Surface Transformation of Carbon Nanofibers via Co-Electrospinning with Natural Rubber and Ni Doping for Carbon Dioxide Adsorption and Supercapacitor Applications

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Abstract

Three distinctive morphologies of carbon nanofibers (CNFs) on the surface were successfully fabricated by electrospinning technique. The polymeric precursor was prepared by dissolving polyacrylonitrile (PAN), natural rubber (NR) cup lump and nickel-pyridine complex in a one-pot solution. The PAN-based polymeric solution, doped with various amounts of Ni, NR and NR-Ni was electrospun to create polymeric fibers, and then stabilized and carbonized to obtain PAN composite nanofibers. Smooth surfaces were found on all NR doped and Ni (5 wt%) doped CNFs. Pores and spots on the CNFs’ surface occurred on Ni doped CNFs at 10 and 15 wt%, respectively. Interestingly, carbon nanotubes (CNTs) growth on the CNF surface was found in NR-10Ni@CNF samples. Depending on preparation technique, Ni\textsuperscript{0} nanoparticles also formed in CNFs with small size (25 nm) promoting CNTs formation, and large size (200-400 nm) creating pores on the CNF surface. CNTs growth on the carbon fiber surface was successfully achieved using trace amounts of NR with Ni samples. From the supercapacitor electrode and CO\textsubscript{2} adsorption tests, the 1NR-10Ni@CNF electrode showed double the specific capacitance of the PAN electrode while the 5Ni@CNF presented a CO\textsubscript{2} adsorption 4.0 and 2.9 times higher than the PAN@CNF at 273 and 298 K, respectively.

Keywords: Carbon Nanofibers; Natural Rubber; Nickel Particles; CO\textsubscript{2} Adsorption, Supercapacitor.
1. Introduction

Carbon nanofibers (CNFs), as a one-dimensional (1D) nanostructured carbon form, are receiving increasing attention as suitable materials for various applications because of their light weight, high physical strength, and chemical resistance.[11] CNFs have potential applications in nanocomposites,[2] catalyst supports,[3] rechargeable batteries,[4] textiles,[5] supercapacitors,[6] energy devices,[7] and hydrogen storage.[8] Each application requires different CNF morphologies to enhance its properties. For example, hydrogen storage or catalytic applications require high surface area and small pores on the CNF surface,[3,9] physical properties depend on the size and surface area of CNFs,[10, 11] while superconductor applications need tunable metal form and controllable particle size inside the CNF matrix. However, controlling the size, surface area, and specific CNF morphology corresponding to each application is a challenging task. Transition metal nanoparticles (Pd, Pt, Rh, Ru, Ir, Ni, …, etc.) supported CNFs have received increasing interest for their use as catalysts.[12] For example, Ni/CNFs were used as a catalyst for methane decomposition[13] and hydrogenation reaction of benzene,[14] 2-tert-butylphenol,[15] and p-nitrophenol.[16] However, the decorated Ni was mostly achieved by conventional preparation methods such as impregnation, deposition-precipitation, and co-precipitation.

Developed CNF fabrication methods include traditional chemical vapor growth and polymeric electrospinning. Chemical vapor growth produces uniform CNFs, but this method is complicated and expensive. By contrast, electrospinning is an effective technique to produce polymeric nanofibers. The electrospinning technique also provides opportunities to develop fiber morphology, chemical composition, architecture, and functionality.[17] Furthermore,
Electrospinning is well-known for its easy operation and universality in processing different polymers to produce functional nanofibers on an industrial scale.\textsuperscript{[18]} Various polymer sources include polyacrylonitrile (PAN),\textsuperscript{[19]} polyvinyl alcohol (PVA),\textsuperscript{[20]} polyvinylpyrrolidone (PVP),\textsuperscript{[21]} pitch,\textsuperscript{[22]} and rayon\textsuperscript{[23]} to fabricate polymeric fibers before the carbonizing process. CNFs obtained from the as-spun PAN precursor give the highest carbon yield, but PAN is an expensive synthetic polymer.\textsuperscript{[24]} Furthermore, the advantage of the as-spun PAN shows lower genotoxicity compared to traditional CNFs for human uses’ application.\textsuperscript{[25-27]} As previously described, carbon nanostructures have been synthesized by several methods in the attempt to develop various surface morphologies. For example, volatile organic solvents drive pore formation,\textsuperscript{[28]} while carbon additives enhance high surface area\textsuperscript{[29]} and mixed polymeric precursors promote branches on the carbon nanofiber surface.\textsuperscript{[30]} Also, applying environmentally friendly, green chemistry is becoming more attractive by replacing hazardous substances with natural resources.\textsuperscript{[31, 32]}

Natural rubber (NR), a bio-resource, has been applied as a filler in many materials, such as polymers, composites, and carbon materials.\textsuperscript{[33-34]} There is no report on using NR as a precursor or additive for electrospun polymeric fibers. The carbon chain of the NR structure may create some advantages to the carbon nanofiber texture, such as increasing carbon content, increasing defects, and creating porosity in the interior carbon fiber. In this work, NR was used as a co-precursor with PAN, while metallic nickel doping was applied to enhance distinctive surface morphologies on CNFs such as carbon nanotubes (CNTs), pores and spots on the CNF surface. Conventional methods to control Ni particles as dopant in metallic form, using PAN-based carbon nanofiber under conventional heat treatment and different behaviors of Ni particles in metallic form in CNFs
were assessed. Three different sets of CNFs (Ni-PAN, NR/PAN, and Ni-NR/PAN) were investigated for the effects of three different amounts of Ni, (5, 10 and 15 wt%), and NR (0.5, 1.0 and 2.0 wt%) on the morphology and properties of fabricated CNFs. Typical characterization techniques including thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy (RS), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and adsorption-desorption analyzer (BET analysis) were performed. Furthermore, the electrochemical performance and CO2 adsorption of the synthesized CNFs were evaluated.

