This article can be cited before page numbers have been issued, to do this please use: K. G. Nair, V. Ramakrishnan and B. Pullithadathil, Mater. Adv., 2021, DOI: 10.1039/D1MA00683E.

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Integrated Co-axial Electrospinning for Single-Step Production of 1D Aligned Bimetallic Carbon Fibers@AuNPs-PtNPs/NiNPs-PtNPs Towards H$_2$ Detection

Keerthi G. Nair$^a$, Ramakrishnan Vishnuraj$^a$ and Biji Pullithadathil$^b$$^*$

Abstract

One dimensional (1D) nanostructure like nanorods, nanowires, nanotubes and nanofibers have aroused great attention owing to their exceptional properties like high surface-to-volume ratio, excellent electron and thermal transport and also plays as interconnects during fabricating nanoscale devices. In this work, one dimensionally aligned Carbon nanofibers (CFs)@AuNPs-PtNPs/NiNPs-PtNPs have been developed via a single step co-axial electrospinning integrated with in-situ photo-reduction. The carbon nanofibers with in-situ functionalized bimetallic nanoparticles possessed well-defined core-shell structure with carbon nanofibers (CFs) as the core and AuNPs-PtNPs/NiNPs-PtNPs as the surface anchored heterojunctions. Homogeneously distributed AuNPs-PtNPs/Ni NPs-Pt NPs, which are identified as chemical sensitizers, triggers the dissociation of H$_2$ through the spill-over effect, by successive diffusion of these H* on carbon nanofiber surface, thereby altering the entire surface of the CFs into reaction sites for H$_2$. Aligned core-shell CFs@Ni NPs-PtNPs possessed high sensitivity of 124% (v/v) at room temperature as compared with aligned core-shell CFs@PtNPs NPs (52%) and aligned core-shell CFs@AuNPs-PtNPs (65%), which may be due to the high catalytic adsorption and desorption properties of Ni and Pt towards hydrogen gas. Moreover, co-axially aligned CFs@NiNPs-PtNPs based sensor also demonstrates outstanding selectivity towards hydrogen compared to other gases like ammonia, ethanol, hydrogen sulphide, and acetone with excellent long-term stability. In addition, hydrogen adsorption kinetics of co-axially aligned CFs@NiNPs-PtNPs based sensor was verified theoretically the adsorption rate constant of (0.42) which showed a comparable experimental value (0.38) of adsorption rate constant. The potential suitability of co-axially aligned CFs@NiNPs-PtNPs based sensor towards H$_2$ at room temperature leading towards real time applications also have been demonstrated.

1. Introduction

Hydrogen is considered as the future clean energy fuel and is widely used in numerous industries, such as, petrochemical refinery, coolant, chemical synthesis, semiconductors, fuel cells, aerospace, automobile and as energy carrier in nuclear fusion power plant. Over the last decade, there have been growing research interests in the use of hydrogen as a zero-emission fuel in automotive applications. H$_2$ as a fuel has already found its potential and is commercially feasible in markets comprising trucks powered by fuel cells and stationary power systems. For the effective deployment of hydrogen as an alternative fuel, it is very significant to develop the infrastructure of hydrogen market carefully and efficiently. Leakage of hydrogen is a serious concern since it could lead to disastrous consequences, and may cause highly damaging explosions even in laboratory scale. Therefore, deployment of H$_2$ detectors is necessary in all such applications, mainly due to its colorless, tasteless and odorless nature. Consequently, efficient monitoring of trace level concentration of hydrogen has become critical. Therefore, hydrogen sensors developed with the parameters of sensitivity, speed, accuracy and reliability are of high demand for storage, production and usage of this forthcoming clean energy carrier. Buttner et al. have summarized the most significant requirements for H$_2$ sensors in market, which includes, the H$_2$ measurement in the range of 0.1%-10% at operating temperature below 80°C, as per the target conditions set by U.S. Department of Energy (DOE) in 2007. In this scenario, developing rapid and stable H$_2$ sensors working at room temperature with broad range of detection is crucial for early hazard prevention before the hydrogen-powered systems are widely exploited. Hydrogen based gas sensors were developed conventionally by numerous semiconducting metal oxides. However, semiconductor based H$_2$ sensors needs high working temperature of 150°C-400°C to accomplish high sensitivity and possess poor selectivity towards H$_2$ gas. Recently, gas sensors based on 1D carbon materials, such as carbon nanofibers(CFs) and carbon nanotubes (CNTs), have achieved considerable importance as ideal candidates for carbon nanostructures based sensors towards room temperature detection of H$_2$, owing to their high surface to volume ratio and directed charge transport properties. Such carbon nanostructures can also be easily functionalized with noble metals or bimetals, leading to improved gas sensor performance. However, only few reports are available on carbon nanofibers based gas sensors compared to CNT based gas sensors. Also, compared to quantum dots (QDs), 1D carbon nanostructures with reduced dimensionality have demonstrated improved electrical properties, which might be due to three aspects: (i) The 1D carbon nanostructures have larger specific surface areas than quantum dots; (ii) 1D carbon nanostructures delivers direct electronic transport pathway and thus reduces the electrical resistance, while the electrical
The production of CNFs is generally carried out by methods such as electrospinning, CVD, templated synthesis, hydrothermal synthesis, catalytic hydrogenation etc.\textsuperscript{10,11} Carbon nanofibers produced by electrospinning are simple, effective, versatile, scalable and low-cost technique that has been employed to fabricate 1D dimensional nanofibers.\textsuperscript{12} Co-axial electrospinning is found to be an effective method to produce core-shell type nanofibers which is a low-cost and continuous production method capable of nanofiber alignment.\textsuperscript{13} Aligned electrospun nanofibers have drawn enormous attention in the fields of sensors, drug delivery, tissue engineering, photoelectric device, supercapacitors and blood vessel engineering since these applications entail highly ordered and well-aligned architecture in addition to the anisotropy and enhanced performance.\textsuperscript{14-16}

