

A NEW APPROACH TO DIRECT PRODUCTION OF CARBON NANOTUBES AND RELATED NANOCARBONS OVER COAL ASH

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Introduction

Nanocarbons have attracted worldwide attention in nanoscience and nanotechnology communities during the past two decades because of their unique mechanical and electrical properties, which make them great potential in catalysis, electrochemical devices, field emission devices and composites[1-2]. However, the high cost and low yield for production of these materials remains the bottleneck for their extensive applications[3].

Physical vapor deposition (PVD) and Chemical vapor deposition (CVD) are the main approaches for the production of CNTs. Generally, the energy-consuming PVD method has been used to produce CNTs with high quality for physical property investigation in lab or specific application, while CVD facilitates the production of CNTs in large-scale. CVD is normally conducted over impregnated silica or alumina substrate with active metal as catalysts. Based on the cost-benefit analysis, catalyst-related cost has been regarded as one of the most expensive portions for the CVD process, including both the active metal and the support[4]. Therefore, a strategy for producing CNTs with cheap yet effective catalyst is in high demand. Small particles of metal and metal oxide, which represent an ideal form of catalyst for the synthesis of CNTs, are almost present in all nature minerals. Up to now, volcanic lava rock, soil, garnet and bentonite have been used as catalyst to grow CNTs efficiently [3].

Coal ash, a solid waste from coal combustion, is produced in an ever increasing amount in China as well as in the world[5]. An environmentally friendly way to disposal coal ash is worldwide concern. Recently, synthesis of CNTs on coal ash derived catalyst via impregnation reported by O.M.Dunens and co-authors[6] may open up a new way to use coal ash. But the impregnate process involved is not environmentally benign and offset the cheap-production effort. Herein, we report an efficient way for growing CNTs directly on coal ash without adding any external active phase, it is found that the yield and structure of the CNTs strongly depend

on the kind of coal ashes. The obtained CNTs/ash composites implicate potential application as building materials.

Experimental

The coal ashes, provided by Institute of Coal Chemistry Chinese Academy of Science, were obtained after complete combustion of coal in air at 815 °C. Synthesis of nanocarbons by CVD process was conducted in a horizontal quartz tube reactor (i.d. 21 mm). Coal ash was put inside a quartz boat which was placed in the middle of the furnace. The temperature was raised to a preset temperature at 10 °C/min in a N₂ flow of 100ml/min, then coal ash was subjected to reduction by H₂ (H₂:100ml/min, N₂:100ml/min) for 1h prior to the CVD process. During the CVD process, a mixture of 60ml/min C₂H₄, 40ml/min H₂ and 100ml/min N₂ was introduced into the reactor for 20 min. Generally, the temperature for the growth of nanocarbon was set between 800 and 900 °C.

An Atomcan-16 Inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine compositions of coal ashes. The morphology of as-synthesis CNTs and related nanocarbon was characterized by Hitachi S4800 scanning electron microscope (SEM) and Philips Tecnai G2 20 transmission electron microscopy(TEM)

Results and Discussion

Table 1. shows the compositions of three different kinds of coal ashes, here we donated the three kinds of coal ashes as CA-1, CA-2 and CA-3, respectively. The most abundant composition contained in ash is SiO₂, which exceeds 50wt% in all three ashes. Besides, Al₂O₃ also shows relatively large loading but varies in different ashes from 16 to 33wt%. The content of Fe, which may act as the only active component in ash for the synthesis of nanocarbon, is relatively high in all these ashes used, between 5.49wt% and 7.91wt% (in the form of Fe₂O₃). The remaining constitutions, such as MgO, TiO₂ and CaO, have been reported to be inert for catalytically produced CNTs and some of them usually used as support for the production of CNTs. But the effect of Na₂O and K₂O on the growth of CNTs has not been explored intensively yet to the best of our knowledge. All of the coal ashes showed brick red, after reduction in H₂ atmosphere, the color changed into grey. After the CVD process, the color would convert to light black, dark black or grey depending on the catalytic activity of

Table 1. Coal Ash Composition and Yield at 900°C

Sample	Ash Composition(wt%)										Yield(wt%)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	
CA-1	50.22	16.41	7.91	11.23	5.08	1.18	5.23	0.93	0.8	0.54	2.5
CA-2	56.02	33.34	5.49	1.20	0.36	1.35	0.58	1.13	0.16	0.07	18
CA-3	55.55	24.39	6.98	7.98	0.83	0.77	1.25	1.23	0.13	0.06	--