2. Experimental section

2.1 Materials

In this research work, all chemicals were commercially available and used without further purification. Polyacrylonitrile (PAN) (ca. MW = 150,000), nickel (II) nitrate hexahydrate (Ni(NO3)2·6H2O), and pyridine (C5H5N) were purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF) was purchased from Carlo-Erba Reagents. Hexane was obtained from Macron Fine Chemicals. Raw natural rubber (NR) cup lumps were harvested from an agricultural farm in Thailand. Nitrogen gas (99.999% UHP) was supplied by S.I. Technology Co., Ltd. (Thailand). Polyvinylidene fluoride (PVDF, 99.9%, Mw ~ 600,000) was purchased from Xiamen Tob New Energy Technology, China. Carbon black (CB, super P conductive, 99+ %) was purchased from Alfa Aesar.
2.2 Preparation of CNFs

2.2.1 Preparation of Ni doped CNFs

Nickel nanoparticles (NiNPs) doped CNFs were fabricated by a polymeric electrospinning process followed by conventional heat treatment, as shown in Fig. 1. First, 8 wt% of PAN solution was prepared by completely dissolving PAN polymer in DMF under magnetic stirrer for 12 h at room temperature.\textsuperscript{[11, 35]} Metal nitrate and pyridine ligand were then added into the prepared solution in complex forms\textsuperscript{[36]} under vigorous stirring at room temperature until a homogeneous solution was obtained. Different amounts of metal complexes, 5, 10, and 15 wt%, were added to the PAN-based solution. Several solutions with varying metal complexes were prepared using nickel (II) nitrate complex with equivalent pyridine ligand (denoted as 5Ni-PAN, 10Ni-PAN and
The polymeric solution precursors with prepared metal complexes were electrospun into polymeric fibers through a stainless-steel gauge needle (1 mm inner diameter) connected to the anode of a DC power supply at a high voltage of 15 kV and flow rate of 1 ml/h. An aluminum foil sheet covered a stainless-steel roller as a collector. The process was carried out in the air at room temperature. The distance between a needle tip and collector was 15 cm. Finally, the as-spun fibers obtained were transformed into carbon nanofibers via thermal treatment. All as-spun fibers were stabilized at 260 °C for 2 h with a heating rate of 1 °C/min and then annealed at 900 °C with a heating rate of 10 °C/min under N₂ atmosphere for 1 h to obtain NiNP doped CNFs (denoted as 5Ni@CNF, 10Ni@CNF and 15Ni@CNF).

2.2.2. Preparation of NR doped CNFs

The NR doped CNFs were fabricated similar to the previous preparation, as 8 wt% of PAN polymer was dissolved in DMF using a magnetic stirrer for 12 h at room temperature. Then, NR solution was prepared by homogeneously dissolving dried NR in hexane under vigorous stirring at room temperature for 12 h. The prepared solution of NR was gradually added into the 8 wt% PAN solution and vigorously stirred for 1 h. For the mixed polymeric solution, different amounts of NR were added to the PAN-based solution at 0.5, 1 and 2 wt% (denoted as 0.5NR-PAN, 1NR-PAN and 2NR-PAN). Then the mixed polymeric solution precursors were electrospun into fibers through a stainless-steel gauge needle (1 mm inner diameter) connected to a DC power supply at high voltage of 20 kV and flow rate of 2 ml/h. An aluminum foil sheet covered a stainless-steel roller as a collector. The process was carried out in the air at 30 °C. The distance between tip and collector was set at 15 cm. Finally, the obtained fibers were transformed into carbon fibers by heat
treatment at the same temperatures, times and heating rates noted in section 2.2.1. The NR-doped CNFs obtained were named 0.5NR@CNF, 1NR@CNF and 2NR@CNF.

### 2.2.3 Preparation of NR and Ni doped CNFs

NR and Ni doped CNFs were prepared by mixing NR-PAN polymer with nickel (II) complex. The 0.5, 1 and 2NR-PAN solution precursors were prepared by the method described in 2.2.2. Then, 10 wt% of nickel (II) nitrate and four equivalents of pyridine ligand were added into three NR-PAN solution precursors to obtain the NR-PAN and Ni complex polymeric precursors (denoted as 0.5NR-10Ni-PAN, 1NR-10Ni-PAN and 2NR-10Ni-PAN). After adding all the components, the solution precursors were vigorously stirred at room temperature for 0.5 h before loading into the syringe and installing in the electrospinning machine. The mixed precursors were electrospun into fibers under the same conditions and parameters of 2.2.1. Finally, the NR and Ni doped fibers obtained were transformed into carbon by heat treatment, following the same process previously described. These CNFs were named as 0.5NR-10Ni@CNF, 1NR-10Ni@CNF and 2NR-10Ni@CNF.