Functionalization of carbon nanostructures with platinum, palladium nanoparticles (NPs) or bimetallic nanoparticles are well-known for H\textsubscript{2} gas detection since these catalytic NPs stimulates the reaction through dissociation of hydrogen molecules into hydrogen atoms. Bimetallics are well recognized due to its synergistic effects. Bimetallic nanoparticles have four plausible types of mixing patterns amid the two metals, they are (i) core-shell structures (ii) sub-cluster segregated (iii) homogeneously mixed alloys and (iv) multi-shell nanoalloys.\textsuperscript{17} Recently, trace level detection of hydrogen was discussed using catalytically active Pt-covered Pd nanowires and Pt-Pd/rGO.\textsuperscript{18} Even though Pt is a notable H\textsubscript{2} sensing material, which helps in H\textsubscript{2} dissociation at the exterior, forming Pt-H, compared to Pd, it remains on the exterior surfaces instead of dispersing into the bulk. Therefore, carbon nanostructures functionalized with Pt NPs, displayed better recovery of H\textsubscript{2} sensor than Pd based sensors. Lately, Baro et al. described the consequence of NPs distribution over graphene wrapped CNTs which displayed 42.8% sensitivity towards 4% of H\textsubscript{2} at RT.\textsuperscript{19} It was noticeable that high loading of catalytic PtNPs on carbon support diminishes the activity of nanocatalyst and so the sensor performance. Our earlier work have explored the bimetallic Au-Pt NPs over CFs synthesized via wet chemical route to sense H\textsubscript{2} gas.\textsuperscript{20} The CFs with AuNPs-PtNPs upgraded the response time of the sensor in comparison with the monometallic PtNPs on CFs. Though CFs@AuNPs-PtNPs displayed exceptional H\textsubscript{2} sensing properties, cost reduction, but, the multi-step fabrication process was found to be its limitations for mass production. In addition, less-PtNPs functionalized carbon support might be more economical and advantageous with improved sensitivity without much shift in the base-resistance. Less-platinum based carbon nanofibers synthesized via two-step method, electrospinning and chemical reduction on flexible substrate for room temperature hydrogen gas detection was discussed in our previous report\textsuperscript{21}. Though, incorporation of less-Pt based low-cost bimetallic systems over CFs on flexible substrates improved the sensor characteristics, but, for real-time applications, easy fabrication methods with improved sensor performance are more desirable. Therefore, for the real-time implementation of these sensors, the fabrication process must be in ease and suitable for mass production. Recently, people have tried to reinforce on-chip fabrication of sensor devices, but such approaches were found to involve multi stage processes, which results in practical issues, a fact which hampers their mass production.\textsuperscript{22}

In this investigation, we have discussed a single-step fabrication strategy based on co-axial electrospinning with in-situ photo-reduction aimed at the production of aligned 1D CFs@AuNPs-PtNPs/NiNPs-PtNPs based heterojunction nanofibers. The surface catalysis related to the noble metal/bimetals (PtNPs, AuNPs-PtNPs and NiNPs-PtNPs) shell layers and carbon nanofibers as core layers leads to an exhaustive understanding of the mechanism for gas-material interactions at the interfaces which was further verified by analysing in-situ electron-transport properties. In addition, a prototype device based on co-axially aligned CFs@NiNPs-PtNPs based sensor was demonstrated towards hydrogen gas detection. This study might furnish significantly about the selection of advanced sensor materials for room temperature H\textsubscript{2} gas sensor device with enhanced sensor performance and process conditions with improved selectivity which favour mass production of H\textsubscript{2} sensors with reduction in overall cost.

2. Experimental Section

2.1 Materials:

Polyacrylonitrile (PAN–Aldrich), Poly Vinyl Pyrrolidone (PVP-Sigma Aldrich), Nickel chloride (NiCl\textsubscript{2}-SigmaAldrich), Chloroauric acid (HAuCl\textsubscript{4}-O-Sigma Aldrich), Hexachloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6}-O-Sigma Aldrich), Dimethyl formamide (DMF-Merck) were used for the fabrication of co-axial CFs@PtNPs.
based nanosystems. All chemicals were used as received without further purification.

### 2.2 Characterization

Morphological characterization of co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs nanofibers were analyzed by transmission electron microscopy (TEM) using JEOL JEM-2010 (Japan, 200 kV) and scanning electron microscopy (SEM) (ZEISS EVO 18, US). Crystal structure and phase analysis were acquired by means of X-ray diffraction (XRD) measurements (Empyrean, Malvern PANalytical, UK) with Cu Kα radiation (λ=1.54 Å) as source. The chemical states of the sensing materials were examined by X-ray photoelectron spectroscopy (XPS) by means of PHI 5000 Versa Probe II (ULVAC-PHI Inc., USA) through monochromatic Al-Kα X-Ray source (hv = 1486.6 eV). The Raman spectral analysis of co-axial CFs@PtNPs based nanosystems were acquired using confocal Raman microscope (WiTec alpha300 RA, Ulm, Germany) using an Nd: YAG laser (Excitation operating at-532 nm).

