



Direct synthesis of high concentration N-doped coiled carbon nanofibers from amine flames and its electrochemical properties

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ABSTRACT

High concentration nitrogen-doped coiled carbon nanofibers (CNFs) were directly synthesized from amine flames upon the NiCl₂ coated substrates. The microstructures and properties of the CNFs were characterized by using scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical workstation. The results revealed that: (1) the percentage portion of the coiled CNFs reached to 80% in the combustion products, and it exhibited a relatively stable screw-pitch with diameters in a range from 40 to 100 nm and length longer than 10 μm. (2) The ratio of N(N + C)⁻¹ proportion within the coiled CNFs was as high as 11% and it was dominated as a 'graphite-like' structure with C≡N bonds (one N atom bonded to three C atoms). (3) After pressing the coiled CNFs onto Ni foam to make an electrode, it showed a larger capacitance and more excellent electrochemical properties than that of the electrode prepared by using conventional carbon nanotubes (CNTs) from CVD process. The present high concentration N-doped coiled CNFs will be promising electrode materials for supercapacitors.

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1. Introduction

In general, one-dimensional carbon nanomaterials can be divided into carbon nanotubes (CNTs), vapor grown carbon fibers (VGCFs) [1] and carbon nanofibers (CNFs) [2] depending on their diameters. That is, diameter of CNTs is less than 50 nm with hollow structures, and diameter of CNFs ranges from 50 nm to 200 nm. When diameters of the one-dimensional carbon materials are larger than 200 nm, they are usually called VGCFs. In our previous work [3–5], it was found that a filament with or without the central hollow core represented different growth mechanism. And therefore, the term CNTs is defined referring to the filament with a center core and exhibits a highly graphitic structure with orientation of the basal carbon planes parallel to the tube axis, while the term CNFs is defined as a filament without a central channel or just a solid-cored fiber, regardless of the graphitic structure.

In general, the mechanical, physical and chemical properties of carbon nanomaterials are determined by their microstructures [6–8]. Extensive researches have been carried out for controlling

microstructures and non-metal (B and N) doping of CNTs, which have broadened potential applications of the carbon materials in catalyst supporter [9,10], biosensor [11], and electrode materials [12].

As we have known, most CNTs possess a straight one-dimensional linear structure. However, if the pentagon and heptagon (P–H) pairs are introduced into the hexagonal carbon rings, the tubular structure of CNTs will be bended and result in a linear spiral structure, which is called the coiled CNTs [13]. It has been demonstrated that the coiled CNTs have unique electrical, magnetic and mechanical properties [14–16]. For example: (1) when current flows through the coiled CNTs, an induced magnetic field will be produced, and this effect can be used to fabricate an electromagnetic transformer or nano-switch. (2) It has been known that the main form of fracture of CNTs/polymer composites is that the CNTs are pulled out from polymer [17], and the coiled CNTs can reduce the slippage between the graphite layers effectively and also enhance the contact strength between carbon materials and substrates at a molecular level. (3) The coiled CNTs are also ideal materials for electromagnetic shielding, due to a great attenuation of energy when electromagnetic waves spread through it.

Up to now, due to its excellent properties, the coiled CNTs have been successfully synthesized from chemical vapor deposition (CVD) [18] and flames [19]. Compared with the coiled CNTs, the coiled CNFs have similar preparation methods and exhibit good mechanical property and chemical inert, and its solid-cored struc-