### 2.3 Characterization

Chemical functional groups of the as-spun fibers were analyzed by Fourier transform infrared spectroscopy (FTIR) using a Spectrum 100 (PerkinElmer, USA). Data were collected using an attenuated total reflection (ATR) technique connected to infrared spectroscopy with 16 scans/samples. Thermal stability and weight loss of the as-spun fiber samples were determined by thermogravimetric analysis (TGA), model TGA2 STARe system (Mettler Toledo, USA).
performed in the range 40 to 700 °C with a heating rate of 10 °C/min under nitrogen flow of 5ml/min. Crystal structures of the samples were measured by Raman spectroscopy (RS) (HORIBA model KH 8700, Japan). Chemical components of all carbon fibers were recorded by powder X-ray diffraction (XRD), model D8 advanced X-ray diffractometer (Bruker, USA) equipped with a Cu Kα sealed tube X-ray source (1.5418 Å). Data were collected in the range 5.0 to 60.0° for 2θ in steps of 0.02° with a scan speed of 0.1 sec/step. The average size of metal particles was estimated from the XRD data by the Scherrer equation, as presented in Equation (1).[^37]

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(1)

where D is the average particle grain size, K is a dimensionless factor (typical value = 0.9), λ is the X-ray wavelength, β is the line broadening at maximum intensity of full width at half maximum (WFHM), and θ is the Bragg angle. Physical morphology of the carbon fiber samples was detected by a field emission scanning electron microscope (FESEM), model Merlin Compact (Zeiss, Germany). Images were captured under an in-lens duo detector (in-lens secondary electron (SE) and energy selective backscattered detection (EsB)) and a transmission electron microscope (TEM), model Tecnai G2 20 S-Twin (FEI, USA) at an operating voltage of 200 kV. The gas adsorption-desorption experiment (up to 1 bar) was performed on a Quantachrome Autosorb automated gas sorption analyzer.

### 2.4 Supercapacitor device assembly and electrochemical performance evaluation
Supercapacitor cells were assembled in two-electrode Swagelok cells using the PAN composite nanofibers (Ni doped CNFs, NR doped CNFs, and NR-Ni doped CNFs) as a major component in electrodes, 2 M sulfuric acid as the electrolyte, and filter paper (Whatman filter paper No. 4) as the membrane separator. The electrode was prepared by casting a slurry containing the PAN composite nanofibers, carbon black, and PVDF binder in a weight ratio of 7:2:1, respectively on stainless-steel foil before drying inside a vacuum oven at 80 °C overnight. The dried electrode was then punched into a circular sheet with a diameter of 80 mm before assembling in the Swagelok cells. All electrochemical characterizations were measured at room temperature. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were conducted by electrochemical workstation (Metrohm Autolab, PGSTAT302N). Specific capacitance of the PAN composite nanofiber electrodes was evaluated from GCD curves according to Equation (2).\[^{38}\]

\[
\text{CSC} = \frac{4I\Delta t}{m\Delta V}
\]  

(2)

where CSC is a specific capacitance (F/g), I is a constant discharge current (A), \(\Delta t\) is a discharge time, m is the electrode mass (g), and \(\Delta V\) is a potential change (V).

### 2.5 CO\(_2\) adsorption measurements

CO\(_2\) adsorption isotherms were measured on an Autosorb iQ-MP/XR (Quantachrome) at 273 and 298 K. 80 mg of sample in a sample cell were degassed at 553 K for 18 h under a He environment before the measurement. The adsorption isotherms were recorded at pressures
ranging from 0-100 kPa while flowing pure CO₂ (99.999 %).

3. Results and discussion

3.1 Characterization of synthesized carbon nanofibers

![TGA curves of 10Ni-PAN (green), 1NR-PAN (brown), and 1NR-10Ni-PAN (blue) as-spun fiber.](image)

**Fig. 2** TGA curves of 10Ni-PAN (green), 1NR-PAN (brown), and 1NR-10Ni-PAN (blue) as-spun fiber.

TGA was performed to investigate the optimal temperature and prevent polymeric decomposition to stabilize the as-spun fibers. Thermograms of selected as-spun fibers are shown in Fig. 2. The 1NR-PAN showed one step of large weight loss at 310 °C (29%) due to the
decomposition of compounds containing oxygen, nitrogen and hydrogen during the carbonization process.\cite{39} Conversely, TGA curves of 10Ni- and 1NR-10Ni-PAN showed three steps of weight loss. The first weight loss occurred at 50 to 110 °C corresponding to humidity removal, while the second step was observed between 175 °C and 260 °C indicating pyridine ligand dissociation. The last step reflected decomposition and carbonization at 300°C. Therefore, the selected temperature for stabilization was 260 °C.