### 2.3 Hydrogen Gas Sensor Property Evaluation

Gas sensing studies of aligned CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs coaxial nanofibers-based sensors towards H₂ were evaluated via a sensor station furnished by a sensor chamber, Digital Multimeter (Agilent, 34410A), Mass flow controllers (MFC, Alicat made, USA) and source meter (Keithley, 2420, SA) coupled with a data procurement system via LabVIEW software. The Au IDA electrodes (~150 μm) were made on alumina (Al₂O₃) used for gas sensing measurements were fabricated via DC sputtering (RHV made, Bangalore). The detection of hydrogen by aligned CFs@PtNPs based bimetallic nanosystems were measured using Agilent Multimeter (Keithley, 2420, SA) coupled with a data procurement system via LabVIEW software. The Au IDA electrodes (~150 μm) were made on alumina (Al₂O₃) used for gas sensing measurements were fabricated via DC sputtering (RHV made, Bangalore). The detection of hydrogen by aligned CFs@PtNPs based bimetallic nanosystems were measured using Agilent Multimeter (Keithley, 2420, SA) coupled with a data procurement system via LabVIEW software.

Figure 1. (a) Photograph of co-axial electrospinning setup for single step production of aligned fibers with in-situ photo reduction, (b) inset shows the photograph of top-view and (c) cross-sectional view of co-axial aligned electrospun carbon nanofibers on Au IDA electrode using in-situ photo reduction followed by stabilization and carbonization process to produced co-axial carbon nanofibers @ platinum based (CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs) nanosystems.

optimized by analysing numerous associations of electrospinning parameters, like, concentration of the polymer solution, distance between nozzle and collector, voltage applied, flow rate, different gauges for core and shell solutions and the diameter of the needle in order to attain even nanofibers. All experiments were accomplished under ambient conditions (RH = 60 %, temperature:29°C). A voltage of 25 kV was used for this study for precursors loaded PVP@PAN solutions with a distance of 21 cm from needle-to-collector. Flow rate used was 1 mL/h using a 22G needle for core and 18G needle for shell material. During the co-axial electrospinning process, the spinning unit was exposed to UV radiation (λ=254 nm) for photoreduction of outer Pt/PVP solution to form metallic Pt nanoparticles, hence to develop heterojunctions on the core fibers. The fiber was directly deposited on IDA electrode (collector) for 10 min to produce a few layers of nanofibers.

These PAN fibers were converted into co-axial CFs@PtNPs based nanosystems via dual-step thermal method comprising of stabilization and carbonization. The stabilization and carbonization of PAN fibers were executed in a tubular furnace containing a Quartz tube. The nanofibers undergo heat treatment in air and N₂ atmosphere in the furnace at controlled temperature with a rate of 2°C/min and 3°C/min retained for
1h. For single–step fabrication of aligned CFs@PtNPs based nanosystems using coaxial electrospinning, the nanofibers were directly collected on Au sputtered IDA such as to form aligned nanofibers. Similarly, aligned CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs based nanosystems were also fabricated directly on Au sputtered IDA by adding Chloroauric acid and Nickel chloride along with Hexachloroplatinic acid and PVP solution respectively to form the shell layers.

3. Results and discussion

Aligned core-shell CFs@PtNPs based nanosystem were fabricated using single step co-axial electrospinning with in-situ photo reduction using polyacrylonitrile (PAN) solution as core material and metals/bimetals (PtNPs, AuNPs-PtNPs and NiNPs-PtNPs) with polyvinyl pyrrolidone (PVP) solution as shell material followed by stabilization (300°C) and carbonization (950°C) as depicted in Figure 1. Monometallic and bimetallic (Au-Pt or Ni-Pt) nanoparticles in the shell layers were formed as a result of in-situ UV irradiation facility (8W) with 254 nm UV source during co-axial electrospinning. The UV source is made to illuminate between positive (needle) and negative (copper sheet-collector) terminals of the electrospinning, which helps to reduce Pt\(^{2+}\) to Pt\(^{0}\) without any accumulation of Pt nanoclusters in the shell layer during thermal decomposition of polymers. Similarly, bimetallic nanoparticles (Au-Pt/Ni-Pt) were also formed during in-situ UV irradiation. The formation of aligned nanoparticles on the collector is depicted in Figure 1. The jet would stretch itself across the gap as the field lines are attracted towards the electrodes. This induces the electrosprun fibers to align themselves across the Au IDA electrode without any additional secondary voltage. Owing to the occurrence of charges on the fibers, mutual repulsion among the deposited fibers will increase the parallel and fairly even distribution of the fibers. This method may well be repetitive and a collection of monoaxial aligned fibers might be assembled on big surface. Through this process, fibers with length in centimeters and diameters in the range of nanometers to micrometers can be developed in an aligned array. Thus, this fabrication method has several unique advantages over the prevailing methods for the fabrication of sensors. This method involves on-chip assembly of the materials onto detector substrates by means of economical co-axial electrospinning. Also, it proposes one-stage process for the development of aligned heterojunction nanofibers with impressive control across the alignment of 1D fibers. In addition, this fabrication process eradicates solvent and impurity effects, that happened during the synthesis of sensing materials via chemical route, thereby improves the sensing properties. The co-axial fabrication, allows suitable monometallic and bimetallic functionalization of carbon nanofibers which improves the selectivity of the sensors. Thus, it offers a typical way for the complete insight towards the interactions amid analyte gas and sensor materials such as to elucidate the complicated sensing mechanism.