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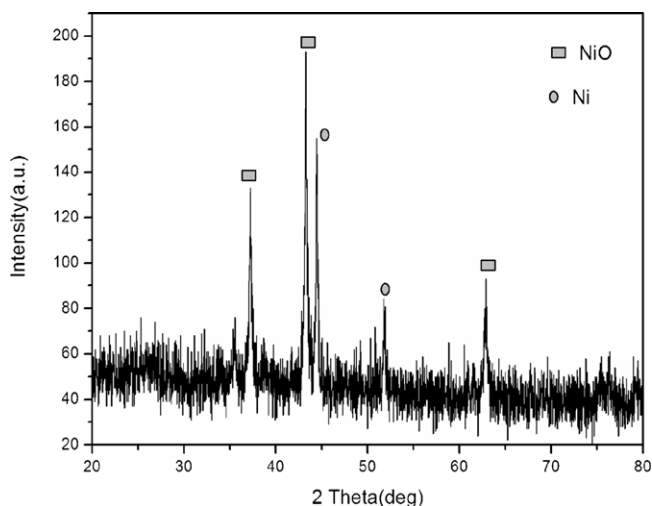


Fig. 1. XRD patterns of the N-doped coiled CNFs from amine flames.

ture provides superior performance in some special applications [20].

Doping is an effective way to change the electrical properties of nano-materials. Doping nitrogen atoms in CNTs can not only change the electrical properties, chemical reactivities and microstructures, but also bring rich functional groups to the CNTs surface [21,22]. Recent research has revealed that the N-doped CNTs increased the interactions between carbon and deposited nanoparticles [23], which show it a candidate for more stable electrode materials for electrochemical devices such as Li-ion batteries and supercapacitors.

In recent years, there are several processes which have been developed for synthesizing N-doped CNTs including CVD [24,25], catalytic pyrolysis [26], arc discharge [27] and substitution reaction [28]. These methods usually require protective atmosphere and high temperature during preparation of N-doped CNTs, which then arise problems such as complicated operation, low N-doping content, easy escape of doped nitrogen atoms from CNTs with time prolonging, and the decrease of nitrogen content with increasing temperature [29].

In our previous work, the N-doped CNTs were successfully prepared from amine flames [19]. It was found that the nitrogen atoms were dominantly 'graphite-like' which were more stable than the 'pyridine-like' structure from CVD and the N-doped CNTs exhibited different properties [19]. In addition, flame method is of advantages, i.e., simple and easy to be carried out in the air, many defects and functional groups in the carbon nano-materials; the fuel provides not only reaction temperature but also C and N sources simultaneously, integrative preparation and doping process, high energy utilization efficiency and reducing environmental pollution [30].

In this paper, the coiled CNFs with high N-doping content were firstly prepared from amine flames. Then, the N-doped coiled CNFs were used to make an electrode for testing its electrochemical properties. The results indicated possessed larger capacitance and excellent electrochemical properties, which show it to be promising electrode materials for supercapacitors.

2. Experimental

In the experiment, pure copper with size 15 mm × 15 mm was chosen as the substrate. The substrate surface was mechanically polished to a mirror finish, then coated by a NiCl₂ ethanol solution and dried in a furnace. Finally, the substrate was put into amine flame for 5 min. The sampling face was against the flame in a

