High Aspect Ratio Nanoscale Multifunctional Materials Derived from Hollow Carbon Nanofiber by Polymer Insertion and Metal Decoration†

Beena K Balan,[a] Vinayak S Kale,[a] Pradnya P Aher,[b] Manjusha V Shelke,[a] Vijayamohanan K Pillai[a] and Sreekumar Kurungot*[a]

[a]*Physical and Materials Chemistry Division, National Chemical Laboratory, Pune, India 411 008.*

[b]*Polymer Science and Engineering Division, National Chemical Laboratory, Pune, India 411 008.*

E-Mail: k.sreekumar@ncl.res.in; Fax: +91 20 2590 2636 Tel: +91 20 2590 2566

Supporting Information

Materials and Methods

Materials:

Hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6.6H_2O$), 3, 3’-diaminobenzidine (DAB), polyphosphoric acid (PPA) and 5-tert-butyl isophthalic acid were procured from M/s. Aldrich Chemicals. N, N-dimethyl acetamide (DMAc), ethylene glycol (EG), perchloric acid ($HClO_4$) were procured from Rankem Chemicals. All the chemicals were used as received without any further purification. A poly (tetrafluoroethylene) (PTFE) filter paper (pore size, 0.45 μm; Rankem) was used for the filtration. A copper grid with a carbon support (Icon Analytical Inc.) was used for the HRTEM observations.

Preparation of Polybenzimidazole (PBI):

Polybenzimidazole was synthesized by solution polycondensation method using polyphosphoric acid (PPA) as the solvent. In a typical procedure, a three-necked flask equipped with a mechanical stirrer, N_2 inlet and $CaCl_2$ drying tube was charged with 500 g of PPA, 10 g (0.0467 mol) of 3, 3’-diaminobenzidine (DAB) and the temperature was elevated to 140 °C. After complete dissolution of DAB, 11.414 g (0.0514 mol) of 5-tert-butylisophthalic acid was added; temperature was slowly raised to 170 °C and maintained for 5 h under constant flow of N_2. The temperature was further raised to 200 °C and maintained for 14 h. After completion of the reaction, temperature was lowered and the highly viscous reaction mixture was poured on to the stirred water. The precipitated polymer was crushed and thoroughly washed with water till neutral to pH. The polymer was then kept overnight in 10% aqueous Na_2CO_3, washed with water until neutral pH and soaked in methanol for 8 h to extract the water. Dried polymer (100 °C, 3 days) was further purified by dissolving in DMAc to get a 0.25 wt. % solution, removing undissolved material, if any, by centrifugation at 3000 rpm for 3 h and reprecipitation on to stirred water. The polymer was kept in methanol for 8 h, filtered, dried at 60 °C for 24 h and then in vacuum oven at 100 °C for a week. The inherent viscosity of the polymer was 0.47 dLg^{-1} using 0.2 gdL^{-1} polymer solution in DMAc.

Preparation of carbon nanofiber supported catalyst:

Decoration of Pt nanoparticles only in the inner cavity and on both the walls is achieved by a modified polyol process using pristine and H_2O_2 treated CNFs respectively. To facilitate metal dispersion into the tubular region of the carbon nanofiber, simultaneous metal ion dispersion and reduction were accomplished through a polyol process by carefully optimizing the polyol-water ratio to achieve balanced surface tension and polarity characteristics. The modification of the polyol process by using a proper composition of polyol and water is a critical step to facilitate reactants entry into the tubular region and homogeneous wetting of the inner wall surface by the solvents. In the typical synthesis, 400 mg of the support material was added to an aqueous ethylene glycol solution (ethylene glycol/water 3:2 v/v, 600 mL) and dispersed by sonication. In the next step, aqueous ethylene glycol solution of H_2PtCl_6 (517 mg in ethylene glycol/water 3:2 v/v, 900 mL) was added drop by drop with stirring. Subsequently, the mixture was kept under stirring for 5 h at ambient temperature to achieve well dispersion of the components in the mixture. In case of nanofibers with straw type morphology, this aging time is important because the precursor solution has to be reached inside the tubes of the support material. After the stirring process, the mixture was refluxed at 140 °C for 8 h. The solid material was then collected by filtration and washed with water and dried under vacuum to obtain the Pt decorated CNF samples.

PBI encapsulation with Electrocatalyst:

The critical parameter that determines the entry of the polymer into the inner cavity is the viscosity and surface tension of the solvent medium. So to ensure the PBI entry into the cavity, PBI solution in DMAc was selected and 1 mg of the catalyst was added to 1 mL of 0.25 wt. % of the polymer solution. To get a uniform dispersion and to initiate the PBI entry into the cavity, the mixture was initially sonicated using a bathtype sonicator for 10 min. and subsequently kept stirring for 10 h at room temperature to facilitate PBI entry into the tubular region and homogeneous coverage along the inner and outer surfaces.