Figure 2 shows the X-ray diffraction pattern of pristine CFs, co-axial CFs@PtNPs, co-axial CFs@AuNPs-PtNPs and CFs@NiNPs-Pt NPs. A wide peak centered at 25.2° was appeared for CFs, co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-Pt NPs, which is attributed to the amorphous phase of the graphitic carbon ((002) plane) prevailing in the CFs (JCPDS card 41-1487).\(^{21,23}\) The XRD pattern of co-axial CFs@PtNPs confirms the existence of the characteristic peaks located at 20 = 39.7°, 45.4°, 67.9° and 81.2°, which were ascribed to the planes (111), (200), (220) and (311) consistent to the fcc platinum (JCPDS card 04-0802), respectively.\(^{24}\) The average particle size (d\(_{\text{av}}\)) of Pt was estimated using with Debye Scherrer equation as 2.4 nm. The d-spacing of co-axial CFs@PtNPs nanosystem was found to be 0.226 nm which is related to Pt (111) plane with lattice parameter, a=0.392 nm and is comparable with previous reports. Furthermore, platinum oxides peaks have not appeared in the XRD patterns depicted in Figure 2.

XRD pattern of co-axial CFs@AuNPs-PtNPs based nanosystem exhibited peaks at 20 values of 40.02°, 46.2°, 68.4° and 81.9° corresponding to (111), (200), (220) and (311) planes of fcc crystal structure of Pt respectively (JCPDS card 04-0802). The inter d-spacing of co-axial CFs@AuNPs-PtNPs was found to be 0.2254 nm which is related to Pt (111) plane with lattice parameter, a=0.3904 nm. Overlapped peaks of Au and Pt further indicates that the nanoparticles are bimetallic in nature.\(^{25,26}\) Similarly, XRD pattern of co-axial CFs@Ni NPs-Pt NPs displayed both strong and sharp peaks at 40.25°, 46.6°, 67.4° and 81.9° corresponding to (111), (200), (220) and (311) planes of fcc crystal structure of Pt respectively (JCPDS card 04-0802). The d-spacing of co-axial CFs@Ni NPs-Pt NPs based nanosystem was found to be 0.2251 nm which is related to Pt.
Figure 3. Raman Spectra of pristine CFs, co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs.

(111) plane with lattice parameter, a=0.389 nm. Overlap of the peaks of Ni and Pt further indicates that the nanoparticles are bimetallic in nature.21,27,28 A close observation of XRD patterns of co-axial bimetallic systems; CFs@AuNPs-PtNPs and CFs@Ni NPs-Pt NPs reveals that the peak corresponding to (111) plane of Pt has shifted to higher Bragg angles. From Figure 2, it can also be confirmed that there is no peak matching to fcc Ni or NiO for co-axial CFs@Ni NPs-Pt NPs. The shift towards higher Bragg angles associated to pristine Pt might be owing to the constraining strain persuaded by formation of bimetallic Pt with Au and Pt with Ni on CFs during the formation of co-axial bimetallic systems; CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs, which can effectively modify the adsorption energy of metal catalysts, and sequentially refining the catalytic activity.29

Raman spectral analysis was executed to understand the chemical identification of pristine CFs and co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@Ni NPs-Pt NPs (Figure 3). For pristine CFs, two characteristic peaks, i.e., D and G bands were spotted at 1335.7 cm⁻¹ and 1580 cm⁻¹, which are ascribed to the structural distortions triggered via the defects existing in the sp² carbon network and E₂g phonon mode of sp² carbon atoms. A red shift was noticed for the D band (1354.6cm⁻¹) and G band (1568.4 cm⁻¹) in co-axial CFs@PtNPs and the I_D/I_G ratio was amplified (1.008) compared to bare CFs (1.003), which can be attributed to the structural alterations owing to the interaction amid platinum nanoparticles with CFs support. Similarly, for co-axial CFs@AuNPs-PtNPs, the D and G bands were found to be at 1360 cm⁻¹ and 1587 cm⁻¹ and for co-axial CFs@NiNPs-PtNPs, the D and G bands were found to be at 1367 cm⁻¹ and 1606.6 cm⁻¹ respectively. I_D/I_G ratio for co-axial CFs@AuNPs-PtNPs was 1.09 and for co-axial CFs@Ni NPs-Pt NPs, it was estimated as 1.0023. The higher intensity of I_D/I_G peak for co-axial CFs@AuNPs-PtNPs may be due to the SERS enhancement upon introduction of plasmonic Au in the CFs based bimetallic nanosystem.20,30

The structural and morphological analysis of the co-axial electrosprun CFs based bimetallic nanosystem were further executed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The electric-field lines in the gap between Cu electrodes are drawn towards the electrode edges as seen in the electric field profile in Figure 4(a). Figure 4(b) shows the SEM image of direct fabricated aligned co-axial CFs@NiNPs-PtNPs on IDA before heat treatment. As spun fibers have the length in micrometers, which aids in continuous charge transport in chemiresistive based gas sensors. Here, the alignment of nanofibers can be explained by “gap electrospinning”.31,32 The as-spun nanofibers are taken as a string of positively charged elements associated through a viscoelastic medium. This may result in experiencing two sets of electrostatic forces by the charged nanoparticle; (i) F_e acting amid the charged fiber and image charges brought on the two parallel grounded electrodes and (ii) F_s formed by the splitting of electric field. As per Coulomb’s law of interaction, the fibers adjacent to the electrodes produce the sturdiest electrostatic force (F_e), which outcomes the elongating of nanofibers across the collector (parallel copper sheets) to produce aligned co-axial nanofibers.