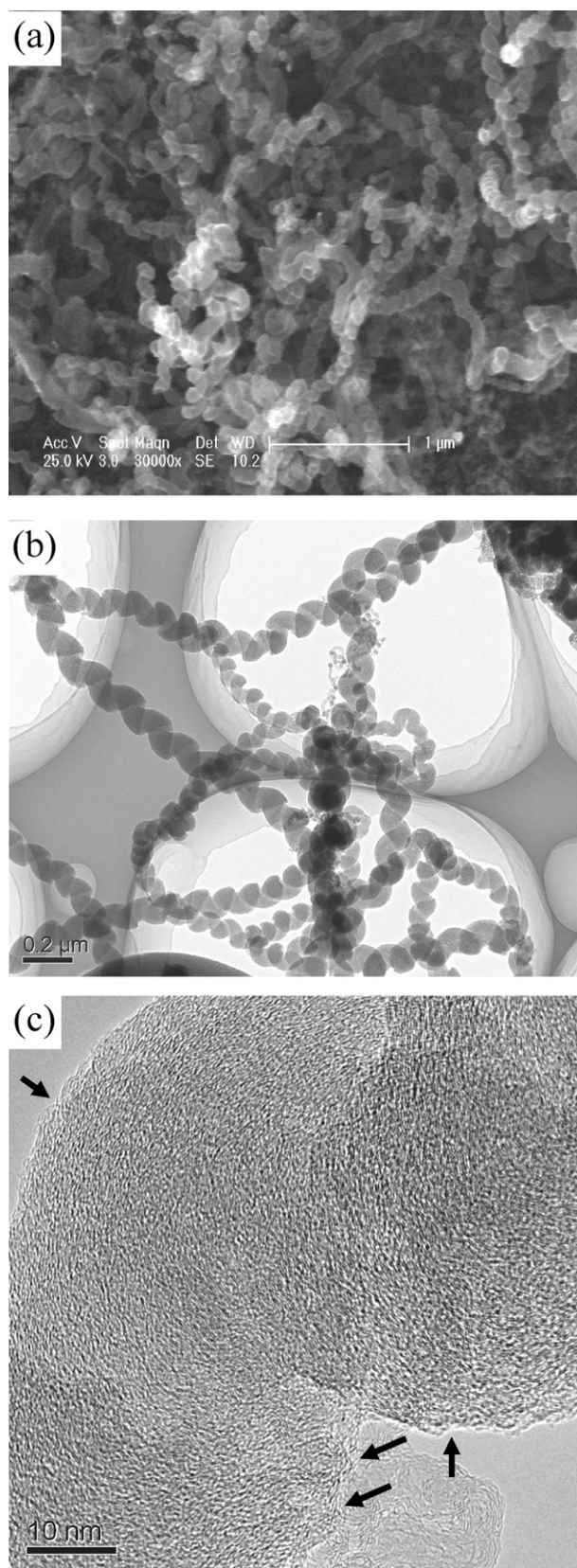


Fig. 2. Characterizations of the N-doped coiled CNFs from amine flames: (a) SEM, (b) TEM, and (c) HRTEM.

height around 1 cm above the lamp of a laboratory burner. A layer of black materials on the substrate was the CNFs. The morphology and microstructure of the CNFs were characterized by using a SEM (FEI SIRION, The Netherlands) and a HRTEM (JEOL JEM 2010FEF, Japan). The variation of the catalyst was carried out by using a XRD (D8 Advanced XRD, Bruker AXS, Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Multilab2000 spectrometer to get the information of chemical binding energy and the elemental compositions of the CNFs. The Fourier transform infrared (FT-IR) spectrum was recorded using a FT-IR spectrometer (Nicolet iS10, Thermo, USA) for detecting the surface functional groups on the CNFs.

In order to measure electrochemical properties, the CNFs were ground and pressed onto Ni foam substrate for making an electrode. During grinding, PTFE solution was added according to weight ratio of 10:1. Grinding time was 1 h. Then, 20 mg of the samples were uniformly distributed upon the Ni foam with chip size $10\text{ mm} \times 10\text{ mm}$. For comparison, CVD method was used to synthesize regular CNTs without N-doping on the Ni foam and made it an electrode. At last, both of the electrodes were studied by cyclic voltammetry (CV) and chronopotentiometry (CP) measurements on an electrochemical workstation (Shanghai Chen-hua CHI666C series). Two different electrodes made from carbon materials worked as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum wire electrode as the counter electrode, the electrolyte is the 6 M KOH solution.

3. Results and discussion

3.1. Morphology of the N-doped coiled CNFs

Fig. 1 shows the XRD patterns of the N-doped coiled CNFs from amine flames upon the NiCl_2 coated substrate. Only NiO and Ni diffraction peaks were obtained, while carbon peak between 20° and 30° was not found. It conforms that the catalyst precursor NiCl_2 has been decomposed inside the flame. That is to say, at high temperature, at first, NiO was generated due to the reaction between NiCl_2 and oxygen in the air; then, Ni nanoparticles were produced due to a reduction reaction when free C atoms in flame reacted with NiO. Because Ni has a strong catalytic activity, the redundant C atoms would be adsorbed into Ni particles, and grew the carbon nanofibers (CNFs). In addition, the XRD diffraction peaks of the carbon materials are generally difficult to be measured because they have low crystallization [4].

