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Preparation, Characterization, and Applications of Electrospun Carbon Nanofibers and Its Composites

Mayakrishnan Gopiraman and Ick Soo Kim

Abstract

Carbon nanofibers (CNFs) and its composites have gained vast attention due to its exceptional chemical and textural properties. So far, various multifunctional carbon nanofibers and its composites are developed with highly unique and tunable morphology. In this chapter, we reviewed unique fabrication methods that are recently reported and its characterization techniques such as SEM, FE-SEM, TEM, WAXD, XPS, AFM, and Raman. In addition, catalytic, energy, and environmental applications of carbon nanofiber composites (metals and/or metal oxide nanoparticles incorporated and/or decorated hybrid carbon nanofibers) are discussed. Preparation and characterization of electrospun carbon nanofiber composites and its applications in catalysis and energy storage are the main focus of this chapter.

Keywords: electrospinning, carbon nanofibers, hollow structures, composites, catalysis

1. Introduction

Carbon nanofibers have received growing interests due to their unique chemical and physical properties, depending upon their size, surface area, and shape [1, 2]. Indeed the attractive structural, electrical, and mechanical properties of carbon nanotubes (CNTs) make it an ideal supporting material for various applications. Particularly, the CNTs can be used as an efficient support for the decoration of catalytic active materials. Carbon nanofibers (CNFs) also have the similar physicochemical properties to CNTs and the diameter varying from some tens of nanometers to 500 nm [3] and are also suitable to be used as catalyst support. Electrospinning is a very simple but powerful method for the fabrication of high-quality carbon nanofibers [4]. In general, the CNFs with sub-micrometer diameters as well as some tens of nanometers to 500 nm are prepared by carbonization of electrospun polymer nanofibers under inert atmosphere at high temperature [5]. Undoubtedly, polyacrylonitrile (PAN) is a well-known and efficient precursor for the fabrication of carbon fibers [6]; therefore, several attempts were made to prepare the electrospun-derived carbon nanofibers from PAN [7]. Several approaches, including wet-chemical synthesis [8, 9], electrodeposition [10, 11], and dry synthesis [12–20], are developed to obtain various multifunctional active materials loaded with carbon nanocomposites. By using these techniques, various types of metal or metal oxide nanoparticles (NPs), such as Au,

Co, Ru, Pt, Pd, Ag, Co, Rh, Ti and Cu, have been decorated or immobilized on/ into the carbon nanofibers. These metal NP-supported CNF nanocomposites have shown great promises in catalysis [21], fuel cells [22], and highly sensitive chemical/ biological sensing applications [23, 24]. In particular, the CNF composites showed excellent results in various catalytic systems such as in photocatalytic activity [25, 26], water gas shift reactions (WGS) [27], enzyme immobilization or biocatalysts [28, 29], and direct oxidation of alcohols [30]. So far, TiO₂-deposited CNFs have gained much attention in the photocatalytic reactions, and a considerable number of reports are available in the literature. Alike, Pd NP-supported CNFs are often preferred for the catalytic organic conversions such as hydrogenation reaction [31] and Heck coupling reaction [8]. It is proven that the CNFs are one of the highly suitable supports for the decoration of Pd NPs and the resultant Pd/CNF composite often demonstrated an enhanced catalytic activity [32]. In fact, the unique structure, high conductivity, huge surface area, and chemical inertness of CNFs often help to obtain high dispersion of metal nanoparticles on CNFs. Most of the Pd NP-supported CNFs showed better activity than the conventional Pd/C catalysts [8, 33].

In this chapter, we discussed the preparation and characterization of electrospun carbon fibers and its composites. The contributions of CNF composites in various catalytic systems (such as photocatalytic activity, water gas shift reactions (WGS), enzyme immobilization or biocatalysts, and direct oxidation of alcohols) are also discussed in detail.

2. Preparation and characterization of carbon nanofiber composites

2.1 Electrospun carbon nanofibers

Electrospinning is a straightforward method to obtain the nanofibers. **Figure 1** shows the fundamental electrospinning setup and the list of important parameters to be controlled. The nanofibers can be produced by applying high voltage to a polymer solution which could create electrostatically repulsive force and an electric field between two electrodes, so that the nanofibers can be formed [34]. Obviously, the formation of nanofibers is highly dependent on the viscosity and electric conductivity of the polymeric fluids, humidity, and applied voltage [35]. To date,

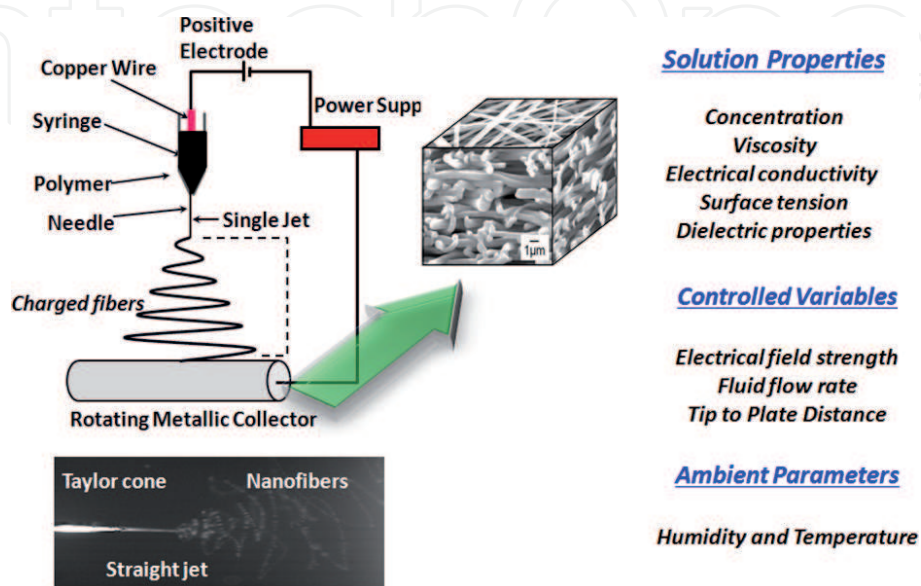


Figure 1. Scheme of fundamental setup for electrospinning and electrospinning parameters.

over 100 kinds of polymers have been employed to produce their nanofibers via electrospinning. However, a very limited number of polymers such as polyacrylonitrile (PAN), polyimide (PI), poly(vinyl alcohol) (PVA), poly(vinylidene fluoride) (PVDF), cellulose acetate, and pitch have been successfully used to obtain carbon nanofibers [36]. The carbon nanofibers are often characterized by various techniques. Scanning electron microscope (SEM) is one of the very common methods to characterize the CNFs. The surface morphology, particularly the fiber diameter, uniformity, and surface smoothness are often studied by SEM analysis. Alike, transmission electron microscopy (TEM) and atomic force microscopy (AFM) are also employed for the detail surface analysis. The crystalline and amorphous nature of the CNFs is often investigated by means of X-ray diffraction (XRD) analysis. Raman spectroscopy is a very useful technique for the analysis of G-band and D-band of CNFs. X-ray photoemission spectroscopy (XPS) was also effectively used to analyze the CNFs. The specific surface area and textural properties such as pore volume and pore size of CNFs are evaluated by using the Brunauer-Emmett-Teller (BET) method.