The co-axial morphology and distribution of the metallic/bimetallic nanoparticles over the fibers was confirmed using TEM as showed in Figure 5. The higher magnification images displayed uniform arrangement of PtNPs, AuNPs-PtNPs and NiNPs-PtNPs formed on CFs with a mean diameter of 4.49, 4.13 and 2.73 nm. The core-shell structure of the co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs was evident from TEM images as depicted in Figure 5(a-b). Fast fourier transform (FFT) was employed by masking to eradicate undesirable noise and hence to disclose the anticipated frequencies by means of Gatan Microscopy Suite Software. In order to get the real image on the masked region in the FFT pattern, an inverse Fourier transform (IFFT) was employed. The IFFT from the HRTEM images of co-axial CFs@PtNPs (Figure 5(c)) revealed a lattice d-spacing of 0.226 nm corresponding to the (111) crystalline plane of fcc Pt anchored on CFs.33

From Figure 5(e), it can be understood that in the case of co-axial CFs@AuNPs-PtNPs, the bimetallic AuNPs-PtNPs were homogeneously
distributed on CFs with a mean diameter of 4.13 nm. The HRTEM and FFT study of core-shell CFs@AuNPs-PtNPs nanosystem were further investigated. IFFT analysis of co-axial CFs@AuNPs-PtNPs (Figure 5g) exhibited a lattice spacing of 0.194 nm and 0.204 nm conforming to the \( d \) spacing values of Pt (200) and Au (200) planes. These results show that AuNPs and PtNPs occur as bimetallic NPs in the co-axial CFs@AuNPs-PtNPs nanosystem. Selected area diffraction (SAED) pattern described in Figure 5h displayed spot patterns allocated to (111), (200), (220), (222) and (420) planes of fcc Pt crystals and the spot patterns allocated to (400) plane of fcc Au deliberated the polycrystalline kind of Au and Pt, that was in virtuous consent with the inferences as attained by XRD patterns of bimetallic Au-Pt nanosystem showing the development of bimetallic AuNPs-PtNPs on CFs.

Similarly, as shown in Figure 5i, co-axial CFs@NiNPs-PtNPs also were found to be successfully formed and were consistently dispersed on CFs with average diameter of 2.9 nm. The HRTEM and FFT images of core-shell CFs@NiNPs-PtNPs based nanosystem was performed for further structural elucidation. IFFT analysis of co-axial CFs@NiNPs-PtNPs (Figure 5k) showed lattice spacing of 0.227 nm and 0.216 nm conforming to the \( d \) values of Pt (111) and Ni (111) planes respectively. These observations specify, that Ni and Pt nanoparticles occur as bimetallic nanoparticles in the co-axial CFs@NiNPs-PtNPs produced through the single-step coaxial Figure 5i displays spot patterns ascribed to (111), (220) and (331) planes of fcc Pt crystals and spot patterns allocated to (111) and (220) plane of fcc Ni crystals discussed the electrosprinning method. SAED pattern analysis showed in polycrystalline nature of Ni and Pt showed a decent agreement with the inferences attained from XRD analysis of co-axial CFs@NiNPs-PtNPs, verifying the bimetallic formation of NiNPs-PtNPs nanostructures on CFs. From the morphological investigations, it is obvious that co-axial bimetallic NiNPs-PtNPs on CFs showed reduced size of nanoparticles and homogeneous distribution over CFs, which can proficiently enable the “spillover effect” during adsorption of \( \text{H}_2 \) than other co-axial CFs@PtNPs based nanosystem and can result in better sensor performance.

In order to understand the surface chemical states of co-axial CFs@PtNPs based nanosystems, XPS analysis was carried out. High-resolution spectra of co-axial CFs@NiNPs-PtNPs consisted of oxygen 1s (O1s), carbon 1s (C1s), nitrogen 1s (N1s), Nickel 2p (Ni2p) and platinum 4f (Pt4f) as depicted in Figure 6. The survey scan spectra of co-axial CFs@NiNPs-PtNPs illustrated in Figure 6a exhibit five prominent peaks at 530.3, 396, 283, 875.2 and 73 eV conforming to O1s, C1s, N1s, Ni2p and Pt4f, that confirmed the existence of elements, such as oxygen, carbon, nitrogen, nickel and platinum. The
C1s peak (Figure 6b) can be deconvoluted into four peaks, attributed to C=C bond (282.6 eV), C=O bond and C-N bond (283.6 eV), C=O bond (285.2 eV) and -COOH (287.4 eV), respectively. The C=C bond (283.6 eV) and 285.2 eV are the distinctive characteristics of C-OH groups and C=O bonds. The high-resolution O1s spectra of co-axial CFs@Ni NPs-Pt NPs (Figure 6d) shows the presence of C=O (530.32 eV), and oxygen vacancies (535.7 eV)\(^{30}\). The Ni 2p spectra (Figure 6c) can be deconvoluted into three peaks at 856.41, 858.5, 401.2 and 403.2 eV attributed to the pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen and pyridinic-N-oxide respectively. Amongst these groups the pyridinic and pyrrolic nitrogen aids in lessening of charge transport resistance and thereby can boost up the catalytic effects due to the sp\(^2\) hybridized nitrogen atom \(^{39}\). The Pt 4f exhibited two peaks emerged at 70.2 and 73.7 eV, which are initiated from the spin orbital coupling of 4f photoelectron transitions as observed from Figure 6f. The lowermost B.E components linked might be ascribed to the zero valent state of metallic platinum NPs\(^{20,21}\).