Fig. 2 shows the SEM, TEM and HRTEM micrographs of the N-doped coiled CNFs. We found that the percentage of the N-doped coiled CNFs in combustion products was very high, above 80%. Their pitch and diameter were quite uniform and stable with both left spiral and right spiral directions. The diameter of the CNFs is in a range of 40–100 nm, and length is up to 10 μm with a large aspect

ratio. TEM and HRTEM observations demonstrated its solid structure with amorphous carbon. Because of instability of the flames and atmospheric environment, the arrangement of the CNFs was chaotic and many defects and functional groups were formed on the CNFs surface.

In order to measure N-doping content in the coiled CNFs, XPS analysis was carried out, as shown in Fig. 3. The survey scan spectrum showed the presence of principal elements C1s, O1s, Ni2p, and N1s core levels. From high-resolution scan of the N1s spectral region, the N1s core level peak can be resolved into five components centered at 405.9, 403.6, 401.2, 399.7 and 398.3 eV, as shown in Fig. 3(b).

According to the reports on N-doped CNTs [29,31,32], the present results revealed that: (1) the strongest peak at 405.9 eV is attributed to N–O bond; (2) the second strongest peak of 399.7 eV is “graphite type nitrogen” with $\text{N}=\text{C}$ bond; (3) the peak at 398.3 eV is the “pyridine type nitrogen” with $\text{N}=\text{C}$ bond; (4) the weakest peaks at 403.6 eV and 401.2 eV are “pyrrolic type nitrogen” and nitrogen gas, respectively.

When analyzed the content of each element in the N-doped CNFs, it is found that the content of N atoms reaches to 7.84 at.%, as shown in Table 1. According to the traditional calculation selecting $\text{N}(\text{C}+\text{N})^{-1}$ as N-doping content, the present N-doping content is as high as 11 at.%, which is much higher than the other methods for synthesizing N-doped CNTs. For example, N content was generally not more than 10% from the substitution of CNTs [28], only 3–5 at.% from CVD [24,25], and not more than 3 at.% from arc discharge [27] and catalytic pyrolysis [26]. Table 2 lists the details of methods, experimental conditions and nitrogen contents. In contrast, the present flaming method obviously provides the most simple preparation conditions but with the highest N-doping content. Two reasons have been proposed for the high N-doping content in the coiled N-doped CNFs:

(1) Formation of the carbon–nitrogen structure of “graphite-type nitrogen” with $\text{N}=\text{C}$ bonds. In amine flame, due to high concentration of nitrogen atoms, nitrogen atoms can merge into CNFs simultaneously during growth, and form the N-doped CNFs. Therefore, nitrogen atoms were difficult to lose from the N-doped CNFs. However, the other methods, such as CVD, usually dope nitrogen atoms in the prepared CNTs. In this case, nitrogen atoms were generally in the interstitial sites of CNTs, which was unstable and easy to lose and even disappeared after a period of time.

(2) Lower temperature of the flames. In general, the temperature inside flame is around 450°C , which is lower than the process, such as CVD and arc discharge. Therefore, the doped nitrogen atoms were kept in a stable condition, and the content was increased.

Therefore, if the higher nitrogen content of fuels are used, it is expected to get the higher content of the N-doped CNFs furtherly.