Kim et al. [37] prepared CNFs via electrospinning by using PVA and DMF as precursor and solvent, respectively. In a typical preparation method, PVA was dissolved in DMF and the polymer mixture was electrospun. In the first step, the resultant nanofiber webs were oxidatively stabilized at 280°C under air flow (heating at 1°C/min). Then the stabilized nanofiber web was activated by steam resulting in activated carbon nanofibers. The stabilized nanofiber webs were heated at a rate of 5°C/min up to 700, 750, and 800°C and activated for 30 min by supplying 30 vol.% of steam in a carrier gas of N₂. They confirmed that the resultant CNFs have well-developed mesopores and the CNFs demonstrated excellent specific capacitance (173 F/g at 10 mA/g).

Kuzmenko and co-workers [38] prepared nitrogen-doped carbon nanofibrous mats from regenerated cellulose impregnated with ammonium chloride. The ammonium chloride provided the thermal stabilization of incompletely regenerated cellulose fibers. In a typical preparation, cellulose acetate solution was prepared in acetone/DMAc mixture which was subsequently electrospun. The voltage was 25 kV, distance between needle and collector was 25 cm, and the process was performed at temperature around 20 ± 2°C and relative humidity 45–60%. Aluminum foil was used for collecting the nanofibers. The prepared cellulose acetate nanofibers were deacetylated by using dilute NaOH solution. Then the regenerated cellulose webs were impregnated with NH₄Cl by immersion in 0.3 M aqueous solution of NH₄Cl for 24 h at 20 ± 2°C. The NH₄Cl-treated regenerated cellulose samples were carbonized in a quartz tube furnace for general annealing in N₂ flow (1 L/min) by heating up to 800°C with the heating rate of 5°C/min. **Figure 2** shows the SEM images of the CNFs synthesized from the regenerated cellulose [38].

2.2 Porous carbon nanofibers with hollow cores

Kim et al. [39] successfully prepared porous CNFs with hollow cores through the thermal treatment of electrospun copolymeric nanofiber webs. **Figure 3** shows the schematic diagram for producing porous CNFs with hollow cores. For the preparation of porous CNFs with hollow cores, PAN and poly(methyl methacrylate) (PMMA) polymers were chosen. The PAN is a widely used precursor for the preparation of CNFs, and the PMMA can be thermally decomposed at elevated temperatures. Dissolving these two polymers (PAN and PMMA) in a solvent would create phase separation [continuous phase (sea) changes into pore walls (or skeletons of nanofibers) and the discontinuous phase (islands) changes into many hollow pores], which results in the *sea-islands* feature. It is well known that

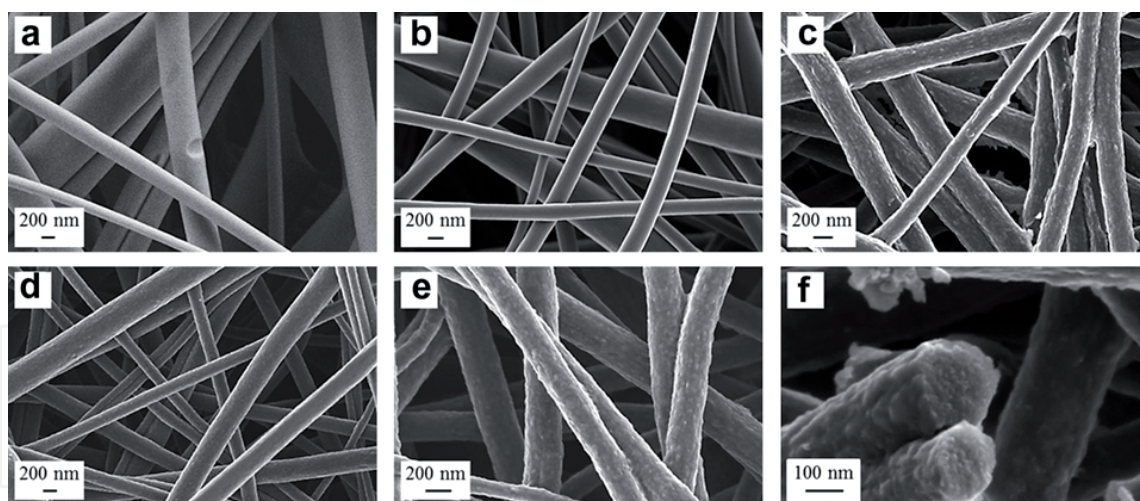


Figure 2. (a-f) SEM images of the CNFs synthesized from the differently regenerated cellulose with additional NH_4Cl impregnation [38].

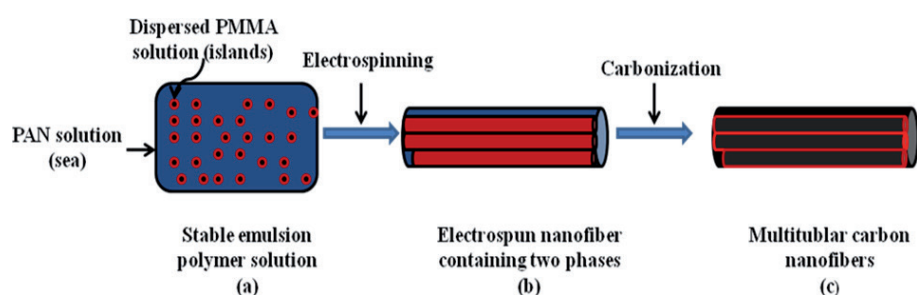


Figure 3. Schematic diagram for the preparation of porous CNFs with hollow cores. (a) Preparation of stable polymer solutions from two separate phases; nanoscale phase separation occurs due to their different molecular weights; PMMA forms the discontinuous phase and PAN forms the continuous phase; (b) nanofiber formation (with two phases) by electrospinning; (c) removal of the PMMA phase at elevated temperatures [39].

the low-surface-tension polymer (PAN) would occupy the continuous phase of the solution (*sea*), while the high-surface-tension polymer (PMMA) forms the discontinuous phase (*islands*). In fact the two separate phases are due to the intrinsic properties (e.g., interfacial tension, viscosity, elasticity) of the polymers [40]. The electrospinning technique was used to obtain the PAN/PMMA nanofibers containing two separate phases. The thermal treatment of PAN/PAMM nanofibers at over 1000°C would eventually form the porous carbon nanofibers with hollow cores. The complete removal of PMMA phase and the transformation continuous PAN phase would result in the formation of porous CNFs with hollow cores (**Figure 4**).

Highly flexible N- and O-containing porous ultrafine CNFs were prepared by Wei and co-workers [41]. The ultrafine porous CNFs were obtained by simply varying the PAN/PMMA ratios (10/0, 7:3, 5:5, and 3:7). Briefly, PAN/PMMA solutions with different ratios (10:0, 7:3, 5:5, and 3:7) are prepared in DMF. For better dispersion, the PAN/PMMA solution was sonicated followed by stirring at 60°C for 2 h. The polymer blend was electrospun under an electric field of 9 kV at a tip-to-collector distance of 15 cm. The resultant electrospun PAN/PMMA nanofibers were stabilized under air flow at 300°C with the heating rate of $1^\circ\text{C}/\text{min}$ for 1 h. Subsequently, the stabilized nanofibers were carbonized under N_2 atmosphere at 900°C with heating rate of $5^\circ\text{C}/\text{min}$ for 1 h. It was proven that the increasing the ratio of PMMA would result in the formation of ultrafine CNFs. **Figure 5** shows the FE-SEM images of CNFs; CNFs, 7:3; CNFs, 5:5; and *u*-CNFs, 7:3. The FE-SEM images show that the morphology of CNFs is homogeneous, continuous, and a typical cylindrical shape.