The Ni 2p spectrum \(^{40,41}\) unveiled two weak peaks emerging at 875.2 and 856.41 eV, ascribed to the binding energies of Ni 2p\(_{3/2}\) and Ni 2p\(_{1/2}\) as shown in Figure 6e. Besides, from the XPS spectra it was confirmed that, there were not any further impurity peaks, and the major Pt 4f and Ni 2p peaks confirmed the emergence of Ni NPs-Pt NPs bimetallic NPs on CFs by single-step co-axial electrospinning method. In addition, Figure 7 compares the Pt 4f spectra of co-axial CFs@PtNPs, co-axial CFs@AuNPs-PtNPs and co-axial CFs@Ni NPs-Pt NPs. The charge transfer occurring in co-axial CFs@Ni NPs-Pt NPs is apparent in XPS (Figure 7) spectra. The high-resolution XPS spectrum of CFs@PtNPs and co-axial CFs@AuNPs-PtNPs are depicted in Figure S1 and Figure S2. In the case of co-axial CFs@AuNPs-PtNPs, the binding energy of Pt 4f spectra was shifted slightly to higher energy, which directs towards the solid interaction prevailing among metallic Au, Pt and the CFs. The B.E shift can pave the way for electron density shift from the bimetallic AuNPs-PtNPs to the CFs. Thereby, the work function lowered for CFs@AuNPs-PtNPs. Therefore, to equilibriate the fermi levels, transfer of charge carriers from PtNPs to AuNPs and then to CFs occurs.\(^{20}\)

Hence, XPS analysis significantly supports the emergence of bimetallic AuNPs-PtNPs on CFs. On contrary, for co-axial CFs@NiNPs-PtNPs, the binding energy of Pt 4f peak was shifted slightly to lower energy (Figure 7), signifying a sturdy interaction prevailing among metallic Ni, Pt and the CFs. This shift may be caused by the transfer of electrons from Ni to Pt owing to the difference in electronegative values of Ni (1.91) and Pt (2.28), which results in a variation in the electronic properties of Pt, i.e., lowering the density of state on the Fermi level in co-axial CFs@NiNPs-PtNPs. Hence, the bimetallic formation with Ni, altered the electronic properties of Pt, resulted in improvement of catalytic performance \(^{42,43}\). Besides, in bimetallic Pt based co-axial CFs nanosystems, the Pt 4f peak gets widened. This possibly would be because of the overlapping of the Ni 3p peak with the Pt 4f\(_{3/2}\) peak. These results also substantiate the observations from with XRD and HRTEM analysis.

**Figure 6.** (a) XPS Survey spectrum of co-axial CFs@NiNPs-PtNPs based nanosystem and High resolution XPS spectrum of (b) C1s (c) N1s (d) O1s (e) Ni 2p and (f) Pt 4f of co-axial CFs@NiNPs-PtNPs based nanosystem.

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axial CFs@PtNPs towards hydrogen in the range of 0.1% to 4%. Figure 8a depicts the dynamic gas sensing response of aligned co-axial CFs@PtNPs, aligned co-axial CFs@AuNPs-PtNPs and aligned co-axial CFs@NiNPs-PtNPs towards hydrogen at room temperature. The sensor response of 1D aligned co-axial CFs@PtNPs was decreased. It might be due to the adsorption of water on the sensor surface by air. However, co-axial CFs@PtNPs sensor took extra time to recover to the baseline resistance as a result of the exposure of platinum hydride amongst nanohybrids. Figure 8b describes the dynamic response of co-axial CFs@AuNPs-PtNPs towards H₂ concentrations ranging from 0.1% to 4% which exhibited sensitivity in the range of 8.9% to 62% at room temperature. During sensor recovery, the resistance of 1D aligned co-axial CFs@AuNPs-PtNPs regained the base resistance more swiftly than co-axial CFs@PtNPs. This might be due to the integration of bimetallic AuNPs-PtNPs catalysts over the core CFs. The bimetallic AuNPs-PtNPs also reduces the emergence of platinum hydride and thereby, increases the catalytic sites offered on the CFs towards H₂ gas which resulted in the improved sensor response and recovery time.

Figure 8c demonstrates the dynamic sensor response of 1D aligned co-axial CFs@NiNPs-PtNPs towards H₂ gas with concentration ranging from 0.1% to 4% at room temperature which exhibited sensitivity in the range of 10.8% to 124% with sensor response time and recovery of 24s and 89s (towards 4% of H₂). Thus, the 1D aligned co-axial CFs@NiNPs-PtNPs sensor exhibited superior adsorption towards H₂ which may be due to the bimetallic NiNPs-PtNPs catalytic active sites present over the core CFs. The sensor performance of co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-Pt NPs are compared in Figure 8d and tabulated in Table S1. The cross-interference of the H₂ sensor towards different gases is a vital parameter for real-time application of the sensors (Figure 9a). The sensor response towards interfering gases such as acetone, ammonia, ethanol and hydrogen sulphide (H₂S), were tested to check the selectivity of 1D aligned co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs. Figure 9b depicts the repeatability of 1D aligned co-axial CFs@Ni NPs-Pt NPs based sensor towards periodic exposure of 0.5% of H₂ at room temperature.

Also, Figure S3 depicts the interference of humidity on the H₂ sensing properties of CFs@NiNPs-PtNPs. It was observed that, with the increase in humidity, the H₂ sensor response of CFs@NiNPs-PtNPs decreased. It might be due to the adsorption of water molecules on the sensor material, which prevents subsequent adsorption of H₂ molecules, leading to decrease in sensor performance. In-situ current-voltage (I-V) studies performed for 1D aligned co-axial CFs@NiNPs-PtNPs sensor exhibited similar responses without any remarkable shift in baseline resistance, upon exposure to 0.5% H₂. 1D aligned co-axial CFs@NiNPs-PtNPs sensor showed similar responses without any remarkable shift in baseline resistance, upon exposure to 0.5% H₂. 1D aligned co-axial CFs@NiNPs-PtNPs sensor performance was compared with recently developed carbon based or metallic based sensors and concisely presented in Table 1. From the recent literature, it was clear that most of the reported H₂ sensors were based on multi-step processes or complex process or expensive method or not suitable for real-time applications. Whereas, the aligned co-axial CFs@NiNPs-PtNPs sensor was developed through a one-step fabrication of sensor material, which can be easily upscaled for mass production for real-time applications. Also, the co-axial CFs@NiNPs-PtNPs sensor showed rapid and stable ON/OFF cycles respectively. Along with the complicated fabrication processes adopted by previous reports, the non-linearity of the sensor responses at higher concentration was an another issue faced by H₂ gas sensors. The aligned co-axial CFs@NiNPs-PtNPs nanosystem not only achieved the ease in fabrication method, but also resolved the problem of non-linearity of
H₂ based gas sensors at higher concentration of H₂ at room temperature. This could be mainly due to the following reasons: (i) the bimetallic catalyst arrangement over the CFs, such that it “spill over” the adsorbed hydrogen on the surface of CFs and (ii) the direct single step fabrication of co-axial bimetallic aligned CFs@NiNPs-PtNPs nanosystem, which eradicates the barrier formation for electron transport, usually occurring during the process of functionalization of carbon support for metal attachment during wet chemical route, which is not required in case of direct co-axial fabrication process.