FT-IR is usually used to characterize the functional elements absorbed by carbon nanomaterials. Fig. 4 shows a FT-IR spectrum

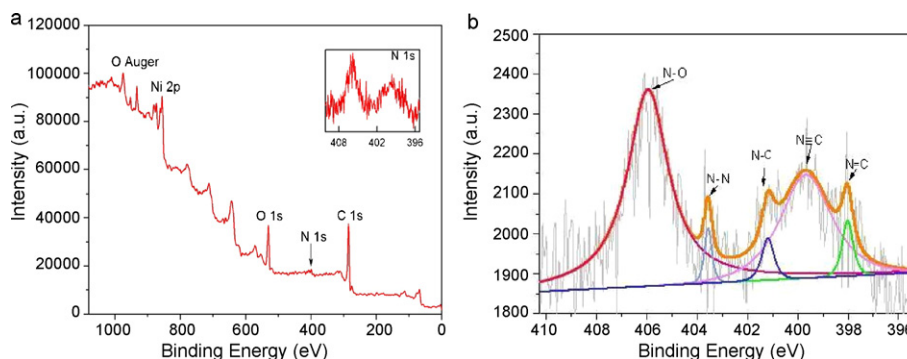


Fig. 3. XPS spectra of the N-doped coiled CNFs from amine flames: (a) survey spectrum and (b) N1s spectrum.

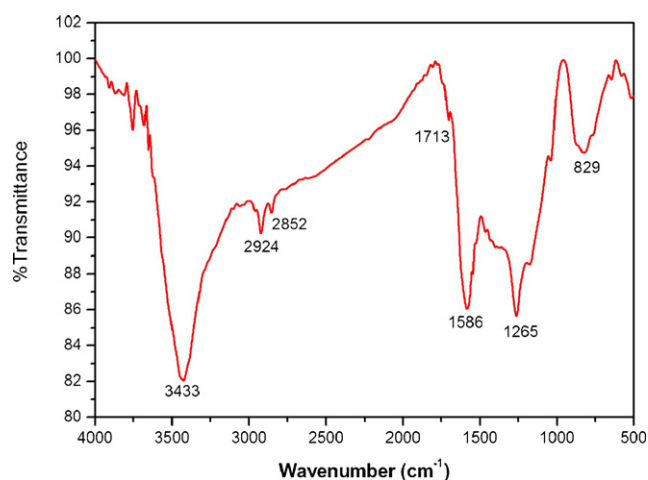
Table 1
XPS comparative parameters for the N-doped coiled CNFs from amine flames.

Name	Peak BE	Height/counts	FWHM/eV	Area (P) CPS/eV	Area (N)	at.%
C1s	284.64	4084.32	2.03	9883.97	3890.74	62.85
O1s	529.65	2773.37	1.4	9618.86	1322.08	21.36
N1s	406.09	500.74	0.34	2196.17	485.42	7.84
Cl2p	199.15	108.08	0.1	323.1	55.28	0.89
Ni2p	854.07	3005.72	1.39	23075.72	436.69	7.05

Table 2
Comparisons among different processes to synthesize N-doped CNTs and N-doped CNFs.

Methods	Experimental conditions	Nitrogen content
CVD – N-doped CNTs [24,25]	700–900 °C, N atmosphere	3–7%
Arc discharge – N-doped CNTs [27]	High voltage, He–N gas	<3%
Catalytic pyrolysis – N-doped CNTs [26]	1000 °C, argon atmosphere	2–3%
Substitution – N-doped CNTs [28]	Above 1200 °C	<10%
Amine flames – N-doped CNFs	450 °C, amine fuels	11%

in the range of 500–4000 cm^{-1} of the coiled CNFs. The bands at 3433, 2924, 2852, 1586, 1265 and 829 cm^{-1} were observed in the spectrum. The bands at 3433 cm^{-1} is attributed to the stretching vibrations of water molecules or O–H groups, the bands at 2924 and 2852 cm^{-1} could be assigned to C–H bonding in amorphous CNFs [33]. The bands at 1586 and 1265 cm^{-1} were related to the