Characterization:

The HRTEM images were taken by a TECNAI-T 30 model instrument operated at an accelerating voltage of 300 kV. Samples for HRTEM imaging were prepared by placing a drop of the catalyst sample in isopropanol onto a carbon-coated Cu grid (3 nm thick, deposited on a commercial copper grid for electron microscope), dried in air and loaded into the electron microscopic chamber. X-ray Diffraction (XRD) was conducted using a Phillips X'pert pro powder X-ray diffractometer (Cu, K_α radiation, Ni filter). Thermogravimetric Analysis (TGA) was performed on a SDT Q600 TG-DTA analyzer under Air atmosphere at a heating rate of 10 °C min^{-1}.

Electrochemical Measurements:

All the electrochemical studies were performed on an Autolab PGSTAT30 (Eco Chemie) equipped with a Pine RDE unit. A conventional three electrode system with a 5 mm diameter glassy carbon (GC) electrode coated with the sample as the working electrode (WE), Ag/AgCl as the reference electrode (RE) and Pt foil as the counter electrode (CE) was used for all the experiments. The GC electrode was polished using 0.3 and 0.05 µm alumina slurries, followed by washing with water and acetone. A 10 µL aliquot of the catalyst slurry prepared by dispersing 5 mg of the catalyst in 1 mL of the PBI solution in DMAc (0.25 wt %) was placed on a polished glassy carbon electrode and then dried in air to remove the solvent. After that, it was dipped in 10 mL of polyphosphoric acid, dried in air and was used as the WE. The same procedure was repeated by varying the catalyst: PBI ratios. To record CV with Nafion coated on the surface, working electrode was prepared as follows: 10 µl aliquot of the slurry made by sonicating 1 mg of the catalyst in 1 mL DMAc was drop-coated on glassy carbon electrode. After this, 2µl of 0.01 wt. % Nafion diluted with ethanol was coated on the surface of the catalyst layer to yield a uniform thin film and was dried in air. The CV was measured in 0.5 M $HClO_4$ deaerated with N_2 at a scan rate of 50 mVs^{-1}. RDE studies were carried out in O_2 saturated 0.5 M $HClO_4$ at a scan rate of 5 mVs^{-1}.

Results

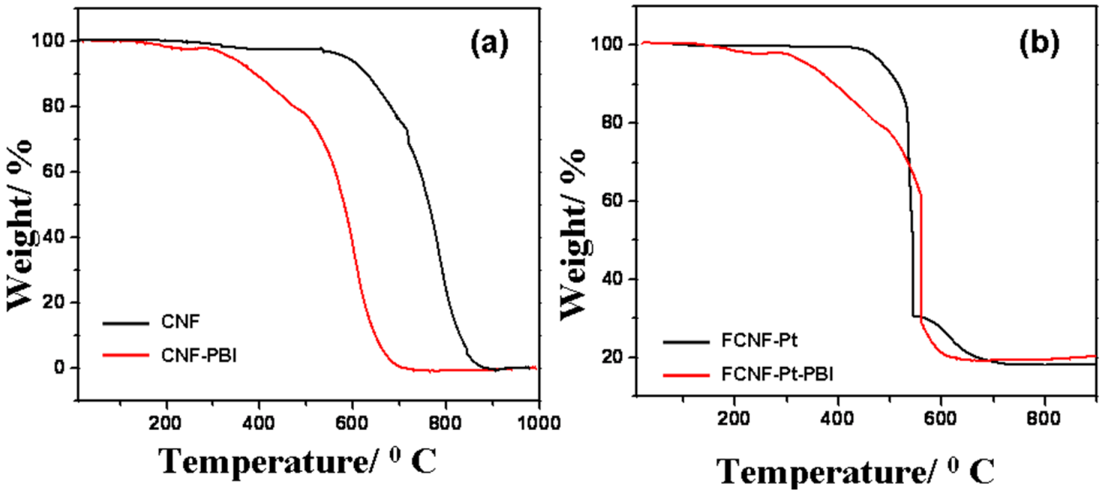

***Fig. S1**: TGA profiles obtained in air up to 1000 °C for (a) CNF before and after PBI incorporation (b) FCNF-Pt before and after PBI incorporation.*