The linear relation between response and the square root of H₂ gas was accredited by Langmuir isotherm theory of dissociative adsorption of gases on metal surfaces. Based on this theory, adsorption and desorption rates are described as $k_1[H_2](1 - \theta)^2$ and $k_2\theta^2$. Where, $[H_2]$ is the hydrogen concentration, $\theta$ is the surface coverage, adsorption and desorption rate constants are denoted by $k_1$ and $k_2$. Upon steadiness, the rate of hydrogen surface coverage, becomes negligible and thus adsorption rate equivalent to desorption rate, i.e., $k_1[H_2](1 - \theta)^2 = k_2\theta^2$. Hence, gas sensor response is relative to surface coverage ($\theta$), by equation 1

$$S = \sqrt{K[H_2]} \quad \text{equation 1}$$

Where, $K$ is fraction of adsorption rate to desorption rate constants. Therefore, equation 1, aids to estimate the ratio of adsorption-desorption rate constants for co-axial CFs@NiNPs-PtNPs based sensor experimentally, that offer insights to the genre of hydrogen adsorption on bimetallic NiNPs-PtNPs present over the core CFs. During equilibrium, the slope of the sensor response against square root of hydrogen concentration gives the rate constant value experimentally. Also, from the concept of adsorption and desorption of H₂ gas on metal surfaces, the rate constant was theoretically calculated as $(k_1/k_2)^{1/2}=0.42$. Adsorption kinetics of hydrogen gas on the surface of 1D aligned co-axial CFs@mono/bimetallic (PtNPs, AuNPs-PtNPs and NiNPs-PtNPs) were studied theoretically and was found to be approximately close to the experimentally derived values, of 1D aligned co-axial CFs@PtNPs (0.36), CFs@AuNPs-PtNPs (0.29) and CFs@NiNPs-PtNPs (0.38) respectively, which indicates that the adsorption reaction follows the fundamental adsorption-desorption reaction, $H_2 \leftrightarrow 2H_{\text{ads}}$. The better agreement of the experimental adsorption rate constant with the theoretically calculated adsorption rate constant points towards the superior H₂ gas sensor response of CFs@NiNPs-PtNPs (Figure 9d).
Table 1 Comparison with previous reports on H₂ sensors.

| sensor material             | fabrication method   | operating temp. (°C) | H₂ conc. (ppm) | sensitivity |
|-----------------------------|----------------------|----------------------|----------------|-------------|
| Graphene-supported Pt/Pd core–shells hybrid⁵¹ | Wet chemical route and air brush spraying | RT | 10,000 | 36% |
| Pt - CNT⁴⁸                  | Spin coating and Electron beam deposition | RT | 23,000 | 16% |
| Pd thin films⁵²             | RF sputtering        | RT | 20,000 | 12% |
| Pd Nanofilms⁵³             | DC sputtering        | RT | 1000 | 5.5% |
| Pt/Pd bimetallic thin film⁵⁴ | PLD                  | 150 | 10,000 | 13.6 |
| (Pt/SiC) Nanoballs⁵⁵       | DC/RF sputtering     | 330 | 100 | 44% |
| Pt-PPy⁶⁶                   | LBL                  | RT | 1000 | 11.6% |
| Pt-MWCNTs⁵⁷               | Electrodeposition   | RT | 3,000,000 | 16% |
| Palladium-Organic Fibers⁵⁸ | Sputtering (DC)      | RT | 25 | 12.2% |
| Pd/Ox/PAH/PPS/PAH⁵⁹       | Layer by layer       | RT | 1000 | 2.04% |
| CFs/ZnO⁶⁰                 | Electrospinning and RF sputtering | 150 | 100 | 73.4% |

In the case of co-axial CFs@PtNPs based nanosystem, H₂ molecules detaches and adsorb on catalytic sites of CFs@PtNPs based systems, (PtNPs, AuNPs-PtNPs and NiNPs-PtNPs) as given by equation 2.

\[
H_{2g} + 2S_0 \rightarrow 2H_u + 2S_0
\]

Where, \( S_0 \) denotes vacant sites on the sensor. The letter “g” denotes the gaseous state and “a” be the adsorbed state. The nonlinearity during higher concentrations of H₂ observed in previous reports was eliminated by single-step fabrication of aligned co-axial bimetallic NiNPs-PtNPs over CFs.⁷⁷,⁶¹ The integration of bimetallic NiNPs-PtNPs have improved the catalytic sites for hydrogen adsorption, along with the enrichment in the carrier concentrations. This improvement in charge carriers, triggers the conductivity proportionally as shown in the sensor response of aligned co-axial CFs@PtNPs, CFs@AuNPs-PtNPs and CFs@NiNPs-PtNPs. The charge transfer in co-axial CFs@PtNPs based nanosystem was evident from high resolution XPS spectra of Pt 4f (Figure 7). The change in B.E can result in electron density change from the NiNPs-PtNPs/AuNPs-PtNPs to the CF supports. This denotes excellent interaction between bimetallic NiNPs-PtNPs/AuNPs-PtNPs nanosystems over CFs. In the presence of H₂, the bimetallic NiNPs-PtNPs dissociates H₂ molecules into H⁺, which readily adsorb on the catalytic active sites, i.e., bimetallic NiNPs-PtNPs, resulting in the decrease in work function as depicted in Figure 10. As a result, electrons transfer from PtNPs to NiNPs and then to CFs such as to equilibrate the fermi level. This generates in depletion of electrons at NiNPs-PtNPs/CFs interfaces and adsorption of hydrogen might be favoured as it is a reducing gas.