**Fig. 3** FTIR spectra of as-spun fibers.

The 8 wt% PAN, 1NR-PAN, 10Ni-PAN and 1NR-10Ni-PAN as-spun fibers were selected to
characterize the chemical functions by FTIR, as shown in Fig. 3. Vibrational frequencies of the as-spun nanofibers were presented in the range 3500 to 750 cm\(^{-1}\). Different dopant fibers showed clear characteristic signals, in agreement with the 8 wt% PAN spectrum at 2923, 2245 and 1454 cm\(^{-1}\) of C–H stretching, C≡N group and C–H bending, respectively.\(^{[40]}\) The spectrum of 1NR-PAN presented the characteristic vibration of PAN and showed a weak absorption band at 2160 cm\(^{-1}\) assigned to C=C stretching and a weak band at 1663 cm\(^{-1}\) assigned to substituted C=C stretching.\(^{[41]}\) The C=C vibrations in the 1NR-PAN spectrum implied that NR had dispersed in PAN fibers. For 10Ni-PAN and 1NR-10Ni-PAN spectra, the vibrational frequencies revealed similar patterns resulting from Ni-pyridine complex addition and poor signal of NR. The distinct weak broad bands around 2160 and 1663 cm\(^{-1}\) were assigned to C=C stretching, while the strong broad vibration at 1319 cm\(^{-1}\) corresponded to the C–N group of disordered pyridine ligands in the Ni-pyridine complex.\(^{[42]}\) Moreover, characteristic aromatic peaks at 1046 and 828 cm\(^{-1}\) were attributed to the pyridine ring structure, while the absorption band at 1740 cm\(^{-1}\) was assigned to C=O stretching of the residue solvent (DMF). The Ni metal signal was not observed in the 1NR-10Ni-PAN spectrum, but vibration of the coordinated pyridine ligand was used as evidence for metal complex addition. The wavenumber of free pyridine ligand (1433 cm\(^{-1}\)) shifted to a lower value when coordinated to the metal core,\(^{[43]}\) while broad frequencies between 1400 and 1322 cm\(^{-1}\) were assigned to coordinated pyridine ligand due to the lower shift and wide wavenumber frequency range.

All fabricated CNF samples were characterized by Raman spectroscopy. In Fig. 4, the D-band (blue region) at 1355 cm\(^{-1}\) reflected disordered graphite in CNF, while the G-band (yellow region) around 1580 cm\(^{-1}\) was caused by ordered graphite or carbon fibers with sp\(^2\) hybridization.\(^{[44]}\) The
presence of the D-band implied that the CNFs had defects due to impurities, incomplete graphitization and sp³ hybridization. Increase in the ratio of D- to G-band intensity revealed the level of defects and impurities in the CNF structure, with a higher ratio indicating lower crystallizability of the carbon fibers. For nNR@CNF samples, the value of D-band/G-band ratio increased at higher NR content because the NR dopants were not carbon-based for graphitization. Therefore, slightly increasing value of D-band/G-band ratio when adding higher amounts of NR affects the lower crystallizability of the samples. The D-/G-band intensity ratio of Ni doped CNFs, 10Ni@CNF was the highest (I_D/I_G =1.03), while 5Ni@CNF gave a moderate ratio (0.97) and 15Ni@CNF had the lowest ratio (0.79). This fluctuation occurred due to Ni particles embedded inside the CNF structure. Interestingly, the combination of NR and Ni CNF ratios (nNR-10Ni@CNF samples) were lower than for pure NR and Ni doped CNF. As mentioned, NR and Ni doped CNFs showed reduced crystallizability, but the ability to enhance graphitization and increase sp² carbon formation.
Fig. 4 Raman spectra of carbon nanofibers.
Fig 5 XRD patterns of carbon nanofibers.

X-ray diffraction patterns obtained from synthesized carbon nanofibers are depicted in Fig. 5. The broad diffraction peaks between 25 and 35 degrees of 2θ confirmed the disordered structure of the carbon phase.[15] The diffraction pattern of synthesized 8 wt%-PAN@CNF showed the carbon phase pattern of carbon nanofibers, corresponding to previous reports.[45] For Ni doped carbon nanofibers, the small peak at 2θ = 26 degrees of the 10Ni@CNF and 15Ni@CNF patterns was attributed to the reflection (002) of carbon due to a more graphitic structure of the carbon fibers or carbon bonded to Ni.[46] All Ni doped CNFs revealed sharp diffraction peaks at 2θ = 44
(111) and 52 (200) degrees as typical peaks of metallic Ni, while 5Ni@CNF comprised diffraction peaks at $\theta = 37$ (111) and 43 (200) degrees of NiO.\cite{46} Interestingly, the XRD patterns of 10Ni@CNF and 15Ni@CNF showed only Ni (0) peaks because the pyridine ligand coordinated around the Ni metal core prevented oxidation of Ni during the thermal process. However, NiO particles were observed in 5Ni@CNF because of incomplete complexation for low concentrated Ni and pyridine in the polymeric solution. 10Ni@CNF had the lowest Ni content in metallic form and was selected to dope with trace NR. As expected, various amounts of NR dopant containing 10 wt% Ni carbon nanofibers provided only the Ni$^0$ pattern without NiO formation.
Average sizes of metal particles were estimated from the XRD data by the Scherrer equation as presented in Table S1. The Ni\(^0\) particle size was calculated at 15-18 nm by applying a common value of K = 0.9, and the calculated particle size of NiO particles in 5Ni@CNF was 15.04 nm. The calculated Ni particle size indicated that this method could measure doped Ni particles on a nanometric scale and showed good particle dispersion. Compared to the TEM
technique as shown in Fig. 6, particle sizes were observed to be distributed between 25 and 30 nm for small size and from 130 to 250 nm for large size. Some large Ni particles aggregated during polymeric solution or graphitization processes.

