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Rhodium Nanoparticle-Carbon Nanosphere Hybrid Material as Electrochemical Hydrogen Sensor

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SI-I: Experimental Details:

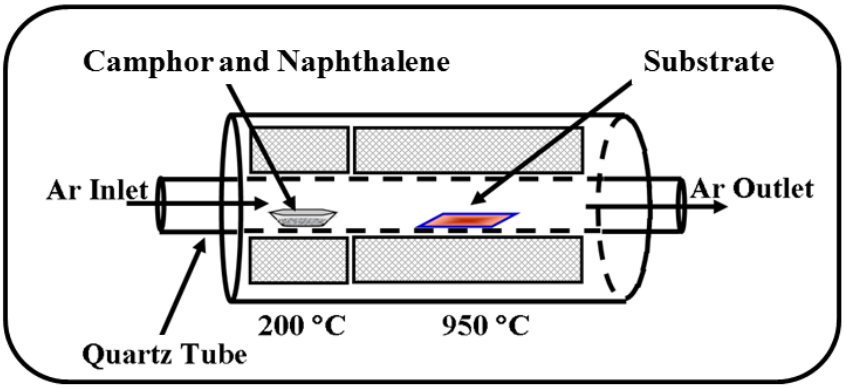
Materials:

Rhodium chloride (99.9%), Multiwalled carbon nanotubes (99.9%; metal free), Al and Cu metal plate were purchased from Aldrich chemicals, camphor (99.9%), naphthalene (99.9%), ethylene glycol, isopropanol, acetone, sulphuric acid, nitric acid, hydrochloric acid were used as received from Merck (AR grade); deionized water (16 MΩ) from Milli-Q system was used for all experiments. H_2 (1% balance with nitrogen) gas used for the experiment was purchased from Deluxe Treading Co., India.

Synthesis of Carbon Nanospheres (CNSs):

An in-house fabricated CVD set-up, capable of attaining temperature of 1200 °C, comprising of a dual zone furnace was used to synthesize the CNSs. In the beginning, a stream of Ar was passed through the quartz tube (i.d. 34 mm) at the flow rate of 100 sccm (standard cubic centimeter) to drive out all impurities till both the zones achieved their respective temperatures (pre heater zone; 200 °C, main zone; 950 °C). A mixture of naphthalene and camphor (90:10 wt%) was used as a precursor. This precursor was kept in the first (pre heater) zone of the dual furnace, maintaining the optimized temperature at ~180-200 °C to ensure the complete sublimation of precursor. The sublimed precursors were then passed into the main zone by means of Ar as a carrier gas with an optimized

flow rate of 250 sccm. The temperature of the main furnace was programmed such that it starts decreasing as soon as the vaporized gases entered the reaction zone without any external cooling aid. The carbon based material deposited on Cu substrate which is kept at the center were obtained by subjecting the system of second zone to the temperature ramp from 950-1000 °C at a natural cooling rate (~10 °C/min).



The material collected on Cu substrate which is kept at the center were collected for further studies; using scanning electron microscopy, high resolution transmission electron microscopy, thermo-gravimetric analysis, x-ray diffraction, Raman analysis, x-ray photoelectron spectroscopy, and electron dispersive x-ray analysis.

Acid Functionalization of Carbon Nanospheres (CNSs):

Initially, 200 mg of as-synthesised CNSs (diameter: ~250 nm,) were carboxylated using microwave (MW) treatment for 4 min at a power of 60 % of total 700 W (separated by 60 s off-time interval). An acid mixture of 98 % H_2SO_4 and 78 % HNO_3 (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 CNSs were then dried at 100 °C in an oven for 5 h and used further

for decoration of Rh nanoparticles.

Decoration of Rh Nanoparticles on Carbon Nanospheres:

In the decoration procedure 100 mg of acid functionalized carbon nanospheres (CNSs) was dispersed in 50 mL of dry ethylene glycol using sonication for 30 min, and 100 mg of $RhCl_3$ was added to this well dispersed suspension. The mixture was stirred for ageing for a 12 hrs at room temperature followed by refluxed at 160 °C for next 12 hrs. Finally, the product was washed several times with acetone to remove the impurities of chloride and ethylene glycol and dried in a vacuum. Same experiment repeated by changing the concentration of $RhCl_3$, to study the concentration dependent decoration of Rh nanoparticles on CNSs surface.

Functionalization of Carbon Nanotubes:

Initially, 200 mg of MWNTs (diameter: 20 ±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% H_2SO_4 and 78% HNO_3 (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 ^{o}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. $RhCl_3$ 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 Rh^{3+}/MWNTs instead of only Rh^{3+} 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).