**Fig. 4.** FT-IR spectrum of the N-doped coiled CNFs from amine flames.

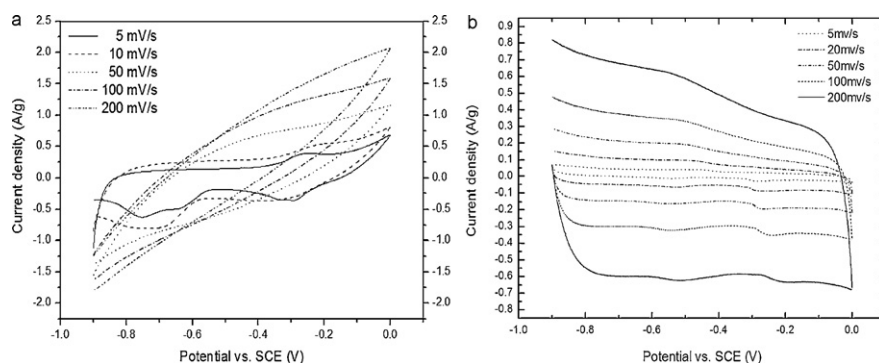
graphite-like structures, they were assigned to N-doped graphite-like structures, such as N≡C bonding and N=C bonding [34]. The band at 829 cm^{-1} was assigned to the bending motion of C–O–C bonding [35]. Obviously, from the FT-IR spectrum, so many atom groups were formed on the CNFs surface, which make it a potential application in special fields.

3.2. Electrochemical properties of the N-doped coiled CNFs

Compared with pure CNTs, N-doped CNTs, as a more novel class of nanomaterials, have been developed recently [36]. The experimental and theoretical researches have shown that N-doped CNTs have many advantages over general CNTs [37,38]. These advantages includes (1) controlling electronic properties of CNTs by introducing different amounts of nitrogen; (2) controlling morphology of CNTs to create extra “structural reactive sites” for deposition of catalytic nanoparticles; (3) enhancement interaction between CNTs surface and the deposited nanoparticles (e.g. Pt) [23]. However, the electrochemical properties of the N-doped coiled CNFs have not been reported.

Fig. 5 shows the cyclic voltammetry (CV) curve of the N-doped coiled CNFs and pure CNTs respectively. The results show that the curve area of the N-doped coiled CNFs is significantly larger than that of CNTs, which suggests that the N-doped coiled CNFs possess a greater capacity [5]. In addition, compared with our previous work on pure CNFs, the appearance of redox peaks at low scan rate indicates that the N-doped coiled CNFs also have pseudo-capacitance [39]. The deformation of the CV curves from rectangle is due to the defects and functional groups on the surfaces of the N-doped coiled CNFs. It was found that at high scanning speeds, some special phenomena happened, that is: (1) the charging and discharging process were accelerated; (2) the electrolyte diffusion in electrode became insufficient; (3) the defects on the surface were in low utilization.

Fig. 6 illustrates a CV curve of the N-doped coiled CNFs for 100 cycles. It was found that the redox peaks appeared in the first cycle, then decreased gradually with increase of cycle, and at last disappeared after 100 cycles. This phenomenon revealed that there were a lot of functional groups on the N-doped coiled CNFs surface, which provided availability for the oxidation–reduction processes. This oxidation–reduction executed in an irreversible one-way direction and contributed to certain amount of pseudo-capacitance. It must

**Fig. 5.** Cyclic voltammetry curve in 6 M KOH solution: (a) N-doped coiled CNFs from amine flames and (b) CNTs from CVD.