![Fig. 6](image)

**Fig. 6** Proposed mechanism for NiNPs formation after coordinated by pyridine ligand.

Based upon the results herein and the precedent reports, a plausible reaction pathway is shown in Fig. 7. At the polymeric solution preparation step, the nickel nitrate (Ni(NO$_3$)$_2$) was surrounded by excess pyridine ligands which led to the formation of square planar [Ni(py)$_4$(NO$_3$)$_2$] complex.$^{[47, 48]}$ However, when excess pyridine was added to the solution precursor, other forms of Ni complexes were created with 2, 3, or 6 pyridine compounds in the solution such as [Ni(py)$_2$(NO$_3$)$_2$], [Ni(py)$_3$(NO$_3$)$_2$], and [Ni(py)$_6$(NO$_3$)$_2$].$^{[49, 50]}$ Subsequently, the Ni (II) complex changed to NiNPs by removing pyridine compounds under high temperature in the stabilization and carbonization steps. In these steps, the pyridine compound that surrounded the Ni$^{2+}$ ion probably prevented oxidation of Ni to nickel oxide.
Morphologies of carbon nanofibers with different dopants were determined by SEM and TEM. As shown in Fig 8(a-c), SEM images of various Ni doped CNFs had different morphologies as smooth surfaces with pores and spots for 5Ni@CNF, 10Ni@CNF and 15Ni@CNF respectively. The 5Ni@CNF had a uniform smooth surface and small diameter size (250-350 nm) with well dispersed Ni$^0$ nanoparticles (25 nm). The two sizes of Ni particle were assigned as Ni$^0$ (25 nm) and NiO (200 nm) forms, corresponding to the XRD result. By contrast, 10Ni@CNF had a porous surface and larger diameter size (average 633 nm). Although Ni doped CNF was observed as only...
Ni\textsuperscript{0} form, these Ni\textsuperscript{0} particles (250 nm) were larger than Ni particles in 5Ni@CNF, indicating that Ni agglomerated to larger particles when increasing the amount of Ni dopant to 10 wt%. Moreover, pores occurred throughout the carbon fiber chain and were affected by Ni nanoparticle drilling.\textsuperscript{[51]} As shown in Fig. 6 (b), the Ni particles destroyed the carbon matrix adjacent to their surface by creating pores on the surface.\textsuperscript{[52-54]} The TEM images reveal some evidence that pore formation on CNFs by Ni\textsuperscript{0} particles drilled the CNF matrix such that NiNPs were found at the bottom site of pores. The 15Ni@CNF particles had a similar diameter (average 849 nm) to 10Ni@CNF sample. Pores were not observed on the surface of 15Ni@CNF, while large spots of Ni particles were found throughout the CNF surface. The high Ni content in CNF encouraged agglomeration of the larger particles and favored NiO formation under thermal conditions.\textsuperscript{[55]}

All three NR doped CNF samples had smooth surfaces. As depicted in Fig. 9(a-c), average diameters of NR doped CNF were 422, 433, and 676 nm for 0.5NR@CNF, 1NR@CNF, and 2NR@CNF, respectively. Increased diameter resulted from the higher content of NR doped in solution during the electrospinning polymeric fiber process. Higher content of NR dopant obstructed the electrospinning process and impacted diameter size. Additionally, as mentioned in Raman characterization, the NR dopant interrupted the graphitization process but also enlarged the diameter size, implying that NR can be used as either a carbon additive or a carbon source for CNF fabrication. However, NR doping over 2 wt% could not be electrospun into fibers because incompatibility between PAN precursor and NR affected particles formation during preparation of polymeric precursor.
Fig. 9 SEM images (left) and diameter size distribution (right) of (a) 0.5NR@CNF, (b) 1NR@CNF and (c) 2NR@CNF samples.