Fig. S1 (a) shows the thermogravimetric analysis (TGA) of CNF before and after the incorporation of PBI in air from room temperature to 1000 °C. The pristine carbon nanofiber shows initially a small weight loss corresponding to residual water followed by a continuous weight loss of carbon upto 800 °C. No detectable amount of residual metals is present in this case. Interestingly, after incorporation PBI, weight loss starts from 300 °C itself attributed to the presence of PBI. The weight loss occurs at lower temperature as compared to those reported in the literature and it may be due to the lower molecular weight of the PBI used (As indicated by its lower inherent viscosity). Moreover, the inner hollow cavity of CNF may provide an intriguing one-dimensional confinement of PBI leading to limited intermolecular H_2 bonding. This effect also supports the above observation of weight loss at low temperature. Fig. S 1 (b) is the TGA corresponding to the electrocatalyst before (FNCF-Pt) and after (FNCF-Pt-PBI) PBI incorporation. In the case of FCNF-Pt, no appreciable weight loss is observed until 420 °C whereas in the case of FCNF-Pt-PBI, the weight loss corresponding to PBI is also observed. From the residue content, the amount of Pt in both these cases is calculated to be ~ 20 wt. %. It can also be noted from the TGA profiles that in case of pristine CNF, the carbon loss occurs at a higher temperature as compared to the other two. This is in accordance with the fact that Pt nanoparticles dispersed on the CNF surfaces can act as the active sites to facilitate the oxidation of carbon, leading to a fast decomposition at a lower temperature compared to the pristine sample.

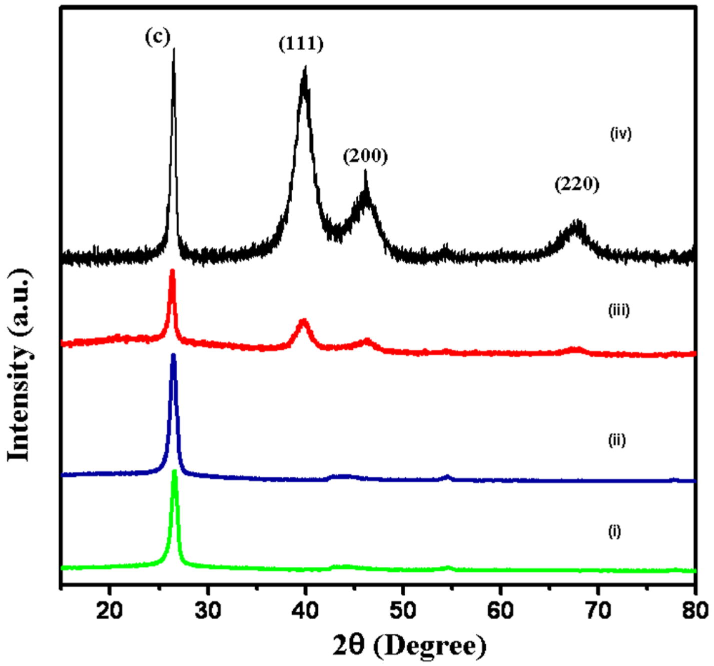

Fig. S2: *X-ray diffraction patterns obtained for (i) pristine CNF (ii) CNF encapsulated with PBI (CNF-PBI), (iii) FCNF-Pt encapsulated with PBI (FCNF-Pt-PBI) and (iv) FCNF-Pt.*

Fig. S2 shows the X-ray diffraction (XRD) patterns of pristine CNF, pristine CNF incorporated with PBI (CNF-PBI), FCNF-Pt and FCNF-Pt incorporated with PBI (FCNF-Pt-PBI), respectively. A comparison of the XRD patterns of pristine CNF before and after incorporation does not show much difference. XRD pattern of FCNF-Pt shows three peaks at 2θ values of 40.10, 46.40 and 67.70, which can be indexed to (111), (200) and (220) planes of Pt, respectively. This is in accordance with the face centered cubic structure, which is consistent with the previous literature reports. After incorporation with PBI solution same features are also retained, despite with less intensity. The intensity difference may be attributed to the formation of a skin layer of polymer on the surface of Pt nanoparticles; also, the XRD patterns in both the cases are broader indicting smaller particles. The average crystalline size of the nanoparticles calculated for FCNF-Pt using Scherrer equation is 3.2 nm and 3.5 nm respectively, before and after the polymer incorporation, indicating only a marginal difference once the sample is subjected to the polymer wrapping process. These sizes are quite close to those from the HRTEM observations.

