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LETTER

Synthesis of carbon coiled micro/nano-structures in the absence of sulphurous promoter

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Introduction

Vapor grown carbon fibers (VGCF) are generally prepared by chemical vapor deposition (CVD) process using hydrocarbon compounds as the carbon source and transition metal powder such as Fe, Co, Ni as the catalyst. VGCF can generally be classified into straight fibers and helical fibers according to their morphology [1–6]. It may reasonably be expected that the helical fibers have novel properties and special applications for their unique helical structure, as in the case of the double helix structure in DNA or α-helix proteins in the human body. However, the growth of the fibers with the 3D helical/spiral forms is quite by accident. For this reason, the fabrication of helical fibers has already attracted much attention among the scientists though it is a topic full of difficulties and challenges [1–6].

Recently, regularly micro-coiled carbon fibers (referred to as ‘‘carbon microcoils’’ hereafter) have been synthesized with high yield and good reproducibility [1–6]. Carbon microcoils are recognized to have high potential for many applications, such as electro-magnetic wave absorbers, electrode materials, tunable micro-devices and so on. There have been many reports of preparation of carbon microcoils, but the conventional methods all require toxic gases i.e., sulfur or phosphorus promoters. In conventional methods for the fabrication of carbon microcoils, fine Ni particles was used as catalysts and acetylene containing a small amount of sulfur or phosphorus compounds was used as carbon source [1–6]. Although the content of these sulfur or phosphorus compounds in total gases was very minute, they were indispensable to form the carbon microcoils because they were used as promoter in the reactions. Furthermore, the dosage would strongly affect the morphologies of the carbon products. However, two obvious disadvantages arise from the use of sulfur or phosphorus compounds. First, these compounds are toxic and have a very unpleasant smell, so the reaction operation is highly hazardous and affects the health of the people in the surroundings. Second, these compounds are liquid at room temperature, so that it is difficult to accurately control the concentration while mixing them into other reaction gases, hence results the uncertain morphologies of the carbon products.

In this work, ball milled Ni-sulphide has been used as catalyst on purpose to avoid the introducing of noxious and unpleasant thiophene during the reaction process also to get the thin film of quasi-aligned carbon microcoils. Although Mukhopadhyay et al. have reported the synthesis of carbon microcoils by catalytic chemical vapor deposition (CCVD) method [5, 6] but those synthesis reports of carbon-coiled structure are based on the use of thiophene as sulphur promoters. The present novel method of fabrication of carbon microcoils does not require the toxic gases, i.e., sulfur or phosphorous promoters, which is really benefit to protecting environment and make it easy to obtain carbon microcoils with perfect morphology.

The regular carbon coiled structures can be quite efficiently obtained with good controllability, so that it

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is suitable and secure to scale up for the production of carbon-coiled structure. The main advantage of our synthetic procedure is that one could get a thin film of aligned carbon micro-spring, which could be useful as shock absorber.

Experimental

Correct amount (~5 gm) of catalyst powder (ball milled Ni-sulphide) was taken on a quartz boat, and was placed in the central zone of the electrically heated horizontal furnace as discussed elsewhere [5–7]. Initially, the furnace was flushed with nitrogen (96% pure) for 30 min. The reaction temperature was kept at 740 °C. Next acetylene (purity 99.9%) along with hydrogen were allowed to flow through the furnace. After 30 min the gas flow was stopped and the furnace was cooled down by flushing nitrogen at 100 ml/min rate. A black fluffy-spongy powder was collected and was examined under Scanning Electron Microscope (SEM—Philips ESEM XL 30 series & CARL-ZEISS-EVO 50 series). Detailed experimental conditions for microcoils, coiled nanofibers and sample containing both microcoils/nanocoiled fibers have been tabulated in Table 1.

Results and discussions

Ball milled Ni-Sulphide has been used as catalyst, which promotes coiled structure synthesis; thereby avoiding the direct use of thiophene vapor having the disadvantages as mentioned above. Mukhopadhyay et al. has already reported [5, 6] that thiophene vapors used on pyrolysis, in the reaction zone produces highly reactive sulphur particles. Then possibly a chemical/physical adsorption/alloy formation occurs between Ni powder and in situ generated sulphur particles. This chemical reaction, based on the diffusion of solid particles, takes place on the catalyst surface-leading to the proposed catalytic anisotropy on the crystal faces of the catalyst grains. Depending on the degree of the anisotropy (of in-situ reactions/combinations between Ni powder and sulphur particles) the coil diameters and the degree of coiling also vary. Larger the anisotropy, more is the degree of coiling and smaller the anisotropy, less is the degree of coiling. The same kind of anisotropy has already been achieved by using ball milled Ni-sulphide particles. Under SEM it has been observed that ball milled Ni-sulphide particles have variation in diameter. Hence the same catalytic anisotropy as mentioned earlier [5, 6] has already presented here. During the reaction condition because of this existing catalytic anisotropy carbon microcoiled have been easily synthesized. Thus the differences in coiling as observed in SEM images can be explained. However, there is no evidence, at present to support the proposed mechanism.