Interestingly, when NR was varied between 0.5, 1 and 2 wt% to Ni (10 wt%) CNF, the three SEM images revealed branches of carbon nanotube growth over their mother CNF, as demonstrated in Fig. 10 (a-c). The average sizes of diameter of CNFs for 0.5NR-10Ni@CNF, 1NR-10Ni@CNF, and 2NR-10Ni@CNF samples were 789.63, 879.52, and 1,890.54 nm, respectively. The observed carbon nanotubes on the CNF surface grew after catalyzation by Ni nanoparticles. Compared to without NR doping for 10Ni@CNF, the agglomerated Ni particles decomposed in the carbon matrix around the Ni particles, while smaller Ni particles (27 nm) with
NR doped 10Ni@CNF favored catalyzed carbon nanotube growth. Ni particles of 5Ni@CNF did not induce carbon nanotube growth because of poor non-graphitized carbon residues in the carbon fiber. Ni particles of NR doped CNF in 10Ni@CNF can behave as a catalyst for carbon nanotube growth because the chemical structure of NR allows carbon decomposition to become a carbon resource. To confirm that Ni nanoparticles catalyzed carbon nanotube growth, the 0.5NR-10Ni@CNF was subjected to TEM characterization. As shown in Fig. 6 (c), Ni nanoparticles were fixed on terminal carbon nanotubes and clearly grew up from their mother surface. Prasiwi et. al.[51] proposed the CNF growth mechanism on Ni and Ni/C catalysts with the decomposition of ethylene. Similarly, at high temperature during the carbonization step, NR was decomposed and Ni nanoparticles on the CNF surface became the active nucleation sites for CNT growth. In addition, the diameter of these carbon nanotubes was close to the Ni size, concurring with previous reports.[56, 57] The 2NR-10Ni@CNF had the lowest carbon nanotube growth and largest diameter of CNF because higher content of non-compatible NR resulted in poor NR dispersion in the PAN polymer and as-spun fiber shape.
Nitrogen adsorption-desorption measurements of all samples were performed following the BET method to probe the surface area of the materials, with results presented in Table 1. Figure 11(a) shows the adsorption-desorption of 5Ni@CNF, 10Ni@CN, and 15Ni@CNF, respectively. 5Ni@CNF exhibited isotherm type I and surface area of 396.72 m$^2$/g related to their smallest size, while 10Ni@CNF and 15Ni@CNF samples were categorized in type IV isotherm with typical characteristics of mesoporous solids proceeding through monolayer and multilayer hysteresis, followed by capillary condensation during desorption.$^{[58,59]}$ The 10Ni@CNF sample showed pores...
on the surface but had the lowest surface area (66.23 m²g⁻¹) because the CNF formed bunches, whereas the 15Ni@CNF sample had moderate surface area (144.07 m²g⁻¹) with fewer CNF bunches than 10Ni@CNF. Specific surface area of the nNi@CNF samples ranged between 60 and 400 m² g⁻¹ depending on the Ni doped concentration.

**Table 1.** Physicochemical properties of Ni doped carbon nanofiber

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Ni@CNF</td>
<td>396.27</td>
<td>0.0312</td>
<td>2.02</td>
</tr>
<tr>
<td>10Ni@CNF</td>
<td>66.23</td>
<td>0.0326</td>
<td>3.45</td>
</tr>
<tr>
<td>15Ni@CNF</td>
<td>144.07</td>
<td>0.0562</td>
<td>2.77</td>
</tr>
<tr>
<td>0.5NR@CNF</td>
<td>26.32</td>
<td>0.0076</td>
<td>2.88</td>
</tr>
<tr>
<td>1NR@CNF</td>
<td>14.60</td>
<td>0.0104</td>
<td>5.28</td>
</tr>
<tr>
<td>2NR@CNF</td>
<td>5.77</td>
<td>0.0102</td>
<td>6.60</td>
</tr>
<tr>
<td>0.5NR-10Ni@CNF</td>
<td>169.99</td>
<td>0.0850</td>
<td>3.13</td>
</tr>
<tr>
<td>1NR-10Ni@CNF</td>
<td>79.38</td>
<td>0.0613</td>
<td>4.07</td>
</tr>
<tr>
<td>2NR-10Ni@CNF</td>
<td>62.91</td>
<td>0.1019</td>
<td>6.53</td>
</tr>
</tbody>
</table>
**Fig. 11** The N$_2$ adsorption-desorption isotherms of (a) nNi@CNF, (b) nNR@CNF and (c) nNR-10Ni@CNF samples.
Figure 11(b) shows nitrogen adsorption-desorption isotherms of 0.5NR@CNF, 1NR@CNF, and 2NR@CNF as type I, indicating uniform CNF surface for all NR doped samples. Specific surface areas of 0.5NR@CNF, 1NR@CNF and 2NR@CNF were 26.23, 14.60 and 5.77 m² g⁻¹, respectively and decreased with increased quantity of NR polymer corresponding to the larger diameter of higher NR doped CNF. Moreover, 1NR@CNF and 2NR@CNF isotherms displayed poor N₂ adsorption on carbon-based materials, which agrees with previous studies.⁶⁰ Figure 11(c) shows the nitrogen adsorption/desorption isotherms of 0.5NR-10Ni@CNF, 1NR-10Ni@CNF, and 2NR-10Ni@CNF. Specific surface areas of 0.5NR-10Ni@CNF, 1NR-10Ni@CNF, and 2NR-10Ni@CNF were 196.99, 97.38, and 62.91 m² g⁻¹ respectively, and decreased with increased NR polymer loading that resulted in larger CNF diameters which influenced lower CNT formation on the mother carbon surface. All samples gave type IV isotherms, indicating narrow cylindrical pores on CNF surface branches.⁵⁸, ⁵⁹

### 3.2. Electrochemical performance of PAN and PAN composite nanofiber electrodes

Among PAN composite nanofibers, NR-Ni-PAN composite nanofibers (NR-Ni@CNF) were selected to evaluate the electrochemical performance as electrodes in supercapacitor cells due to their specific surface and mechanical characteristics. The performances of PAN and NR-Ni-PAN composite nanofibers were evaluated by CV within a range of 0 – 1.2 V at a scan rate of 50 mV/s before observing their specific capacitance by GCD. Overall, the voltammogram of PAN nanofiber electrode showed similarity to quasi-rectangular shape (Fig. 12(a)), while the PAN composite nanofiber electrode presented pseudocapacitive characteristics.⁶¹ The PAN composite electrode
with the lowest natural rubber content, 0.5NR-10Ni@CNF, showed small redox peaks at ~0.52 and ~0.67 V (Fig. 12(b)). Increasing natural rubber to 1 and 2 wt% in the PAN composite nanofibers resulted in larger voltammogram areas with redox peaks (Figs. 12(c) and 12(d)). For 1NR-10Ni@CNF electrode, a small redox peak was observed at ~0.52 V, while the 2NR-10Ni-PAN electrode presented ~0.58 and ~0.85 V. It was hypothesized that Ni nanoparticles promoted ion conduction, while natural rubber increased porosity of the electrode.