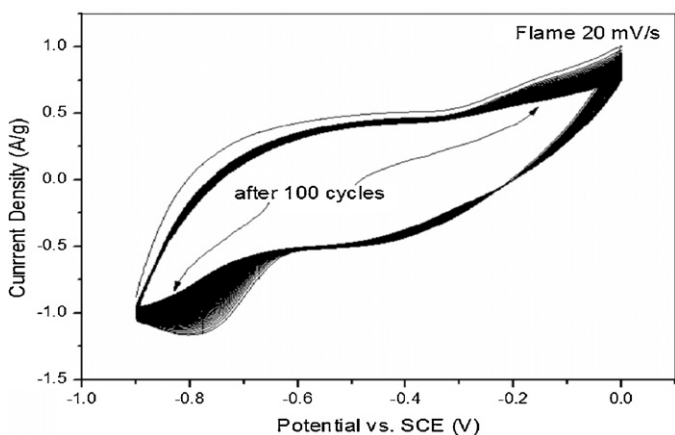


Fig. 6. Cyclic voltammetry curve of the N-doped coiled CNFs for 100 cycles.

be emphasized that the CV curve were still kept in a large area and closed to a rectangular shape after repetitious cycles. Therefore, the N-doped coiled CNFs not only exhibit a high capacity, but also exhibit high stability after the operation environment becoming stable.

Fig. 7 gives the chronopotentiometry (CP) curves of the N-doped coiled CNFs and pure CNTs with current density 0.25 A g^{-1} . Obviously, the shapes of these two curves are symmetrical, which indicates that both materials possess a good capacitance. However, it was found that the time for charge and discharge of the N-doped coiled CNFs electrode was significantly longer than that of the pure CNTs, which showed that the N-doped coiled CNFs electrode exhibit a much larger capacity. These results were also consistent with the above CV curves. In addition, there was a stage during voltage reducing, which means that the N-doped coiled CNFs have pseudocapacitance. When the CNFs were pressed onto Ni foam, the poor contact might happen among the CNFs. Due to the surface atoms groups on the CNFs and the amorphous coiled structure, the electronic conductivity was reduced and this big internal resistance caused the "IR drop".

In summary, the N-doped coiled CNFs from amine flames exhibit excellent electrochemical properties due to its special characteristics such as high nitrogen doping, lots of defects on the surface and the coiled morphology, which make it easier to absorb functional groups for the oxidation–reduction reaction. The superficial defective sites and functional groups can effectively release the chemical inertness of the CNFs and help to the aqueous KOH electrolyte wetting and the formation of electric double layer at the

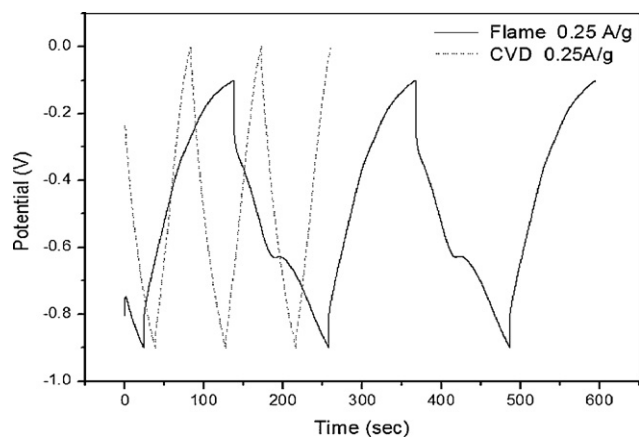


Fig. 7. Chronopotentiometry (CP) curves of the N-doped coiled CNFs from amine flames and CNTs from CVD in 6 M KOH solution.

electrode/electrolyte interface. Therefore, the N-doped coiled CNFs show a potential application in supercapacitors.

3.3. Growth mechanism of the N-doped coiled CNFs in amine flame

It is well-known that the growth mechanism of spiral one-dimensional carbon materials is mainly based on the anisotropic theory of catalyst particles [40]. For the coiled CNTs, Motojima et al. [41] proposed a mechanism, that is, carbon atoms have different deposition rate on the different crystal surface of the catalyst particles; and with carbon atoms deposition and diffusion accumulating over time, the CNTs bend regularly and lead to the formation of the coiled CNTs. Compared with CNTs, only difference is that the N-doped coiled possess a "solid-cored" structure, which imply that it needs more free carbon atoms. Here, two factors are proposed for growth of the N-doped coiled CNFs: (1) interaction between flame temperatures and anisotropic of the catalyst crystal faces [42] and (2) existence of nitrogen atoms in the CNFs.