It should be noted that in order to create the reported catalytic anisotropy [5, 6] over Ni-particles much higher temperature (~900 °C) is required. It is simply because at first thiophene has to crack and generate sulphur particles which in turn will combine Ni-particles to cause the catalytic anisotropy and hence the coiled networks. In the present work since the same catalytic anisotropy as mentioned earlier [6, 7] has already present with the used ball milled Ni-sulphide particles (thus avoiding the cracking of thiophene and combination steps as mentioned above) and the same are responsible for the synthesis of carbon microcoils at low temperature (740 °C) as compared to 900 °C reported earlier [5, 6].

The SEM images are shown in Figs. 1, 2. For comparison analysis SEM image of overall yield of carbon microcoiled samples synthesized in the presence of sulphur promoter (i.e., thiophene) has been shown in Fig. 1a. Figure 1b shows the overall yield of helical carbon micro coils synthesized in absence of thiophene impurity (i.e., sulphur promoter). Figure 2a shows the magnified view of one typical double helical carbon microcoil (DHCMC) synthesized in absence of thiophene impurity. Figure 2b shows a unique image of coiled carbon nanofiber structure synthesized under optimized conditions in absence of thiophene impurity. Figure 2c shows the magnified view of some portion of the sample, which contains both carbon microcoils as well as coiled carbon nanofibers synthesized under

Table 1 Summary of synthesis conditions of coiled carbon nano/micro structures

Type of product	Acetylene flow rate (ml/min)	Hydrogen flow rate (ml/min)	Nitrogen flow rate (ml/min)	Temperature and time of reaction (°C and 30 min)
Carbon microcoils	200	300	100	740
Carbon nanocoiled fibers	100	100	100	740
Sample containing both micro coiled and nanocoiled fibers	200	50	300	740

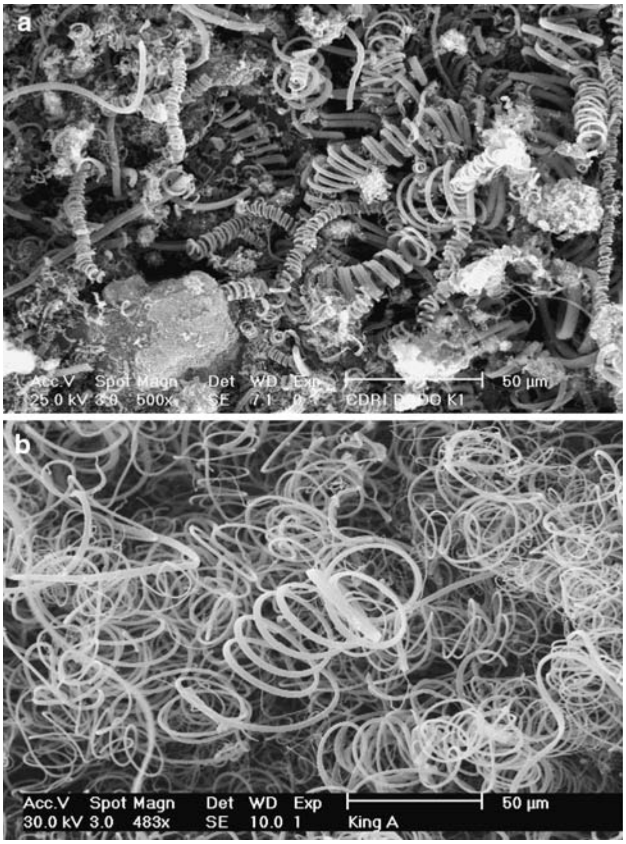


Fig. 1 SEM images of carbon microcoils synthesized (**a**) in the presence of sulphur promoter (i.e., thiophene), (**b**) in the absence of a sulphur promoter