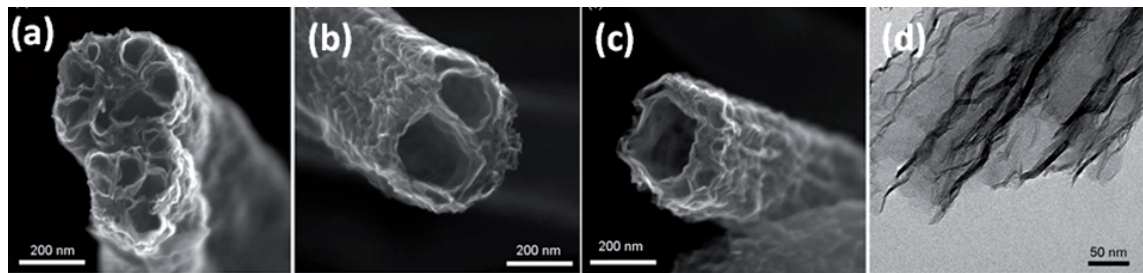


Figure 4.
(a–c) Cross-sectional TEM images of CNFs thermally treated at 2800°C [PAN:PMMA (a) 5:5, (b) 7:3, and (c) 9:1] and (d) TEM image of CNFs showing structurally developed core walls after thermal treatment [39].

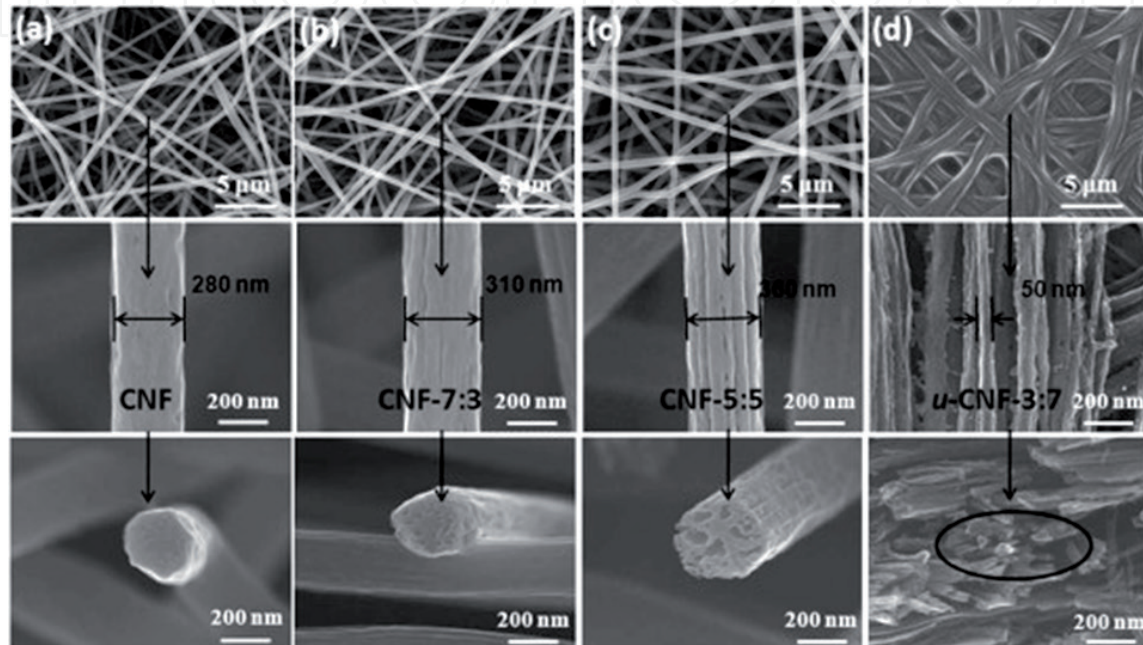


Figure 5.
FE-SEM images of electrospun PAN/PMMA nanofibers with different mixing ratios. (a) CNFs; (b) PAN/PMMA, 7:3; (c) PAN/PMMA, 5:5; and (d) PAN/PMMA, 3:7 [41].

The FE-SEM images of CNFs, 7:3, and CNFs, 5:5, showed that the CNFs have several hollow cores along the fiber axis. Notably, the morphology of the u-CNFs (3:7) was completely changed. The morphology of CNFs (3:7) fibers was homogenous, continuous, and a cylindrical shape with an average diameter of ~50 nm. In fact, the complete decomposition of PMMA during the thermal treatment is the main reason. The BET specific surface area of the u-CNFs-3,7 was determined to be 467.57 m²/g and pore volume of 1.15 cm³ g⁻¹ and an average pore size of 9.48 nm.

Chang et al. [42] introduced a novel technique of centrifuged-electrospinning for the preparation of ultrathin carbon fibers. **Figure 6** shows the preparation diagram of the ultrathin porous CNFs by centrifuged-electrospinning. In a typical procedure, PAN/PMMA polymer blend was prepared in DMF at different weight ratios of 80/20 (PAN80/PMMA20) and 10/90 (PAN10/PMMA90). The polymer blends were used for the preparation of PAN/PMMA nanofibers by centrifuged electrospinning. The centrifuged-electrospinning conditions were as follows: an applied positive voltage of 45 kV, a three-phase induction motor spinning at 4000 rpm, a syringe feed rate of 1.5 mL/min, and a stainless steel ring with a diameter of 50 cm as the collector. Finally, the resultant PAN/PMMA nanofibers were stabilized at 280°C for 2 h at a heating rate 0.5°C/min in air atmosphere and then carbonized at 800°C for 4 h under argon atmosphere at a heating rate of 5°C/min. **Figure 6** (b, c, and d) shows the TEM images of ultrathin micro-/mesoporous CNFs.