In the present work, the Ni nanoparticles from the coated NiCl_2 in flames are considered to be catalysts for growing the CNFs. It has a face-centered cubic (FCC) structure and exhibits a high solubility and low diffusion rate for carbon atoms. Therefore, when the carbon atoms reached to saturation in the Ni nanoparticle, they began to precipitate along the crystal planes. For different crystal planes, carbon atoms precipitate in different speeds. In general, carbon atoms in FCC structure tend to precipitate along the $\{111\}$ close-packed plane and the $\{110\}$ close-packed direction. Because of low temperature (about 450°C) of propylamine flame, a low concentration of free carbon atoms was expected in the flame, which led to a slowing growth speed of the CNFs. Then, for different crystal planes, there was a large diversity of the growth speed of the CNFs. For example, the $\{111\}$ plane provided a stronger epitaxial fit with graphite than the $\{100\}$ and $\{110\}$ planes. Then, the main growth direction of the CNFs was along the $\{111\}$ plane, while the carbon atoms precipitate from the $\{100\}$ and $\{110\}$ planes would force the CNFs bending in other directions. At last, a coiled structure was formed.

Additionally, growth of the coiled CNTs also depends on the formation of pentagon and heptagon (P–H) carbon pairs, because the

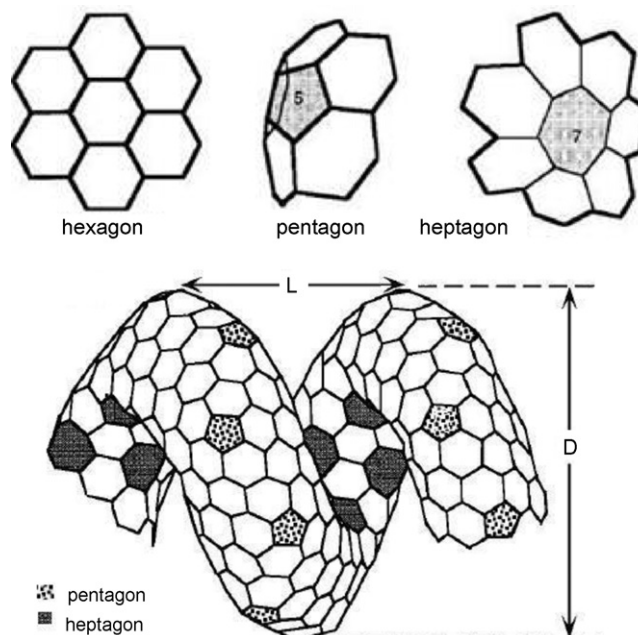


Fig. 8. Formation mechanism of the coiled CNFs [43].

pentagon makes the CNTs bend inwards and heptagon outwards [43], as shown in Fig. 8. In the present case, many defects were introduced upon the surface of the CNFs due to high content of nitrogen doping, as shown in Fig. 2c. These defects could damage the hexagon carbon structure of graphite, and formed the P–H carbon pairs in the CNFs, and then resulted in the growth of the N-doped coiled CNFs.

4. Conclusions

The N-doped coiled CNFs can be simply and effectively prepared from nitrogen-containing amine flames. Comparing with the other process, this CNFs possess advantages such as high N doping content, 'graphite-like' C≡N bonds, coiled structure, rich surface defects and atom groups, due to the co-existence of carbon and nitrogen atoms from amine, and low temperature in flames. Experimental results reveal that the N-doped coiled CNFs exhibit excellent electrochemical properties, and are expected to be a potential application of electrode materials in new energy field and wave absorption.

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