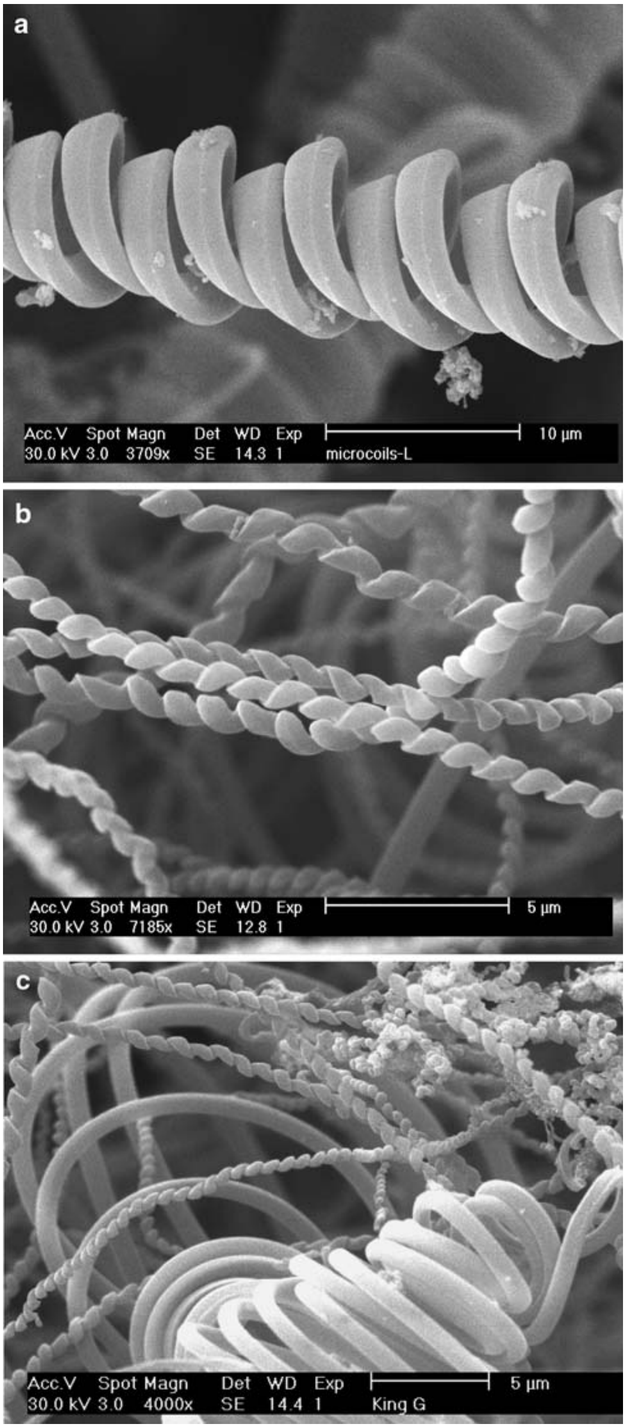


Fig. 2 SEM images of (**a**) a typical double helical carbon microcoil, (**b**) a coiled carbon nanofiber synthesized under optimized conditions in the absence of thiophene, (**c**) part of sample containing both microcoils and coiled carbon nanofibers synthesized in the absence of thiophene

different conditions in absence of thiophene impurity (i.e., sulphur promoter). From SEM observation it has been found out that both kinds of coils are present almost 1:1 ratio (as per quantity). Though the carbon microcoils have relative large cavum (diameter of 3–4 μm), there is no pore along the fiber axis of the carbon fiber, which construct the microcoil. The as-grown carbon microcoils are almost amorphous state as confirmed by Raman spectroscopy and also by Transmission electron microscopy analysis. Two wide peaks, G-band peak at 1,597 cm^{-1} and D-band peak at 1,327 cm^{-1}, has been observed in the Raman spectra representing graphitized carbon and disordered carbon respectively (Fig. 4). The intensity ratio of G-band to D-band (IG/ID) is ~0.90 to 0.92 which is far less than that of multi-walled carbon nanotubes. SEM image of a bundle of double helical carbon micro coils is shown in Fig. 3a. Magnified angular projection through the channel of double helical carbon microcoil under SEM is shown in Fig. 3b. Broken tips of the coil are clearly visible in this image (marked by arrow) (Fig. 4).