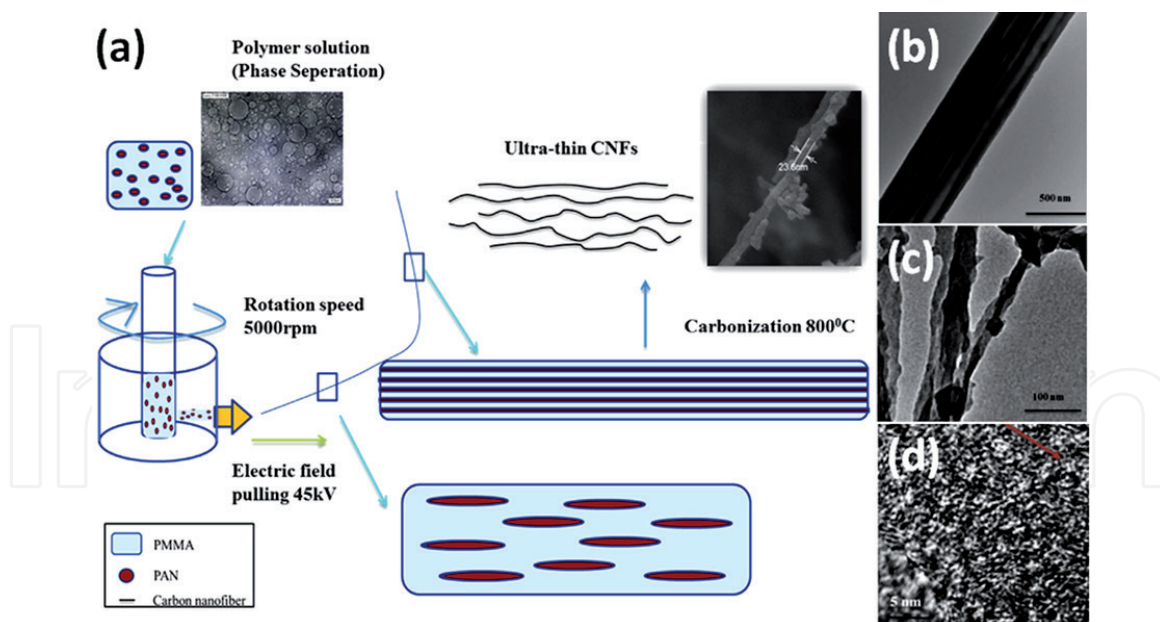


Figure 6.

(a) Schematic diagram for the preparation of ultrathin micro-/mesoporous CNFs by centrifuged-electrospinning followed by carbonization and (b, c, and d) TEM images of ultrathin micro-/mesoporous CNFs [42].

2.3 Carbon nanofiber composites

Recently, preparation of metal oxide-supported carbon nanofiber composites via electrospinning has been extensively studied. The carbon nanocomposites are used in various applications such as energy conversion and storage, capacitive deionization, catalysis, adsorption/separation, and in the field of biomedicine. In order to achieve higher activity, various synthetic routes were developed to achieve porous carbon nanofibers composites with high surface area and tunable pore size distribution. Most of the preparation methods involve carbonization process at elevated temperatures of typically above 1200°C. So far, various metal or metal oxide nanoparticle (Pd, Pt, Ti, Ag, Au, Cu, Ni, Zn, and Ru)-supported CNF nanocomposites were reported [21, 43].

Atchison et al. [44] prepared metal carbide-supported carbon nanocomposites through carbothermal reduction process. Zirconium carbide/carbon nanocomposite (ZrC/C), titanium carbide/carbon nanocomposite (TiC/C), and niobium carbide/carbon nanocomposite (NbC/C) were prepared by electrospinning followed by carbothermal reduction at elevated temperatures. Cellulose acetate and PVP were used as precursor.

Chen et al. [45] prepared Pd nanoparticle-supported carbon nanofibers (Pd-NP/CEPFs: Pd-NP/CEPFs) through the electrospinning process. Shortly, electrospinning solution was prepared by using 10 wt% PAN and 3.3 wt% Pd(OAc)₂ in DMF. The electrospinning process was performed in an electric field of 30 kV and the tip-to-collector distance of 30 cm. Then the electrospun PAN/Pd(OAc)₂ nanofiber involved three steps as follows: (1) 210°C annealing for 1 h under air flow for the oxidation of PAN, (2) heating up to 400°C at a rate of 5°C/min and annealing for 2 h in H₂ and Ar mixture (H₂/Ar = 1/3) atmosphere for the reduction of Pd²⁺, and (3) heating up to 550°C at a rate of 5°C/min and annealing for 1 h in Ar for the formation of metal nanoparticles on/in the carbonized nanofibers (Figure 7).

Zhang et al. [46] obtained AgNP-immobilized carbon nanocomposite by a two-step preparation: electrospinning followed by the hydrothermal growth of the AgNPs on the CNFs (Figure 8). In a typical procedure, the electrospinning solution

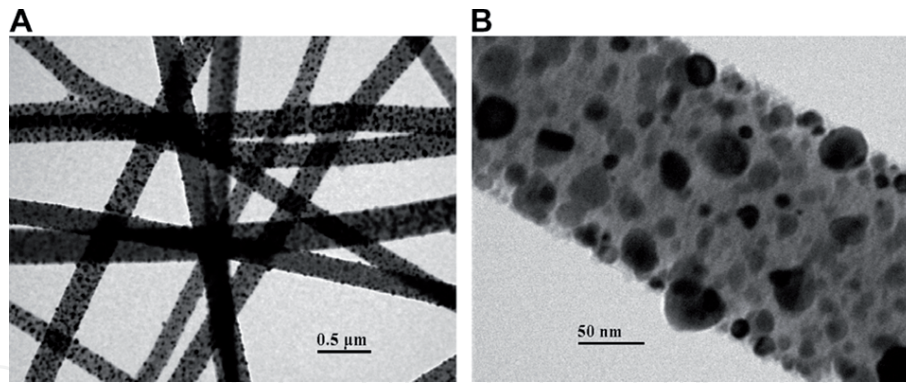


Figure 7. TEM images of Pd-NP/CNFs. (A) Lower magnification; (B) higher magnification [45].

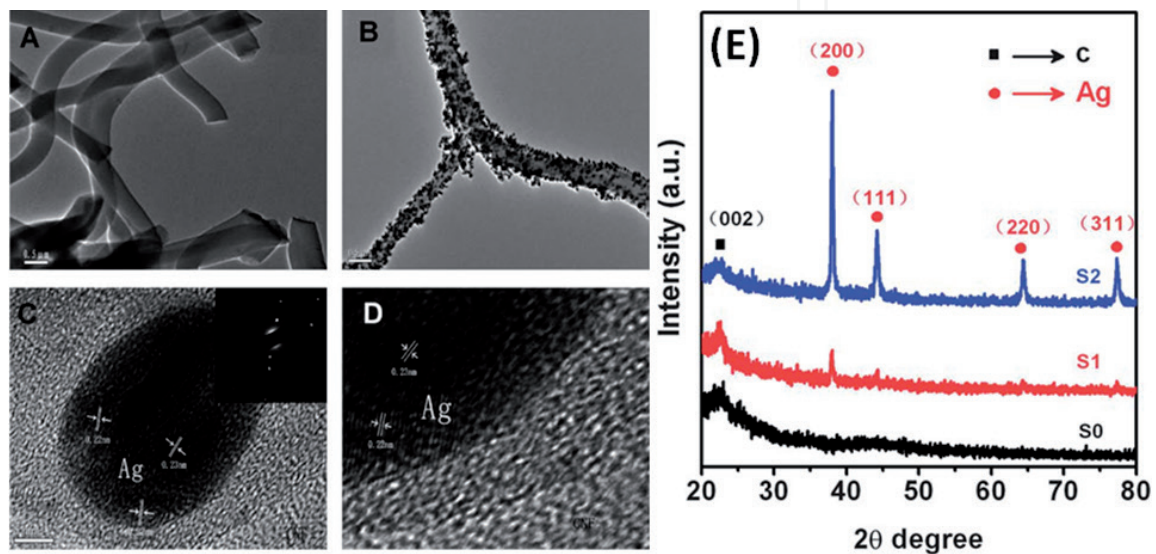


Figure 8. TEM images of sample (A) CNFs and (B) CNFs/AgNPs, (C) HRTEM images of CNFs/AgNPs, and (E) XRD patterns of CNFs/AgNPs and CNFs.

of PAN was prepared in DMF, and it was electrospun at an applied electric voltage of 10 kV. The PAN nanofibers were then stabilized under air flow at 270°C for 1 h and subsequently carbonized under N₂ atmosphere at 1000°C for 1 h at the rate of 5°C/min. After the preparation of CNFs from PAN nanofibers, the CNFs were treated with HNO₃, centrifuged, and washed with water for several times. Finally an aqueous mixture of glucose, Ag(NH₃)₂OH, and CNFs was stirred for 5 min. After being stirred for more than 5 min, the mixture was transferred into a Teflon-lined autoclave, and it was sealed in a stainless steel tank and heated at 180°C for 3 h. Finally the AgNP-immobilized CNFs (Ag/CNFs) were obtained.