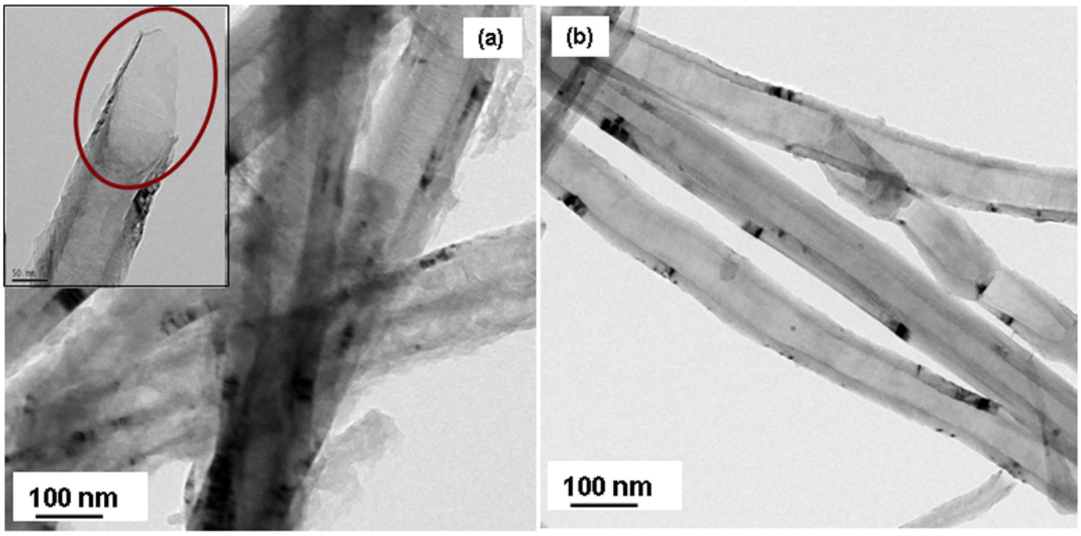

Fig. S3: *HRTEM images of (a) CNFs incorporated with PBI (b) pristine CNFs. Inset of (a) Indicates the open tip of CNF, which facilitated PBI entry by capillary action.*

Since HRTEM can directly determine the morphology transformations of materials in nanospace and has the potential to be a powerful technique for understanding the behaviour of materials encapsulated inside the cavity, no other technique is best suited as this for the present purpose. Accordingly, Fig. S3 (a) shows an overall view of pristine CNFs after incorporating PBI and the figure in the inset of the same clearly confirms that the polymer has entered from the open tip through capillary action. For an effective comparison of the contrast after incorporating PBI, HRTEM image of pristine CNFs prior to PBI incorporation is also shown in Figure S3 (b). Moreover, Fig S4 (a) and (b) give a direct comparison of a single carbon nanofiber before and after PBI incorporation. The difference in the image contrasts of Fig. S3, S4 (a) and (b) gives a clear picture that PBI solution is entered inside the cavities of CNFs. Images clearly depict that no change in the morphology of CNFs like swelling or busting is observed and the diameter (100 nm) remains the same even after the entry of the polymer. It is also observed that PBI is present on the outer wall of the CNFs as well, which could be due to the high wettability of the PBI solution. This observation confirms the theoretical prediction that wetting is a prerequisite for insertion by capillary action.

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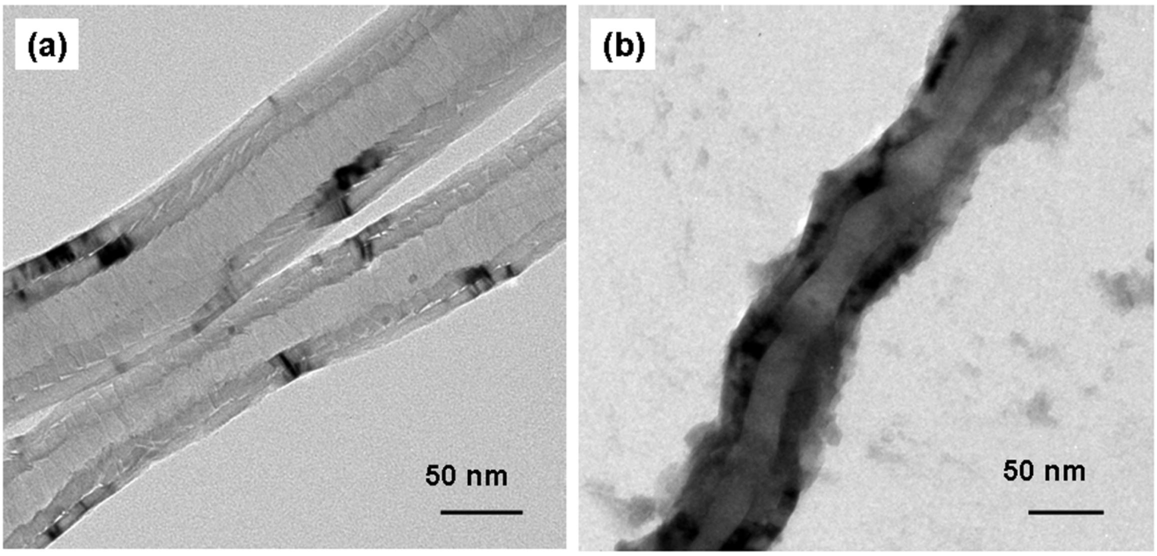

Fig. S4: *HRTEM images of a single CNF (a) before PBI incorporation (b) after PBI incorporation.*