Fig. 12 Electrochemical performance of PAN and PAN composite electrodes. Cyclic voltammograms at scan rates of 50 mV/s of (a) PAN@CNF, (b) 0.5NR-10Ni@CNF, (c) 1NR-10Ni@CNF, and (d) 2NR-10Ni@CNF.
Fig. 13 Electrochemical performance of PAN and PAN composite electrodes. Galvanostatic charge–discharge profiles at current density of 0.1 A of (a) PAN@CNF, (b) 0.5NR-10Ni@CNF, (c) 1NR-10Ni@CNF, and (d) 2NR-10Ni@CNF.

Figure 13 presents the specific capacitance of PAN and PAN composite electrodes evaluated at current density of 0.1 A/g and calculated using Equation (2). Overall, the specific capacitance results were strongly related to the CV performance. The PAN electrode presented an average specific capacitance of ~40 F/g, while the 0.5NR-10Ni@CNF, 1NR-10Ni@CNF, and 2NR-10Ni@CNF electrodes showed average specific capacitances of ~25, ~84, and ~61 F/g, respectively. Among the PAN composite electrodes, the 1NR-10Ni@CNF presented a specific...
capacitance double that of the PAN electrode. The increased specific capacitance could be related
to pore characteristics of the PAN composite nanofibers.[65, 66] Even though the charge-discharge
performance was not as high as the previously published results,[67, 68] it could be seen that
incorporating natural rubbers and Ni nanoparticles into the PAN nanofiber electrode significantly
improved the electrochemical performance. In addition, the physical characteristics of PAN
composite electrode after measuring the electrochemical performance were checked. Non-
homogeneity of electrode between the PAN composite nanofibers and conductive carbon was
found (Fig. S1). To improve the electrochemical performance of the PAN composite electrodes,
optimization of electrode preparation processes was required.

3.3. CO₂ adsorption isotherms

The CO₂ adsorption capacities of nNi@CNF samples are in the order of 5Ni@CNF >
PAN@CNF > 15Ni@CNF > 10Ni@CNF (Fig. 14). The CO₂ adsorption isotherm of 5Ni@CNF
shows greatest CO₂ uptake at 273 K (137.95 cc/g) and 298 K (95.94 cc/g) with a steep rise at low
relative pressure, which the value is much higher than PAN@CNF at 273 K (33.91 cc/g) and 298
K (32.80 cc/g). Moreover, the adsorption amounts of CO₂ on 5Ni@CNF were 6.15 and 4.28
mmol/g at 273 K and 298 K, respectively which were superior to that of commercial activated
carbon fibers (1.92 mmol/g).[69] These samples have similar smooth surface, but the 5Ni@CNF
demonstrated high CO₂ uptake capacity because the NiNPs might have some interactions between
the CO₂ molecules and NiNPs interactions. Compared with previous reports, the CO₂ adsorption
capacity at both temperatures of 5Ni@CNF was highest while those CNF samples possessed high
surface area, high porosity, and hollow cylindrical shape.[70-74] The adsorption capacity of CO$_2$ by different dopants and morphologies of CNFs is tabulated in Table 2. Compared with the reported NiO/CNFs and MgO/ACNF, this 5Ni@CNF displays the moderate $S_{BET}$ but the sample shows the highest adsorption performance of CO$_2$ at 298 K and 1 bar. When compared to porous CNF without metal oxide dopants, the 5Ni@CNF material has the lowest $S_{BET}$ and the adsorption performance of this sample presents the highest CO$_2$ uptake at both temperatures (273 K and 298 K). However, 15Ni@CNF and 10Ni@CNF showed low CO$_2$ adsorption amounts at both temperatures due to their surface morphologies. The 15Ni@CNF had Ni/NiO spots over the surface which had free space between the carbon matrix and particles to adsorb CO$_2$ molecules. The 10Ni@CNF surface, which had high surface porosity, gave the lowest CO$_2$ uptake capacity since the pore size was too large to capture CO$_2$ molecules.
Fig. 14 CO₂ adsorption equilibrium isotherms for nNi@CNF (a) at 273 K and (b) at 298 K.
Table 2 Comparisons of CO$_2$ uptakes at 1 bar on the adsorbents with various support materials.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>SSA (m$^2$/g)</th>
<th>Temp.(K)</th>
<th>CO$_2$ uptake (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN@CNF</td>
<td>306</td>
<td>298</td>
<td>2.52</td>
<td>[74]</td>
</tr>
<tr>
<td>Activated-CNCF</td>
<td>897</td>
<td>298</td>
<td>3.17</td>
<td>[75]</td>
</tr>
<tr>
<td>Hollow ACNF</td>
<td>884</td>
<td>298</td>
<td>3.16</td>
<td>[76]</td>
</tr>
<tr>
<td>NiO/CNF</td>
<td>330</td>
<td>298</td>
<td>1.11</td>
<td>[77]</td>
</tr>
<tr>
<td>MgO/ACNF</td>
<td>413</td>
<td>298</td>
<td>2.67</td>
<td>[78]</td>
</tr>
<tr>
<td>PCNF-2-1000</td>
<td>417</td>
<td>298</td>
<td>3.11</td>
<td>[79]</td>
</tr>
<tr>
<td>Porous CNF/C-H</td>
<td>1084</td>
<td>273</td>
<td>5.08</td>
<td>[80]</td>
</tr>
<tr>
<td>Porous CNF/C-S</td>
<td>990</td>
<td>273</td>
<td>4.63</td>
<td>[80]</td>
</tr>
<tr>
<td>5Ni@CNF</td>
<td>396</td>
<td>273</td>
<td>6.15</td>
<td>This work</td>
</tr>
<tr>
<td>5Ni@CNF</td>
<td>396</td>
<td>298</td>
<td>4.28</td>
<td>This work</td>
</tr>
<tr>
<td>10Ni@CNF</td>
<td>66</td>
<td>273</td>
<td>0.28</td>
<td>This work</td>
</tr>
<tr>
<td>10Ni@CNF</td>
<td>66</td>
<td>298</td>
<td>0.18</td>
<td>This work</td>
</tr>
<tr>
<td>1NR-10Ni@CNF</td>
<td>79</td>
<td>273</td>
<td>1.19</td>
<td>This work</td>
</tr>
<tr>
<td>1NR-10Ni@CNF</td>
<td>79</td>
<td>298</td>
<td>1.18</td>
<td>This work</td>
</tr>
</tbody>
</table>