Yu and co-workers [47] prepared electrospun Ag/g-C₃N₄-loaded composite carbon nanofibers (Ag/g-C₃N₄/CNFs) through combing the electrospinning technology and carbonization treatment. The microstructure of Ag/g-C₃N₄/CNFs was characterized by XRD, FE-SEM, EDS, TEM, and XPS.

Ghouri et al. [48] achieved Co/CeO₂-decorated carbon nanofibers (Co/CeO₂/CNFs) by calcination of electrospun nanofibers composed of cerium (III) acetate hydrate, cobalt (II) acetate tetrahydrate, and poly(vinyl alcohol) in nitrogen environment at 700°C. PVA was used as carbon source due to its high carbon content. In a typical preparation, CoAc and CeAc aqueous solutions were prepared in distilled water. The resultant aqueous solutions were mixed with PVA aqueous solution. After stirring for 6 h, the mixture was electrospun at high voltage of 22 kV using DC

power supply at room temperature with 65% relative humidity. The tip-to-collector distance of 22 cm was fixed. Finally, the dried nanofiber mats were calcined at 700°C for 6 h in N₂ flow with a heating rate of 2.0°C/min. The physicochemical properties of the Co/CeO₂/CNFs were characterized by XRD, FE-SEM, EDS, TEM, XPS, and Raman.

The utilization of noble metals in green technologies has garnered an increasing level of research interest. Particularly, the Pt-based nanocomposites are often preferred as the anode because of their excellent performance in catalyzing the dehydrogenation of methanol. For example, Formo et al. [49] achieved Pt nanostructure-supported CNF nanofibers through electrospinning followed by calcination in air at 510°C for 6 h.

3. Applications of carbon nanofiber composites

Electrospun carbon nanofibers have proven to be efficient catalytic supports owing to the high porosity and large surface areas. The high porosity in a nonwoven mat of nanofibers enables direct growth of catalytic nanostructures. Till date, there are number of applications found for the electrospun carbon nanofibers and its composites.

3.1 Carbon nanocomposites in organic transformations

Owing to high surface area, porosity, stability, metal-support interaction, smaller particle size, and high dispersion in reaction medium, the metal nanoparticle-supported carbon nanocomposites demonstrated excellent activity in organic reactions. They can be highly reusable due its stability which is one of the hallmarks of the carbon nanocomposites.

Palladium-catalyzed Sonogashira coupling reaction is the most straightforward and powerful method used for the construction of C(sp₂)-C(sp) bond, drugs, and polymeric materials [50]. The conventional protocols of the Sonogashira reactions are carried out in the homogeneous phase, using soluble palladium (Pd) complexes such as Pd(PPh₃)₄, Pd(PPh₃)₂Cl₂, and Pd(OAc)₂ as catalysts in the presence of CuI as co-catalyst. Even with the high reaction rate and high turnover numbers, homogeneous catalysis has a number of disadvantages, in particular the lack of reuse of the catalyst. Chen et al. [45] developed Pd-supported CNF catalytic system for the Sonogashira reaction. **Figure 9** shows Pd-NP/CNF catalyzed Sonogashira reaction of iodobenzene and phenylacetylene in liquid phase. The catalyst showed superior catalytic activity toward the Sonogashira reaction. In addition, the catalyst was found to be highly reusable, at least for 10 runs without any significant loss in its catalytic activity.

Alike, electrospun Ag/g-C₃N₄-loaded composite carbon nanofibers (Ag/g-C₃N₄/CNFs) were used for the conversion of 4-nitrophenol to 4-aminophenol and benzylamine to N-benzylbenzaldimine [44]. The Ag/g-C₃N₄/CNFs offered the significant advantages, such as low catalyst use, high activity, easy recycling, and excellent stability. In fact, the synergistic effect between catalytic activity of Ag nanoparticles

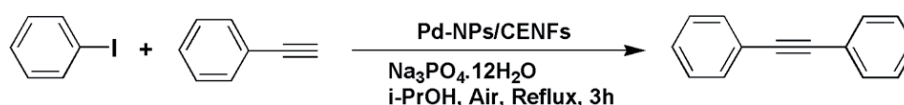


Figure 9. The Sonogashira reaction equation of iodobenzene and phenylacetylene in liquid phase catalyzed by Pd-NP-supported CNFs [45].

(NPs) and g-C₃N₄ and excellent adsorption capacity of carbon nanofibers are the main reason for the excellent catalytic activity.

3.2 Carbon nanocomposites in catalytic reduction of 4-nitrophenol

Catalytic transformation of 4-nitrophenol to 4-aminophenol is one of the very significant reactions in green chemistry [51]. It is well known that the nitrophenols are harmful to the environment, and therefore the US Environmental Protection Agency has listed it as 114th organic pollutant [52]. In recent days, catalytic conversion of nitrophenols to aminophenols is widely studied. In fact, the catalytic product, aminophenols, can be used as an excellent intermediate in synthesizing various drugs and reducing agent. The 4-nitrophenols are often employed as a photographic developer, corrosion inhibitor, anticorrosion lubricant, and hair-dyeing agent [53]. Although the reaction is very simple, greener, and most efficient, the reaction without metal catalysts is not achievable. To perform this reaction, various metal catalysts (based on graphene oxide, silica, alumina, activated carbon, CNTs, fullerenes, and so on) are developed and proven to be an excellent candidate for the reduction of 4-nitrophenols to 4-aminophenol. For example, RGO-ZnWO₄-Fe₃O₄, AgNPs-rGO, PdNiP/RGO, and NiNPs/silica are reported for the reduction of nitrophenol [20].

Carbon nanofibers/silver nanoparticle (CNFs/AgNPs) composite nanofibers were used for the reduction of 4-nitrophenol (4-NP) with NaBH₄ [46]. The reaction was tracked by time-dependent UV-visible spectroscopy (**Figure 10**). It was found that the CNF/AgNP composite demonstrated an excellent catalytic activity in the reduction of 4-nitrophenol. The catalytic efficiency was found to be enhanced with the increasing of the content of silver on the CNF/AgNP catalyst. Reaction kinetic was studied for the CNF/AgNP reduction of 4-nitrophenol. It was reported that the rate constant of $6.2 \times 10^{-3} \text{ s}^{-1}$ was determined for the reduction of 4-nitrophenol over CNF/AgNP catalyst. The excellent active might be attributed to the high surface areas of Ag NPs and synergistic effect on delivery of electrons between CNFs and AgNPs. The CNF/AgNP composite nanofibers can be easily recycled and reused without any significant loss in its catalytic activity.

