of Rh-Carbon Nanotube based Heterostructures and their Enhanced Field Emission Characteristics

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I-Experimental

Synthesis of rhodium nanostructures:

Here the Rh nanostructures were synthesized using 99.9% pure Al (after etching) plate (thickness 75 μ m) having bilateral surface area of 2 cm² as the substrate and aq. 1mM RhCl₃ (99.9% Aldrich) as the source of Rh by Galvanic displacement approach. The Al plate (99.9% from Loba chemicals Pvt. Ltd India) was first cleaned by 50 % nitric acid with sonication for 2 min. to remove the native oxide layer from surface and then rinsed vigorously with distilled water (~18 M Ω cm) and the residual adsorbed organic impurities were removed by ethanol and dried with nitrogen. This plate was then immersed in 100 mL of 1 mM aq. RhCl₃ solution at room temperature. The material growing on the surface of Al was collected, washed first with 1M NaOH to remove the impurities of Al₂O₃ imbedded into the nanostructures followed by deionized water and finally with ethanol to remove the impurities like chloride ions and excess of RhCl₃.

Functionalization of Carbon Nanotubes:

Initially, 200 mg of MWNTs (diameter: 20 \pm 1 nm, purchased from CHEMAPOL industries, Mumbai, India) were carboxylated using microwave (MW) treatment for 4 minutes at a

power of 60% of total 700 W (separated by 60 s off-time interval). An acid mixture of 98% H₂SO₄ and 78% HNO₃ (1:1) was used for microwave treatment. The mixture was then filtered through Polytetraethylene (PTFE) membrane (pore size of 200 nm) and the carbon residue was washed thoroughly with deionized water until the pH of the filtrate became neutral (pH 7). Acidified MWNTs were then dried at 100 °C in an oven for 5 h and used for further treatment.

Synthesis of Rhodium Nanospheres Decorated Nanotubes:

10 mg of these carboxylated MWNTs (solubility of 0.1 mg/mL) mixed with 500 mL of 1 mM aq. RhCl₃ and ultrasonicated (33 kHz) for 30 min for a homogeneous dispersion. Further same procedure of nanospheres synthesis was carried out for the decoration of the Rh on MWNTs by using mixture of Rh³⁺/MWNTs instead of only Rh³⁺ with as-treated Al plate as a source of reducing agent using same above approach. However, slowly color change of initial blackish orange to black of solution after the exposure of Al indicated complete adsorption of ions followed by reduction on functionalized/defect sites of the on MWNTs side walls, which could be due to more defect sites and active -COO⁻ groups on the side walls of MWNTs. After 10 min of the reaction time Al is removed from reaction mixture and Rh/MWNTs material was purified by the same above method. These as-synthesized and chemically modified materials were then characterized using several techniques like scanning electron microscope attached electron dispersive spectroscopy (SEM-EDS). High resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), X-photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (DRIFT mode; FTIR), and thermogravimetry analysis (TGA).

Field emission Studies:

Field electron emission measurements on Rh-MWNTs hybrid, Rh nanospheres and functionalized MWNTs samples were carried out in planar diode configuration under ultra high vacuum. A vacuum in the order of 1×10^{-9} mbar and below was routinely obtained and maintained in the field emission system with the help of sputter ion pump and titanium sublimation pump. The current-voltage (I-V) characteristics were recorded using a high voltage power supply (0-40 kV, Spellman, USA) and a picoammeter (Keithley 614) at room temperature. Fowler-Nordheim (F-N) plots were obtained from the recorded I-V data. The cathode anode separation was kept at ~ 2 mm for both the samples. All field emission experiments were carried out in under identical conditions and were repeated at least three times and the results were found to be highly reproducible.