It should be noted that Table 1 presents the optimum conditions for the synthesis of different carbon coiled structure. These conditions were achieved after performing a series of experiments against each product and analyzing the results. The

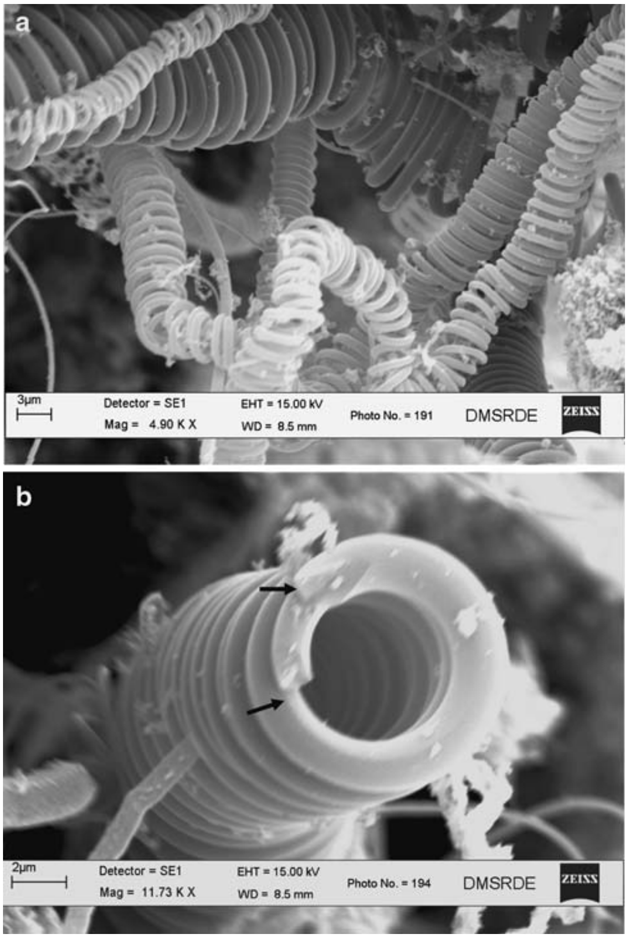


Fig. 3 (**a**) Magnified view of bunch of double helical carbon microcoils present in the sample under SEM while (**b**) vertical projection through the channel of double helical carbon micro coils under SEM

amount of catalyst used against each experiment is 5 gm because of the limitation of furnace size. One could go much larger amount depending on the size of the furnace.

A close look at the SEM images shows

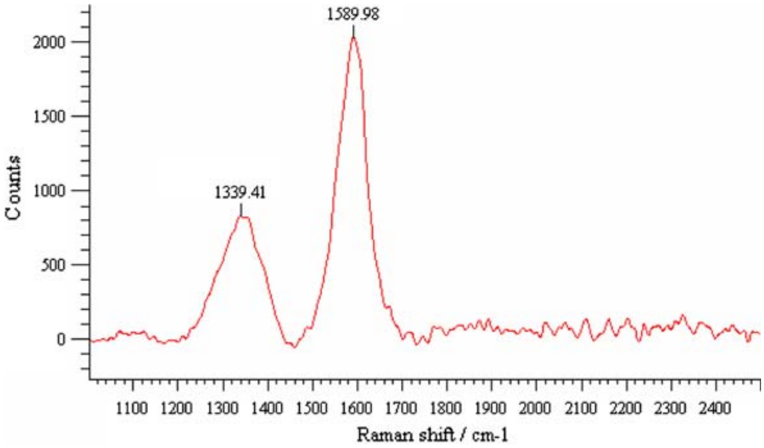
- The yield is very high (~95%).
- The sample is quite pure (with minute presence of impurities such as amorphous carbon and catalyst particles. The presence of Ni and S has been conformed by EDAX. The atomic % ratio of C, S and Ni as observed under EDAX is – 98.39:0.96:0.65).
- Two types of coils are present and have diameter between 3–4 μm and 300–500 nm—depending on the type of nickel particles used (small variation are also present).
- Their lengths are in mm.

It should be mentioned that all the products have been applied for em absorber coatings. It has been found that sample which contains both carbon microcoils as well as coiled carbon nanofibers has better effect than the samples which contains either carbon micro coils or carbon coiled nanofibers. The possible reason for this observation is that in the case of samples containing either carbon micro coils or coiled carbon nanofibers—very narrow rage of diameter distribution was present (e.g., in the case of carbon micro coils diameter ~3 to 4 μm and in the case of coiled carbon nanofibers diameter ~300 to 400 nm). However, in the case of sample containing both carbon micro coils and coiled carbon nanofibers, wide range of diameter distribution was present (e.g., ranging from 300 nm up to ~5 μm) and hence resulting a good reflection loss in 8–12 GHz region.

Conclusion

Here a simple method to synthesize coiled carbon networks by CCVD route in absence of any sulphur/

Fig. 4 Raman spectrum of the synthesized carbon microcoils



phosphorous promoters as well as electromagnetic/microwave field has been presented which has the possibilities of easy scaling up. Subsequent work is being undertaken for the detailed morphological features and will be reported in subsequent publications along with other characterization results.

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