3.3 Carbon nanofiber composites in energy applications

Due to the excellent properties such as high surface area, conductivity, and porosity, the CNF-based nanocomposites are widely used for the energy applications. Without a doubt, the development of electrochemical energy storage systems (EES)

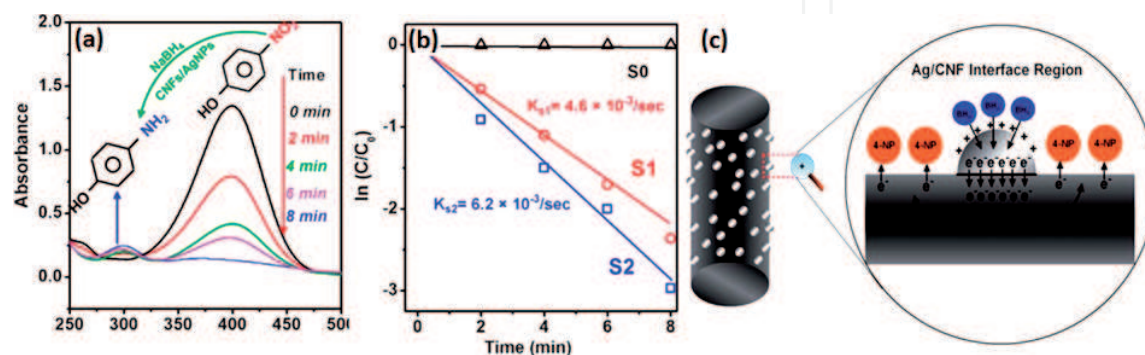


Figure 10. Catalytic evolution of CNFs/AgNPs. (a) UV-vis absorption spectra during the reduction of 4-nitrophenol over CNFs/AgNPs; (b) $\ln(C/C_0)$ and C/C_0 vs. reaction time for the reduction of 4-nitrophenol, S₀ = fresh CNFs, S₁ = CNFs/AgNPs, and S₂ = CNFs/AgNPs; (c) proposed mechanism of the catalytic reduction of 4-nitrophenol with the CNF/AgNP composite nanofibers [46].

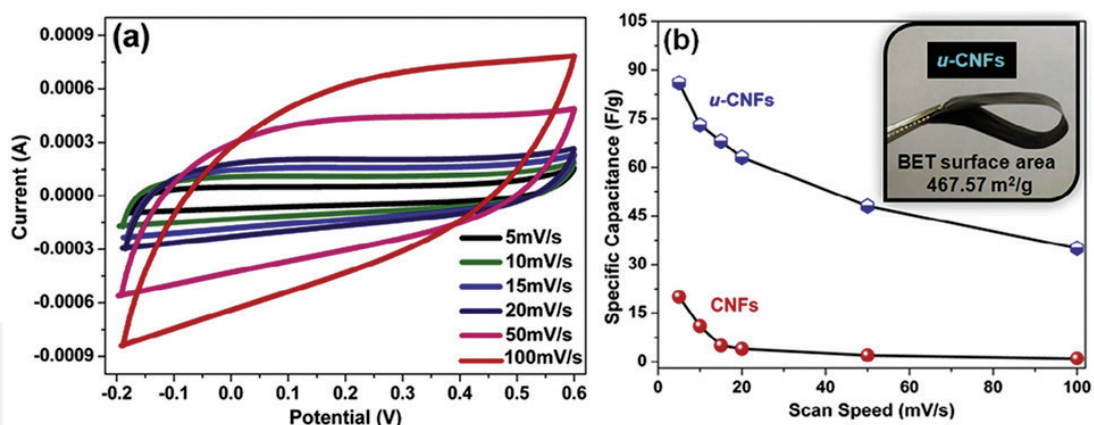


Figure 11.

(a) Cyclic voltammety results for the ultrafine CNFs at different scan rates in 1.0 mol/L H_2SO_4 and; (b) specific capacitance for the u-CNFs (3:7) and CNFs at different scan rates in 1.0 mol/L H_2SO_4 .

is largely focused due to its vital demand for clean and sustainable energy. Mainly three types of devices are very important and most commercialized energy storage systems such as batteries, electrochemical capacitors (ECs), and fuel cells [54].

The ultrafine CNFs prepared via electrospinning of PAN/PMMA blend followed by thermal treatment in inert atmosphere were used as a flexible electrode material for the supercapacitor applications [41]. **Figure 11** shows the cyclic voltammety results for the ultrafine CNFs at different scan rates in 1.0 mol/L H_2SO_4 and specific capacitance for the ultrafine CNFs at different scan rates in 1.0 mol/L H_2SO_4 . The ultrafine CNFs demonstrated an enhanced specific capacitance of 86 F g^{-1} in 1 mol/L H_2SO_4 . Being a flexible electrode material, this is the highest specific capacitance for the CNFs reported so far. The excellent specific capacitance of ultrafine CNFs is due to its unique properties. The results proved that the fiber diameter of ultrafine CNFs was about 50 nm. The XPS and Raman studies confirmed the presence of N and O in the form of various functional groups such as pyridinic, benzenoid amine, graphitic N, and N-oxides. High specific surface area of $467.57 \text{ m}^2/\text{g}$ with an excellent pore volume ($1.15 \text{ cm}^3 \text{ g}^{-1}$) and pore size (9.48 nm) was determined for the ultrafine CNFs. The BET results confirmed the interconnected micro-/meso-/macropores on the surface of the ultrafine CNFs.

The Pt nanostructure-supported CNF nanocomposite was employed for the direct oxidation of methanol [49]. It was found that the Pt nanostructure-supported CNF nanocomposite showed better activity than the commercial Pt/C which may be due to the synergistic effect of the underlying anatase surface and the Pt nanostructures with well-defined facets. Alike, Co/CeO₂-decorated carbon nanofibers were developed for the methanol oxidation [48]. The results showed that the electrocatalytic activity of the Co/CeO₂-decorated carbon nanofibers toward methanol oxidation was excellent. Interestingly, the introduced catalyst revealed negative onset potential (50 mV vs. Ag/AgCl) which is a superior value among the reported non-precious electrocatalyst.

4. Conclusion

Electrospinning is one of the simple and effective techniques for the fabrication of carbon nanofiber. Certainly, metal-supported carbon nanofibers demonstrated excellent activity in various applications such as catalysis, energy, and environmental. In this chapter, we have summarized the recent progress in the research on the preparation methods, characterization, and applications of electrospun carbon nanofibers and its composites.