Characterization:

XRD was carried out on a Rigaku, D/MAX IIIB diffractometer using Cu Kα radiation from a rotating anode X-ray generator operating at 30 kV and 15 mA at room temperature. Scanning electron microscopic (SEM) measurements were carried out with a Leica Stereoscan-440 instrument equipped with a Phoenix energy dispersive analysis of X-ray (EDX) attachment. The X-ray photoelectron spectroscopic (XPS) measurements were carried out on a VG MicroTech ESCA 3000 instrument at a pressure of $>1\times10^{-9}$ Torr (pass energy of 50 eV, electron takeoff angle 60º, and overall resolution ~1 eV). The spectra were fitted by using a combined polynomial and Shirley-type background function using "XPS Peak Fitting Program for WIN95/98 XPSPEAK Version 4.1"

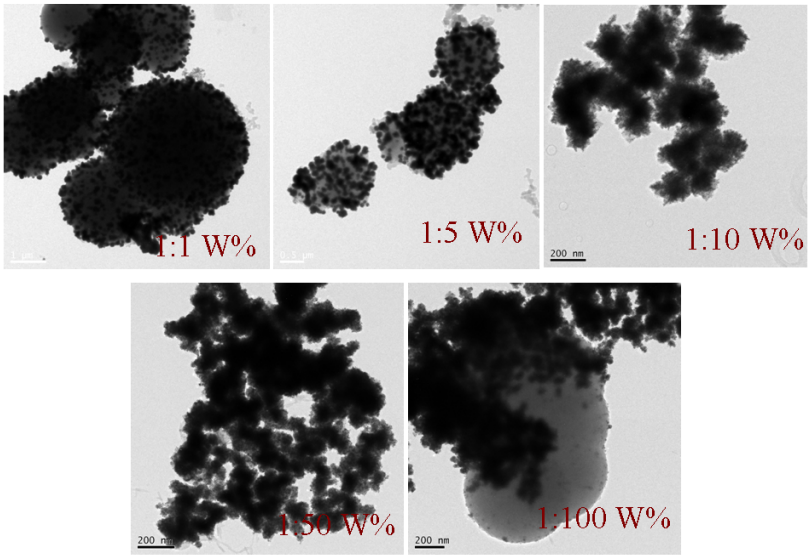
software. The Shirley-type background fitting function used here having asymmetric Gaussian-Lorentzian sum function. Thermogravimetric analysis was carried out on TGA Q5000V2.4 TA instruments, build 2-3 thermal analyzer by heating about 2 mg of sample from 50 °C to 900 °C at a rate of 10 °C/min in Ar. All electrochemical studies were performed on an Autolab PGSTAT30 (Eco Chemie) instrument using a conventional three electrode test cell with a reversible hydrogen electrode (RHE) electrode and a platinum foil as the reference and counter electrodes, respectively. A 3 mm dia. glassy carbon (GC) electrode for working electrode was polished using 0.3 and 0.05 μm alumina powders, followed by washing with water and acetone. The working electrode was prepared as follows: 10 μL aliquot of the slurry made by sonication of 1 mg of the catalyst in 1 mL isopropyl alcohol was drop-coated on glassy carbon electrode. After this, 2 μL of 0.01 wt% Nafion diluted with ethanol was coated on the surface of the electrocatalyst layer to yield a uniform thin film. This electrode was then dried in air and was used as the working electrode for all electrochemical studies. An aqueous solution of 0.5 M H_2SO_4 was used as the electrolyte for normal cyclic voltammetric studies to determine the electro-active surface area. Further, the current densities normalized by using calculated amount of Rh loading from TGA analysis.

Electrode Fabrication for Electrochemical H_2 Oxidation Studies:

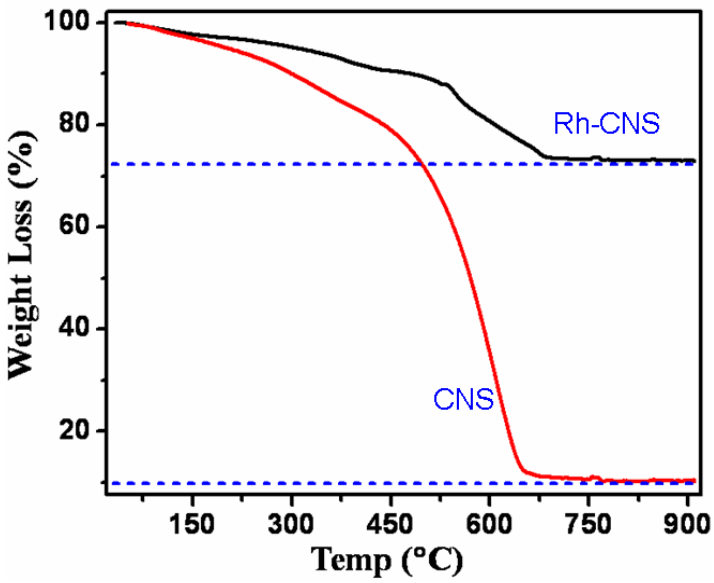
The electrodes were fabricated on PTFE- PM28Y membrane pretreated by placing the membrane in 50 % isopropyl alcohol for 24 hrs before applying catalytic (CNSs, Rh-MWNTs and Rh-CNSs) ink consisting of a homogeneous paste of anode material, nafion and aqueous isopropyl alcohol. The binder was selected to acquire good adhesion of electrode material to the membrane improving the catalyst attachment to the membrane

simultaneously reducing the wrinkling. The catalytic ink was printed on a PTFE membrane and was first cold pressed and then hot pressed at 80 ^{o}C. An 18 mm diameter printed electrode was used as a sensing electrode. A 12 mm diameter area punched from the center of one electrode was used as a reference electrode while remaining annular part acted as a counter electrode. The sensing electrode was placed with the printed electrode part facing downwards and below this a separator and a wick (electrolyte reservoir using 0.5 M sulphuric acid) were kept followed by lastly the reference electrode, ensuring that all these parts rest on the surface of the electrolyte holder. Separate platinum contacts were taken from the sensing, reference and counter electrodes connected to marked pins at the bottom.

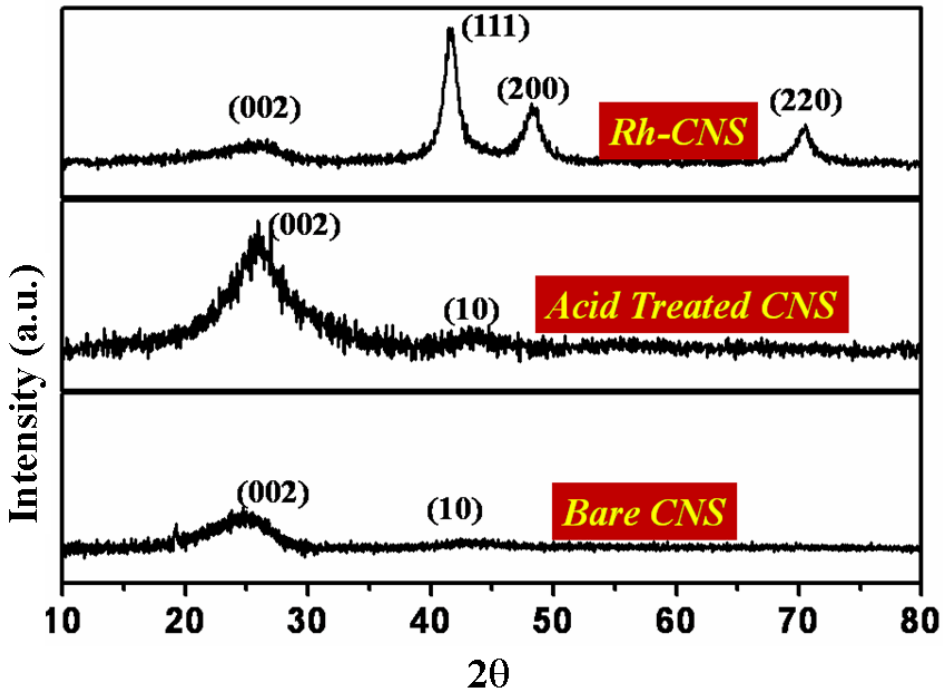
SI-II: Concentration dependent decoration of Rh on Carbon Nanospheres:



SI-III: Thermogravimetric Analysis:



SI-IV: X-ray Diffraction

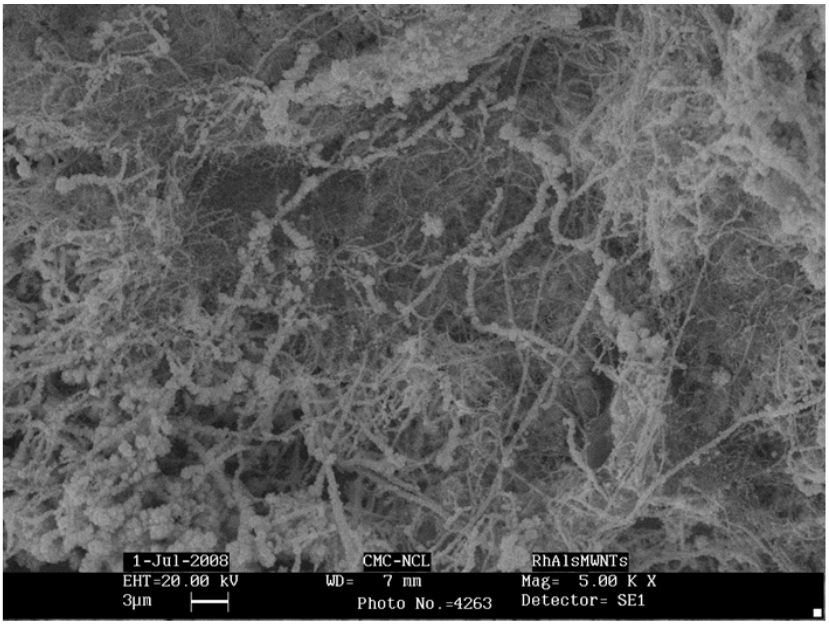


A comparison of the X-ray diffraction patterns in reveals a high degree of crystallinity in cases of all the samples, which provides valuable information on their size distribution. Accordingly, pattern and for the carbon nanospheres (CNSs) and carbon based Rh

heterostructures (Rh-CNSs) exhibit strong peaks at around 2θ 26.6° and at 42° that could be attributed to that of carbon nanostructures. Superimposed X-ray diffraction for (I) CNSs showing inter-planar (002), turbostratic (10) reflections corresponding to graphene stacking of CNSs, Rh nanoparticles exhibiting FCC structure and (III) Rh-CNSs showing mixed reflections including (002), (111), (200) and (220) planes.

Moreover, patterns Rh-CNSs exhibit strong diffractions at around 40°, 46° and 68° which can be indexed as Rh (111), (200) and (220) reflections, suggesting the single phase nature of Rh (0). Further, the crystallite sizes of Rh nanoparticles obtained from the FWHM of these patterns are in good agreement with that observed in HR-TEM studies. The crystallite size of Rh in case of as-prepared Rh -CNSs are found to be ~2.3 nm and ~2.45 nm respectively as inferred from the FWHM of 43.54º peak (corresponding to *d* value of 2.25 Å and 2.27 Å), which are in excellent agreed with the corresponding size from TEM images as shown in Fig 1.

SI-V: Scanning Electron Microscopic (SEM) image of Rh-MWNTs



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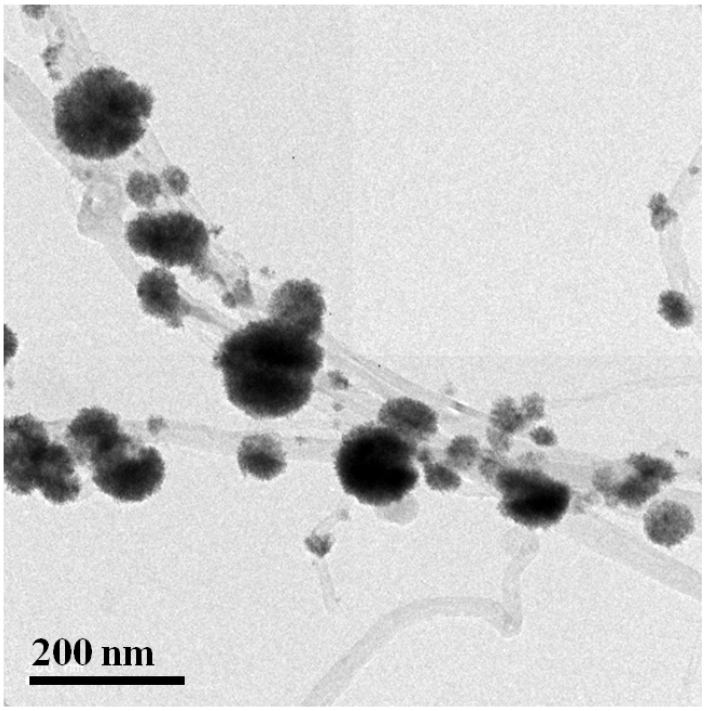
SI-VI: Transmission Electron Microscopic (SEM) image of Rh-MWNTs