The CO$_2$ adsorption isotherms on nNR-10Ni@CNF samples at different temperatures (273 K and 298 K) are presented in Fig. 15. With increasing amounts of NR content, the amount of CO$_2$ adsorbed increased. At both temperatures, the adsorption of CO$_2$ on NR doped 10Ni@CNF were in the order of 2NR-10Ni@CNF > 1NR-10Ni@CNF > 0.5NR-10Ni@CNF. When loading trace amounts of NR to 10Ni@CNF, the CO$_2$ uptake capacity increased. This demonstrates that the NR may create small pores in the carbon matrix of these CNF samples and allow CO$_2$ molecules to adsorb. Compared with those reported in Table 2, the CO$_2$ adsorption capacity of nNR-10Ni@CNF samples is lower than any porous CNF or metal doped CNF samples due to the lower surface area and lower porosity. Additionally, all samples gave a CO$_2$ uptake value higher than 10Ni@CNF.
This implies that NR can enhance CO$_2$ adsorption by generating suitable pores on the CNF surface. Besides, the CNT branches on their CNF surface may contribute to adsorb CO$_2$.

**Fig. 15** CO$_2$ adsorption equilibrium isotherms for nNR-10Ni@CNF (a) at 273 K and (b) at 298 K.
When comparing CO$_2$ capture performance with other adsorbent materials reported at ambient air (298 K at 1 bar) such Metal-Organic Frameworks (MOFs), zeolite-based, and silica-based materials, the 5Ni@CNF sample provides the greatest CO$_2$ uptake capacity (4.28 mmol g$^{-1}$).[81] Compared to the highest CO$_2$ uptake of functionalized MOF materials, the MOFs named 1-en-Mg$_2$(dobpdc) provides the capacity value of 2.83 mmol g$^{-1}$ lower than 5Ni@CNF. Compared to the adsorbents without surface modification such zeolite (Li-LSK) and silica (K$_2$CO$_3$/γ-Al$_2$O$_3$) materials which show the uptake value of 1.34 mmol g$^{-1}$ and 1.20 mmol g$^{-1}$, respectively, the 5Ni@CNF sample still present higher CO$_2$ capture performance. Interestingly, this sample provides the CO$_2$ capture performance close to the ionic liquid (ILs) absorbents such as Sar (5.4 mmol g$^{-1}$), GlyGly (3.8 mmol g$^{-1}$), TBAB (3.8 mmol g$^{-1}$), and BTIG (3.0 mmol g$^{-1}$).

4. Conclusions

Diverse Ni@CNF, NR@CNF, and NR-10Ni@CNF samples were successfully prepared by the electrospinning technique, followed by conventional thermal treatment. The Ni$^0$ form was controlled by incorporating a pyridine ligand. Different Ni nanoparticle sizes influenced pore and spot formation on the CNF surface. NR showed promise as a new carbon additive and natural polymer resource for utilization as a carbon source in the PAN precursor for carbon nanotube fabrication. NR doped in PAN-based CNF increased the diameter of the CNF and produced a smooth surface. Fabricating carbon nanotube growth on carbon nanofibers was achieved by mixing NR (0.5 to 2 wt%) and Ni (10 wt%), while both metallic Ni nanoparticles and NiO nanoparticles were well dispersed in the carbon nanofiber. Furthermore, small amounts of NR could enhance the specific capacitance (from 40 F/g to 84 F/g) and CO$_2$ adsorption performance (from 0.28 and 0.18
mmol/g to 1.19 and 1.18 mmol/g at 273 and 298 K, respectively) in 1NR-10Ni@CNF.

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Supporting information

Available at

Conflict of interest

There are no conflicts to declare.

Reference


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