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References

- [1] Burda C, Chen XB, Narayanan R, El-Sayed MA. Chemistry and properties of nanocrystals of different shapes. *Chemical Reviews*. 2005;**105**:1025-1102. DOI: 10.1021/cr030063a
- [2] De Jong KP, Geus JW. Carbon nanofibers: Catalytic synthesis and applications. *Catalysis Reviews*. 2000;**42**:481-510. DOI: 10.1081/CR-100101954
- [3] Vamvakaki V, Tsagaraki K, Chaniotakis N. Carbon nanofiber-based glucose biosensor. *Analytical Chemistry*. 2006;**78**:5538-5542. DOI: 10.1021/ac060551t
- [4] Kim C, Yang KS, Kojima M, Yoshida K, Kim YJ, Kim YA, et al. Fabrication of electrospinning-derived carbon nanofiber webs for the anode material of lithium-ion secondary batteries. *Advanced Functional Materials*. 2006;**16**:2393-2397. DOI: 10.1002/adfm.200500911
- [5] Huang CB, Chen SL, Reneker DH, Lai CL, Hou HQ. High-strength mats from electrospun poly(p-phenylene biphenyltetracarboximide) nanofibers. *Advanced Materials*. 2006;**18**:668-671. DOI: 10.1002/adma.200501806
- [6] Donnet JB, Bansal RC. *Carbon Fibers*. New York: Marcel Dekker; 1990
- [7] Wang Y, Santiago-Aviles JJ. Conductivity measurement of electrospun PAN-based carbon nanofiber. *Journal of Materials Science Letters*. 2002;**21**:1055-1057
- [8] Yoon B, Wai CM. Microemulsion-templated synthesis of carbon nanotube-supported Pd and Rh nanoparticles for catalytic applications. *Journal of the American Chemical Society*. 2005;**127**(49):17174-17175. DOI: 10.1021/ja055530f
- [9] Selvamani A, Babu CM, Ramkumar V, Sundaravel B. Reduced graphene oxide decorated Au nanoparticles as an efficient electrode for the determination of hydroquinone. *Nano Progress*. 2019;**1**:9-14
- [10] Day TM, Unwin PR, Macpherson JV. Factors controlling the electrodeposition of metal nanoparticles on pristine single walled carbon nanotubes. *Nano Letters*. 2007;**7**:51-57. DOI: 10.1021/nl061974d
- [11] Lin Z, Ji L, Zhang X. Electrodeposition of platinum nanoparticles onto carbon nanofibers for electrocatalytic oxidation of methanol. *Materials Letters*. 2009;**63**:2115-2118. DOI: 10.1016/j.matlet.2009.07.005
- [12] Yuan G, Gopiraman M, Cha HJ, Soo HD, Chung IM, Kim IS. Interconnected ruthenium dioxide nanoparticles anchored on graphite oxide: Highly efficient candidate for solvent-free oxidative synthesis of imines. *Journal of Industrial and Engineering Chemistry*. 2017;**46**:279-288. DOI: 10.1016/j.jiec.2016.10.040
- [13] Gopiraman M, Deng D, Babu SG, Hayashi T, Karvembu R, Kim IS. Sustainable and versatile CuO/GNS nanocatalyst for highly efficient base free coupling reactions. *ACS Sustainable Chemical Engineering*. 2015;**3**:2478-2488. DOI: 10.1021/acssuschemeng.5b00542
- [14] Gopiraman M, Babu SG, Khatri Z, Kai W, Kim YA, Endo M, et al. Dry synthesis of easily tunable nano ruthenium supported on graphene: Novel nanocatalysts for aerial oxidation of alcohols and transfer hydrogenation of ketones. *The Journal of Physical Chemistry C*. 2013;**117**:23582-23596. DOI: 10.1021/jp402978q

- [15] Gopiraman M, Babu SG, Khatri Z, Kai W, Kim YA, Endo M, et al. An efficient, reusable copper-oxide/carbon-nanotube catalyst for N-arylation of imidazole. *Carbon*. 2013;**62**:135-148. DOI: 10.1016/j.carbon.2013.06.005
- [16] Gopiraman M, Babu SG, Karvembu R, Kim IS. Nanostructured RuO₂ on MWCNTs: Efficient catalyst for transfer hydrogenation of carbonyl compounds and aerial oxidation of alcohols. *Applied Catalysis A: General*. 2014;**484**:84-96. DOI: 10.1016/j.apcata.2014.06.032
- [17] Gopiraman M, Bang H, Babu SG, Wei K, Karvembu R, Kim IS. Catalytic N-oxidation of tertiary amines on RuO₂ NPs anchored graphene nanoplatelets. *Catalytic Science and Technology*. 2014;**4**:2099-2106. DOI: 10.1039/C3CY00963G
- [18] Gopiraman M, Karvembu R, Kim IS. Highly active, selective, and reusable RuO₂/SWCNT catalyst for Heck olefination of aryl halides. *ACS Catalysis*. 2014;**4**:2118-2129. DOI: 10.1021/cs500460m
- [19] Gopiraman M, Babu SG, Khatri Z, Kai W, Kim YA, Endo M, et al. Facile and homogeneous decoration of RuO₂ nanorods on graphene nanoplatelets for transfer hydrogenation of carbonyl compounds. *Catalysis Science and Technology*. 2013;**3**:1485-1489. DOI: 10.1039/C3CY20735H
- [20] Saravanamoorthy S, Chung IM, Ramkumar V, Ramaganth B, Gopiraman M. Highly active and reducing agent-free preparation of cost-effective NiO-based carbon nanocomposite and its application in reduction reactions under mild conditions. *Journal of Industrial and Engineering Chemistry*. 2018;**60**:91-101. DOI: 10.1016/j.jiec.2017.10.006
- [21] van der Lee MK, van Dillen J, Bitter JH, de Jong KP. Deposition precipitation for the preparation of carbon nanofiber supported nickel catalysts. *Journal of the American Chemical Society*. 2005;**127**:13573-13582. DOI: 10.1021/ja053038q
- [22] Cao L, Scheiba F, Roth C, Schweiger F, Cremers C, Stimming U, et al. Novel nanocomposite Pt/RuO₂ × H₂O/carbon nanotube catalysts for direct methanol fuel cells. *Angewandte Chemie International Edition*. 2006;**45**:5315-5319. DOI: 10.1002/anie.200601301
- [23] Hrapovic S, Liu Y, Male KB, Luong JH. Electrochemical biosensing platforms using platinum nanoparticles and carbon nanotubes. *Analytical Chemistry*. 2004;**76**:1083-1088. DOI: 10.1021/ac035143t
- [24] Yang M, Yang Y, Liu Y, Shen G, Yu R. Platinum nanoparticles-doped sol-gel/carbon nanotubes composite electrochemical sensors and biosensors. *Biosensors and Bioelectronics*. 2006;**21**:1125-1131. DOI: 10.1016/j.bios.2005.04.009
- [25] Zhang Z, Shao C, Li X, Wang C, Zhang M, Liu Y. Electrospun nanofibers of p-type NiO/n-type ZnO heterojunctions with enhanced photocatalytic activity. *ACS Applied Materials and Interfaces*. 2010;**2**:2915-2923. DOI: 10.1021/am100618h
- [26] Chuangchote S, Jitputti J, Sagawa T, Yoshikawa S. Photocatalytic activity for hydrogen evolution of electrospun TiO₂ nanofibers. *ACS Applied Materials and Interfaces*. 2009;**1**:1140-1143. DOI: 10.1021/am9001474
- [27] Kim H, Choi Y, Kanuka N, Kinoshita H, Nishiyama T, Usami T. Preparation of Pt-loaded TiO₂ nanofibers by electrospinning and their application for WGS reactions. *Applied Catalysis A: General*. 2009;**352**:265-270. DOI: 10.1016/j.apcata.2008.10.016