SI-II Transmission Electron Microscopes (TEM) of Rh Nanospheres

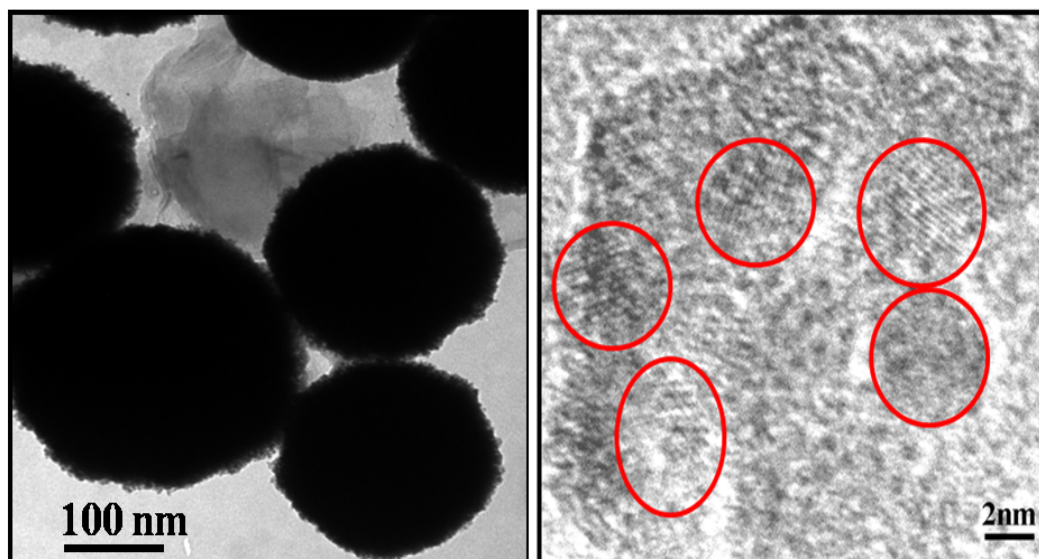


Fig SI-I: Bright field transmission electron micrographs (TEM) of Rh nanospheres (~ 150 nm) at different magnifications revealing the assembly of smaller particles of ~ 2.3 nm.

SI -III Scanning Electron Micrograph (SEM) and Transmission Electron Microscopes (TEM) of MWNTs

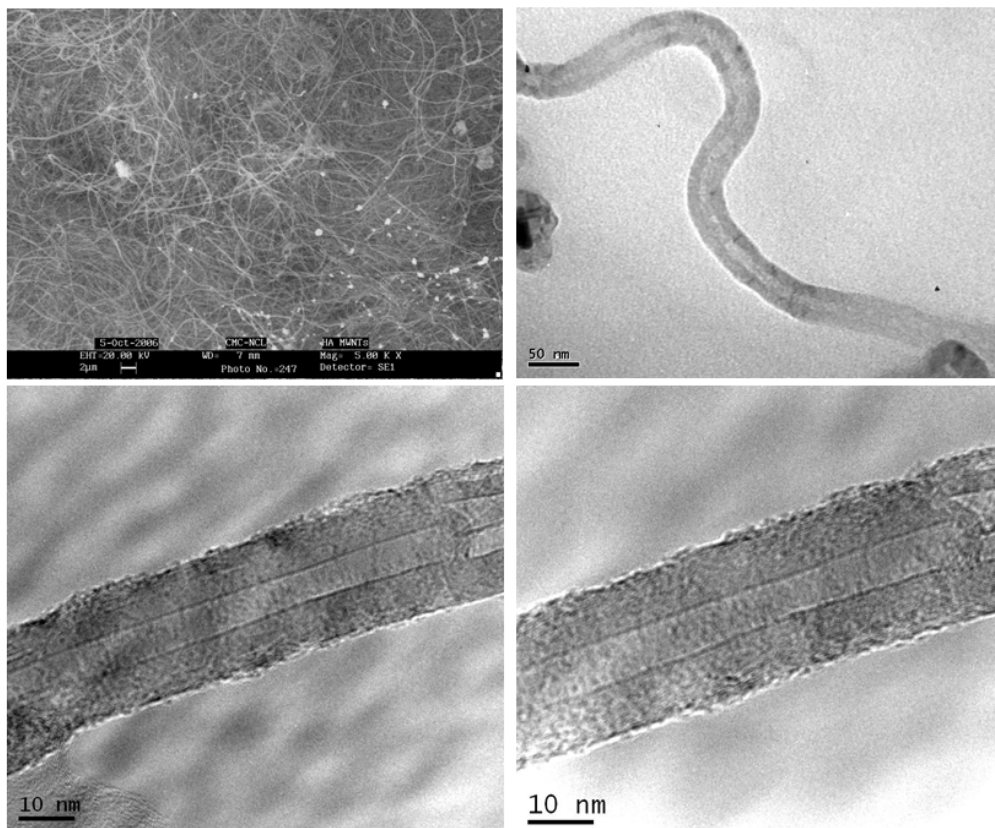


Fig: S-II Scanning Electron Micrograph (SEM) of as purified MWNTs (microwave treated) having higher monodispersity and yield and Transmission Electron Microscopes (TEM) of single nanotubes having size of ~ 30 nm.