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Letter to the Editor

Controlled synthesis of carbon nanocoils and carbon nanotubes on common paper substrates

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ABSTRACT

The commercially available copy papers and pure papers have been adopted to synthesize carbon nanomaterials. It is found that carbon nanocoils (CNCs) are efficiently synthesized on the copy paper substrates using $Fe_2(SO_4)_3/SnCl_2$ catalyst by a thermal chemical vapor deposition method, while only carbon nanotubes (CNTs) are obtained on the pure paper substrate using the same process. It is evidenced that the particles of calcium carbonate existing in copy paper aggregate catalyst and adsorb more sulfur elements which promote the growth of CNCs. In addition, CNCs can successfully grow out from the pure paper by adding calcium carbonate.

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Carbon nanotubes (CNTs) are recognized to have amazing mechanical, electrical and thermal characteristics [1]. Owing to a 3D helical structure, carbon nanocoils (CNCs) exhibit more excellent mechanical and electromagnetic properties than CNTs, which are expected to be used as important basic units of micro/nano systems [2,3]. Regarding the synthesis methods of CNCs [4–7], a lot of researches have been reported. Due to the facts that catalyst particles should be carried or supported by a substrate [8], and different types of carbon coils could be obtained on different substrates, selection of a suitable substrate to synthesize carbon coils of desired type is an important issue. Pan et al. patterned Fe films on indium tin oxide-coated glasses to achieve high yield CNCs [5]. A method to synthesize coiled carbon structures with controlled diameter on an alumina substrate was reported by Bai [6]. Li et al. succeeded in using SiO_2 substrates dispersed with Fe–Sn–O catalyst prepared by a sol–gel process to efficiently synthesize CNCs [7]. It is noted that the substrates used in these researches are in high cost, none flexible or size limited. With the commercial needs, economic or flexible substrates are required to synthesize carbon coils in large quantity. Based on the above considerations, paper may be a good candidate for synthesizing CNTs and CNCs in a large quantity.

$Fe_2(SO_4)_3{\cdot}9H_2O$ and $SnCl_2{\cdot}5H_2O$ mixture dissolved in deionized water was served as the catalyst precursor. Three kinds of paper substrates, i.e., commercially available copy paper, pure paper and the pure paper added calcium carbonate particles were used as substrates. The pure paper added with calcium carbonate particles was prepared by the following procedure: Mixed turbid liquid of calcium carbonate with deionized water were prepared; Then the pure paper was immerged in the turbid liquid dispersed with ultrasonification for 5 min; at last the paper was taken out from the liquid and dried at 40 °C in air. These paper substrates were firstly calcined at 710 °C for 30 min in an argon atmosphere with an

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Ar flow rate of 365 sccm. After that the calcined papers were immersed in the solution of catalyst precursor for 10 min and dried. The samples were then calcined once again under the same conditions of the paper calcination as mentioned above. At last, the carbon deposits were achieved in a chemical vapor deposition system at 710 °C for 1 h by introducing acetylene and argon gases with flow rates of 15 and 325 sccm, respectively.

Fig. 1(a) and (b) show the SEM images of carbon deposits grown on the pure paper and copy paper substrates, respectively. Only CNTs can be obtained on the pure paper substrates, as shown in Fig. 1(a). Fig. 1(c) shows the TEM image of the CNTs in Fig. 1(a). These CNTs possess hollow structures with low crystallinity and the graphite layers tend to orientate along its growth direction. These CNTs have an average inner diameter and outer diameter of 50 and 15 nm, respectively. It is clearly observed from Fig. 1(b) that a great quantity of CNCs have grown from the copy paper substrate. More than 80% deposits are carbon coils with various diameters, ranging from several hundreds of nanometers to several micrometers. The magnified images in Fig. 1(b) and (d) show that the catalyst particles are at the tips of the CNCs indicating a tip growth mechanism. The rest of deposits on the copy paper are CNTs as shown in Fig. 1(e). These CNTs have the similar feature with those on the pure paper substrates. The Raman spectra of the carbon products grown on the pure papers and the copy papers also show the different growth results (see Fig. S1 in Supplementary materials). These results are conjectured to be caused by the differences in composition and structure between the two kinds of papers.

The differences in structure and composition between the two kinds of calcined paper substrates were analyzed by SEM and EDX mapping. Only carbon fibers can be observed on the pure paper shown in Fig. 2(a). The distributions of carbon, oxygen and calcium elements in the area indicated by the box are shown in Figs. 2(b)–(d), respectively. It is observed that carbon and oxygen elements distribute in the pure paper uniformly. However, carbon fibers and micro particles coexist in the copy paper as showed in Fig. 2(e). The EDX mappings of carbon, oxygen and calcium elements in the area indicated by the box are respectively shown in Figs. 2(f)–(h). It is observed that the carbon fiber mainly consists of carbon element, but micro particles mainly consist of calcium and oxygen elements. It is preliminary estimated that the micro particles could be calcium oxide or calcium carbonate. The Raman spectra for the micro particles and the fibers in calcined copy paper show that micro particle area arises four characteristic peaks, which are mainly originated from the