- [28] Wang ZG, Wan LS, Liu ZM, Huang XJ, Xu ZK. Enzyme immobilization on electrospun polymer nanofibers: An overview. *Journal of Molecular Catalysis B: Enzymatic*. 2009;**56**:189-195. DOI: 10.1016/j.molcatb.2008.05.005
- [29] Wan LS, Ke BB, Wu J, Xu ZK. Catalase immobilization on electrospun nanofibers: Effects of porphyrin pendants and carbon nanotubes. *The Journal of Physical Chemistry C*. 2007;**111**:14091-14097. DOI: 10.1021/jp070983n
- [30] Barakat NA, El-Newehy M, Al-Deyab SS, Kim HY. Cobalt/copper-decorated carbon nanofibers as novel non-precious electrocatalyst for methanol electrooxidation. *Nanoscale Research Letters*. 2014;**9**:2. DOI: 10.1186/1556-276X-9-2
- [31] Ye XR, Lin Y, Wang C, Engelhard MH, Wang Y, Wai CM. Supercritical fluid synthesis and characterization of catalytic metal nanoparticles on carbon nanotubes. *Journal of Materials Chemistry*. 2004;**14**(5):908-913. DOI: 10.1039/B308124A
- [32] Yang W, Yang S, Guo J, Sun G, Xin Q. Comparison of CNF and XC-72 carbon supported palladium electrocatalysts for magnesium air fuel cell. *Carbon*. 2007;**45**:397-401. DOI: 10.1016/j.carbon.2006.09.003
- [33] Guo DJ, Li HL. Electrochemical synthesis of Pd nanoparticles on functional MWNT surfaces. *Electrochemistry Communications*. 2004;**6**:999-1003. DOI: 10.1016/j.elecom.2004.07.014
- [34] Li D, Xia Y. Electrospinning of nanofibers: Reinventing the wheel? *Advanced Materials*. 2004;**16**:1151-1170. DOI: 10.1002/adma.200400719
- [35] Park JY, Lee IH, Bea GN. Optimization of the electrospinning conditions for preparation of nanofibers from polyvinylacetate (PVAc) in ethanol solvent. *Journal of Industrial and Engineering Chemistry*. 2008;**14**:707-713. DOI: 10.1016/j.jiec.2008.03.006
- [36] Inagaki M, Yang Y, Kang F. Carbon nanofibers prepared via electrospinning. *Advanced Materials*. 2012;**24**:2547-2566. DOI: 10.1002/adma.201104940
- [37] Kim C, Yang KS. Electrochemical properties of carbon nanofiber web as an electrode for supercapacitor prepared by electrospinning. *Applied Physics Letters*. 2003;**83**:1216-1218. DOI: 10.1063/1.1599963
- [38] Kuzmenko V, Naboka O, Gatenholm P, Enoksson P. Ammonium chloride promoted synthesis of carbon nanofibers from electrospun cellulose acetate. *Carbon*. 2014;**67**:694-703. DOI: 10.1016/j.carbon.2013.10.061
- [39] Kim C, Jeong YI, Ngoc BTN, Yang KS, Kojima M, Kim YA, et al. Synthesis and characterization of porous carbon nanofibers with hollow cores through the thermal treatment of electrospun copolymeric nanofiber webs. *Small*. 2007;**3**:91-95. DOI: 10.1002/smll.200600243
- [40] Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR, editors. *Polymer Handbook*. Vol. 89. New York: Wiley; 1999
- [41] Wei K, Kim KO, Song KH, Kang CY, Lee JS, Gopiraman M, et al. Nitrogen- and oxygen-containing porous ultrafine carbon nanofiber: A highly flexible electrode material for supercapacitor. *Journal of Materials Science and Technology*. 2017;**33**:424-431. DOI: 10.1016/j.jmst.2016.03.014
- [42] Chang WM, Wang CC, Chen CY. Fabrication of ultra-thin carbon nanofibers by centrifuged-electrospinning for application in high-rate supercapacitors. *Electrochimica*

Acta. 2019;**296**:268-275. DOI: 10.1016/j.electacta.2018.08.048

[43] Endo M, Kim YA, Ezaka M, Osada K, Yanagisawa T, Hayashi T, et al. Selective and efficient impregnation of metal nanoparticles on cup-stacked-type carbon nanofibers. *Nano Letters*. 2003;**3**:723-726. DOI: 10.1021/nl034136h

[44] Atchison JS, Zeiger M, Tolosa A, Funke LM, Jäckel N, Presser V. Electrospinning of ultrafine metal oxide/carbon and metal carbide/carbon nanocomposite fibers. *RSC Advances*. 2015;**5**:35683-35692. DOI: 10.1039/C5RA05409E

[45] Chen L, Hong S, Zhou X, Zhou Z, Hou H. Novel Pd-carrying composite carbon nanofibers based on polyacrylonitrile as a catalyst for Sonogashira coupling reaction. *Catalysis Communications*. 2008;**9**:2221-2225. DOI: 10.1016/j.catcom.2008.05.002

[46] Zhang P, Shao C, Zhang Z, Zhang M, Mu J, Guo Z, et al. In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol. *Nanoscale*. 2011;**3**:357-3363. DOI: 10.1039/C1NR10405E

[47] Yu B, Liu Y, Jiang G, Liu D, Yu W, Chen H, et al. Preparation of electrospun Ag/g-C₃N₄ loaded composite carbon nanofibers for catalytic applications. *Materials Research Express*. 2017;**4**:015603

[48] Ghouri ZK, Barakat NA, Obaid M, Lee JH, Kim HY. Co/CeO₂-decorated carbon nanofibers as effective non-precious electro-catalyst for fuel cells application in alkaline medium. *Ceramics International*. 2015;**41**:2271-2278. DOI: 10.1016/j.ceramint.2014.10.031

[49] Formo E, Peng Z, Lee E, Lu X, Yang H, Xia Y. Direct oxidation

of methanol on Pt nanostructures supported on electrospun nanofibers of anatase. *The Journal of Physical Chemistry C*. 2008;**112**:9970-9975. DOI: 10.1021/jp803763q

[50] Sonogashira K. Development of Pd-Cu catalyzed cross-coupling of terminal acetylenes with sp₂-carbon halides. *Journal of Organometallic Chemistry*. 2002;**653**:46-49. DOI: 10.1016/S0022-328X(02)01158-0

[51] Gopiraman M, Deng D, Saravanamoorthy S, Chung IM, Kim IS. Gold, silver and nickel nanoparticle anchored cellulose nanofiber composites as highly active catalysts for the rapid and selective reduction of nitrophenols in water. *RSC Advances*. 2018;**8**:3014-3023. DOI: 10.1039/C7RA10489H

[52] Chang YC, Chen DH. Catalytic reduction of 4-nitrophenol by magnetically recoverable Au nanocatalyst. *Journal of Hazardous Materials*. 2009;**165**:664-669. DOI: 10.1016/j.jhazmat.2008.10.034

[53] Gopiraman M, Saravanamoorthy S, Chung IM. Highly active human-hair-supported noble metal (Ag or Ru) nanocomposites for rapid and selective reduction of p-nitrophenol to p-aminophenol. *Research on Chemical Intermediates*. 2017;**43**:5601-5614. DOI: 10.1007/s11164-017-2950-3

[54] Gopiraman M, Deng D, Kim BS, Chung IM, Kim IS. Three-dimensional cheese-like carbon nanoarchitecture with tremendous surface area and pore construction derived from corn as superior electrode materials for supercapacitors. *Applied Surface Science*. 2017;**409**:52-59. DOI: 10.1016/j.apsusc.2017.02.209