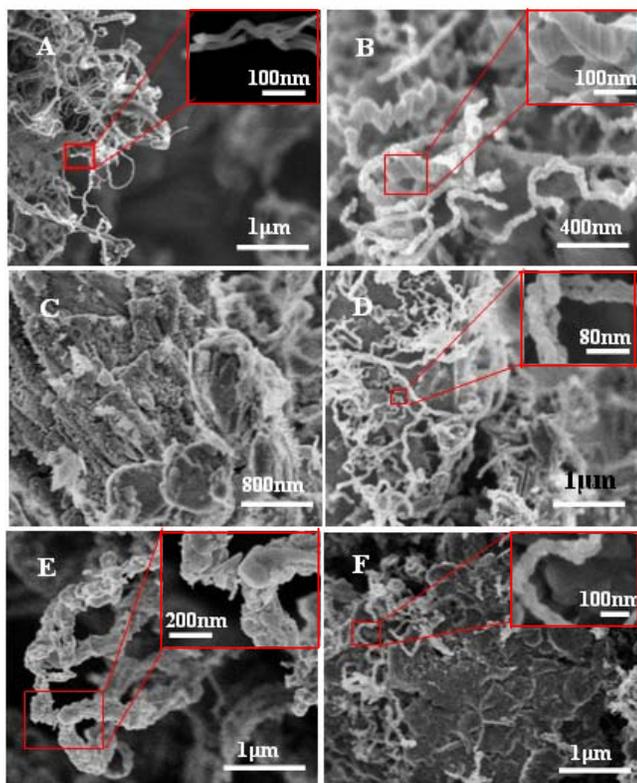


Fig1. FESEM images of (a) CNTs synthesized on CA-1; (b) nanocarbon synthesized on CA-2; (c) CA-3 with almost no carbon covered after a CVD process. Samples of (a), (b), (c) were obtained at CVD process of 900°C. FESEM image of (d) nanocarbon synthesis on CA-1 at 850 °C; (e) nanocarbon synthesis on CA-2 at 800 °C; (f) nanocarbon synthesis on CA-2 at 850 °C

different ashes. The CNT yields after the CVD procedure at 900°C were listed in Table 1.

Interestingly, various nanocarbons were obtained over the coal ashes, and the yield of nanocarbon on the coal ash was found to be non-proportional to the amount of Fe in the starting coal ashes as expected. For example, CA-2 has the lowest Fe content (5.49wt%), however, exhibits the highest activity among the three coal ashes. We assume part of the iron in the ashes may exist in the form of inert compounds, as a result, part of iron could not effectively decompose the carbon source.

Besides the difference in activity, the structure synthesized over different coal ashes varies remarkably. Fig.1(a)~(c) shows the nanostructure synthesized on different coal ashes at 900 °C. From Fig.1(a), we found that the nanostructure grown on CA-1 were mainly CNTs, but with a spiral structure from the inset of Fig.1(a). The nanostructure synthesized on CA-2 showed a total different one-dimensional structure from CNTs. These structures were further characterized by TEM as shown in Fig. 2. It can be observed that the one-dimensional structure constructed by piling small graphene plates along one direction revealed by the interlayers

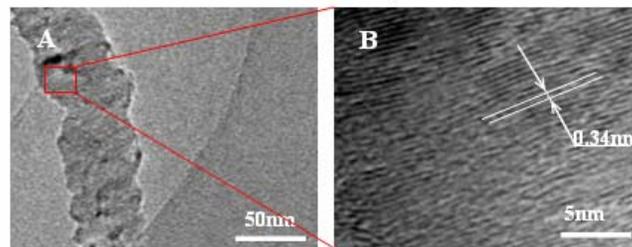


Fig2. Typical TEM of Nanostructure synthesized on CA-2 at 900°C

spacing of 0.34nm. From Fig.1(c), almost no deposited carbon can be observed although with the highest Fe content in CA-3.

The structures of the nanocarbons also changed remarkably with the temperatures employed in the CVD process, as shown in Fig.1(d)~(e). Fig. 1(d) shows an intertwined structure synthesized on CA-1 at 850°C, while rope-structures were obtained on CA-2 at 800 °C (Fig. 1 (e)), the ropes have a relative large diameter as much as over 100nm. As we raised the reaction temperature to 850 °C on CA-2, an intertwined structure could be formed on the ash surface shown in Fig.1(f).

Conclusions

We have demonstrated CNTs and nanocarbons with novel structures could directly grow over coal ashes. The final yield of nanocarbon was not strictly proportional to the amount of active phase iron in the starting coal ashes. The structure can be easily controlled by adjusting the reaction temperature or/and by using different coal ashes. This method was proved to be cheap and versatile to synthesize CNTs and other novel nanocarbons.

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