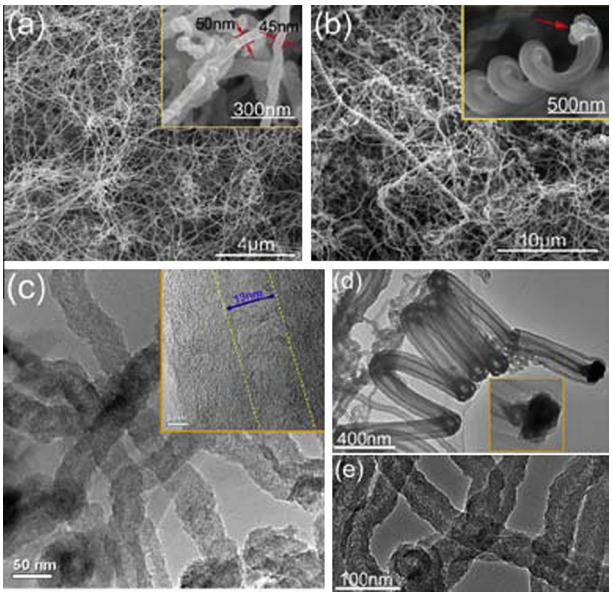

Fig. 1 – SEM images of the CNC/CNTs synthesis on (a) pure paper and (b) copy paper; (c) TEM images of the CNTs in (a); (d) and (e) TEM images of CNCs/CNTs in (b). The inset in each figure is the enlarged SEM or TEM image of local region. (A color version of this figure can be viewed online.)

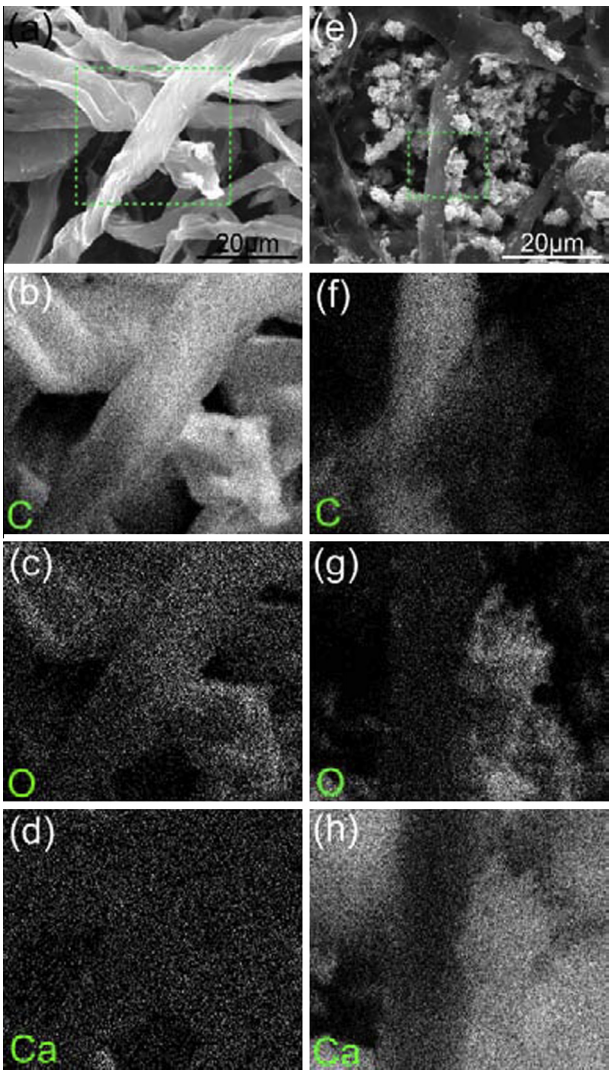

Fig. 2 – (a) SEM image of the calcined pure paper, and EDX mappings of (b) carbon, (c) oxygen and (d) calcium elements in the area indicated by the box in (a). (e) SEM image of the calcined copy paper and EDX mappings of (f) carbon, (g) oxygen and (h) calcium elements in the area indicated by the box in (e). (A color version of this figure can be viewed online.)