Also, the response and recovery time of aligned co-axial CFs@NiNPs-PtNPs based sensor pronounce to be remarkably improved compared to 1D aligned co-axial CFs@PtNPs and CFs@AuNPs-PtNPs.

During the sensor recovery, existence of oxygen in the air enabled the water formation with adsorbed H₂ at the NiNPs-PtNPs surface. The nature of sensor recovery stipulates that the, surface chemistry plays a vital factor in the execution of successful chemi-resistive

Figure 9. (a) Selectivity towards exposure to interfering gases and (b) repeatability of 1D aligned co-axial CFs@NiNPs-PtNPs towards H₂ at room temperature (c) Current-Voltage characteristics of co-axial CFs@NiNPs-PtNPs in N₂, H₂ and air atmosphere and (d) sensor response as a function of (hydrogen concentration)²/² at RT.
with improved catalytic activity is potentially suitable as H₂ sensing material at room temperature. Henceforth, the prototype of H₂ sensor based on 1D aligned co-axial CFs@Ni NPs-PtNPs was carried out for the development of read-out electronic circuits. Thus, for real-time applications, single-step fabrication of 1D aligned co-axial CFs@bimetallic NiNPs-PtNPs on the sensor device is a convenient and cost-effective method towards H₂ gas sensor development.

The prototype device based on aligned co-axial CFs@NiNPs-PtNPs sensor was fabricated based on the equivalent electronic circuit diagram depicted in Figure 11. The connections were made on a prototype universal printed circuit board (PCB). Real time detection of H₂ gas was established with aligned co-axial CFs@NiNPs-PtNPs sensor with the fabricated electronic circuit configuration. An LM741 operational amplifier IC was used, which works as a comparator circuit. Power supply of 9V was given from the battery to the op-amp. The comparator compares voltages/resistance at inputs and produces an output with the voltage/resistance comparison. Therefore, in this comparator circuit, a potentiometer (1MΩ) was connected to the non-inverting input, which is the reference voltage/resistance (V₀). To the inverting input, the potential across a series resistance (1 MΩ) and output of 1D aligned co-axial CFs@NiNPs-PtNPs sensor was given, which forms Vᵢᵣ. Since, the input was given to the inverting configuration, it is called as negative voltage comparator. That is, when the input signal is more negative than the reference voltage Vᵢᵣ, it results in a high output voltage, Vout. When H₂ is in the OFF state, the sensor unit displayed constant resistance and therefore the LED will be in OFF condition. When the H₂ is introduced to the sensor device, a change in resistance of the sensor occurs (resistance decreases), which vary the comparator input, resulting in glowing of LED. Hence, the real time monitoring of H₂ gas at room temperature authenticates that the proposed device can be used for achieving ideal sensor characteristics.

3. Conclusions

To summarize, direct single-step fabrication strategy for the synthesis of 1D aligned electrospun co-axial CFs@PtNPs, co-axial CFs@AuNPs-PtNPs and co-axial CFs@NiNPs-PtNPs were demonstrated towards H₂ gas sensing at RT. Broad detection of H₂ (0.1% to 4%) using aligned co-axial CFs@Ni NPs-Pt NPs showed superior H₂ gas sensing performance (124%) compared to CFs@PtNPs (52%) and CFs@AuNPs-PtNPs (65.4%) at room temperature which may be due to the superior catalytic property of both Ni and Pt. The hydrogen adsorption kinetics disclosed that the adsorbed hydrogen on the surface of bimetallic NPs, modifies the work function of aligned co-axial CFs@NiNPs-PtNPs sensor, which subsequently modifies the resistance. The non-linearity in sensitivity of H₂ based gas sensors at higher concentration was however eliminated by implementing direct fabricated core-shell structure of CFs@NiNPs-PtNPs. In addition, the aligned fabrication of core-shell nanofibers aids to abolish the obstruction during the electron transport throughout the sensor, which thereby resulted in enhanced sensor performance. The theoretical prediction of the
adssorption rate constant was analogous to the experimental value attained for aligned \textit{co-axial CFs@NiNPs-PtNPs} based nanosystem. The on-screen monitoring of H$_2$ interaction with aligned \textit{co-axial CFs@NiNPs-PtNPs} was studied using \textit{in-situ} current voltage characteristics, which bestowed the authentication of interaction of H$_2$ with the sensor material. Furthermore, a prototype device was successfully fabricated using \textit{1D aligned co-axial CFs@NiNPs-PtNPs} based sensor towards H$_2$ gas detection at room temperature, which opens up its relevance for real time monitoring applications.

**Author Contributions**
The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

**Conflicts of interest**
There are no conflicts to declare.

**Funding Sources**
This work is funded by DST-SERB (Ref: SB/S3/CE/038/2015).

**Acknowledgment**
Authors wish to acknowledge DST-SERB (Ref: SB/S3/CE/038/2015) for financial support. The authors also acknowledge the facilities and support provided by the management, PSG Sons and Charities, Coimbatore.

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