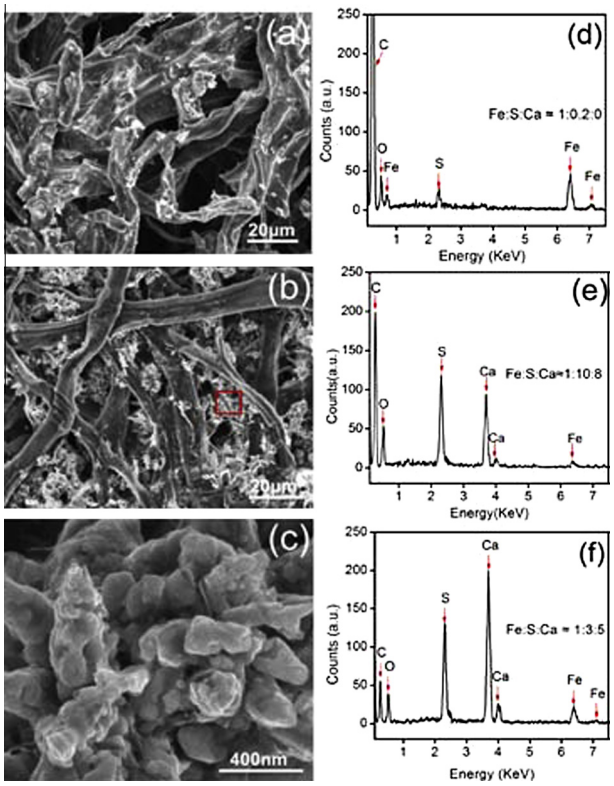

Fig. 3 – SEM images of (a) the pure paper dip-coated with catalyst, (b) the copy paper dip-coated with catalyst and (c) the enlarged image of particles in the area indicated by the box in (b). EDX spectra of (d) the pure paper dip-coated with catalyst, (e) the fiber area and (f) particle area in the copy paper dip-coated with catalyst. (A color version of this figure can be viewed online.)

calcium carbonate [9] (see Fig. S2 in Supplementary materials). The above experimental results indicate that calcium carbonate is the main difference between two kinds of paper substrates and own a crucial influence on the growth of CNCs on paper substrates.

SEM and EDX spectra of the paper substrates dip-coated with catalyst were also measured. Only a few of catalyst clusters attached on the fibers in the pure paper as shown in Fig. 3(a). While in the copy paper, the catalyst particles prefer to be agglomerated around the calcium carbonate particles rather than to be adsorbed on the carbon fibers as shown in Fig. 3(b). The enlarged SEM image in Fig. 3(c) demonstrates that these micro particles with rough surface can promote the deposition of catalyst particles [10] and aggregate them to the sizes suitable for the growth of CNCs. The EDX spectrum taken from the pure paper dip-coated with catalyst, the fiber and particle areas in the copy paper dip-coated with catalyst are respectively shown in Figs. 3(d)–(f). The EDX spectrum in Fig. 3(d) gives the atomic ratio for Fe:S:Ca of 1:0.2:0. The uniformly dispersed small Fe particles on the surface of carbon fiber result in the growth of CNTs. On the other hand, the atomic ratio for Fe:S:Ca is changed to 1:10:8 and 1:3:5 on the copy paper substrates as shown in Fig. 3(e) and (f), which indicates great increases in the atomic ratio for Fe and S and proportion of sulfur element. It is reported that the addition

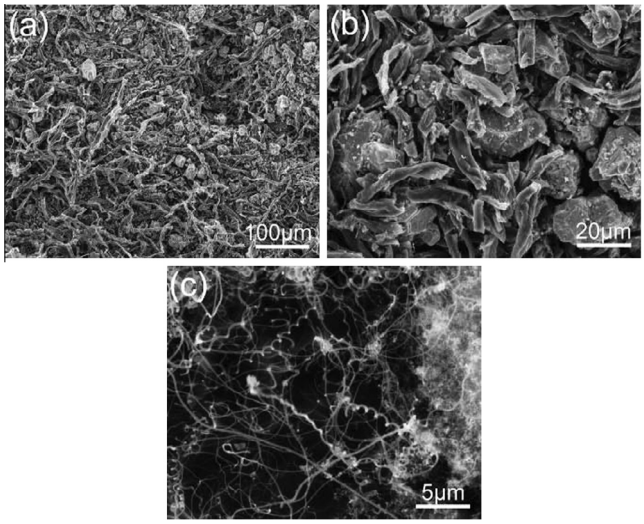

Fig. 4 – SEM images of (a) the pure paper coated with calcium carbonate and (b) the enlarged image of (a). (c) SEM image of the deposits on the copy paper substrates coated with calcium carbonate.

of a small amount of sulfur in catalyst can promote the spiral growth of carbon nanofibers or nanotubes [11], which is another reason for the growth of CNCs on the copy paper substrates.

The commercially available calcium carbonate powder was added into the pure paper to synthesize CNCs. The morphology of the pure paper coated with calcium carbonate is shown in Fig. 4(a) and the enlarged image of Fig. 4(b). It is found that the hybrid structure of carbon fibers and calcium carbonate particles in the decorated pure paper is similar with that in copy paper. It is observed in Fig. 4(c) that CNCs are really grown out from such decorated pure paper substrates as expected.

In summary we have synthesized CNTs on pure papers and CNTs/CNCs on copy papers by a thermal CVD. Compared with the differences in composition and structure between the two kinds of paper substrates, calcium carbonate particles in the copy paper is found to have ability to aggregate catalyst more efficiently and adsorb more sulfur elements which promote the growth of CNCs. The growth of CNCs has also been achieved on the calcium carbonate decorated pure paper substrate. Therefore, this method enable to synthesize carbon nanomaterials selectively on different kinds of cheap paper substrates in large area and quantity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.04.072.

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