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Formation of single and multi-walled carbon nanotubes and graphene from Indian bituminous coal

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HIGHLIGHTS

- We have synthesized single and multi-walled CNTs and graphene from Indian coal.
- Graphene sheets have been synthesized first time by arc discharge using coal electrode.
- The occurrence of several groups in coal has been confirmed by the FTIR spectra.
- A mechanism of CNTs formation from coal described here.

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ABSTRACT

Single-walled carbon nanotubes (SWCNTs) have been synthesized by electric arc discharge method using annealed coal electrode in the presence of Fe as well as Ni–Y as catalysts. Multi-walled carbon nanotubes (MWCNTs) have been synthesized without using any catalysts. The efforts have also been made to synthesized graphene like nanosheets from bituminous coal. The as-synthesized samples have been characterized through scanning and transmission electron microscopy, Raman and Fourier transform infrared spectroscopy. The formation of SWCNTs which holds nearly perfect one dimensional structure is confirmed by the presence of radial breathing mode. A feasible mechanism of CNTs formation from coal described here with the help of Fourier transform infrared spectroscopy.

1. Introduction

Due to their unique properties from the time of discovery [1] in 1991 till date, carbon nanotubes (CNTs) have found myriad many applications. The most important ones are as filler materials for making composites which have unexpected mechanical strength, potential materials to replace old age silicon in electronic devices (e.g. TUBEFET instead of MOSFET), drug carrier for targeted drug delivery, field emitters, as CNTs sensors, hydrogen storage materials and many others [2–4]. There are several methods for synthesizing CNTs viz., the arc discharge between graphite electrodes, laser ablation and chemical vapor deposition etc. [5] Compared with other methods, the arc discharge method is easier to operate and has been used because of its potential merits to produce a high-quality CNTs. However, in the arc discharge process, high purity graphite as carbon source is much expensive, which is used as electrodes. As the applications of CNTs increase, there will naturally be a demand to produce CNTs at the industrial level and also at manageable cost. The cost of nanotubes arises from several aspects, the cost of the source materials, production processes, level of yield, and process of purification. The cost of raw materials will become more significant when nanotubes are required in industrial scales in the future [6,7]. Coal, the cheapest and most abundantly available carbon source can be used to achieve this expectation. Comparatively sparse studies have been made in this regard for preparing CNTs from coal, a nature gifted abundant and inexpensive material. Another reason for using coal is the fact that it contains several foreign species/impurities in addition to carbon. The native species/impurities like H, N, S, O etc. may help in the formation of CNTs. For example H is proven to initiate graphitization which leads to the CNT formation. The use of coal as the source material to make carbon nano-materials started in early 90 s, following the report of successful synthesis of fullerenes from coke by Pang et al. [8]. After that, several groups were reported the

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synthesis of nanotubes from coal or coke, mostly using arc discharge method [9–16]. Qiu et al. synthesized high-purity SWCNTs and double-walled CNTs (DWCNTs) from an anthracite coal by arc discharge method with iron (Fe) catalyst [17,18]. They have also synthesized SWCNTs from coal gas by catalytic chemical vapor deposition method with ferrocene as Fe catalyst [19]. In another study, graphite rod filled with anthracite coal and CuO mixture has been used to produce branched CNTs and Cu-filled CNTs [20,21]. The DWCNTs and SWCNTs have been synthesized from fullerene waste soot (FWS) by the arc discharge method [22,23]. Recently, Moothi et al. have summarized the various methods used in the synthesis of CNTs from different types of coal (anthracite, bituminous, etc.) and on the role played by coal as carbon source in the production of CNTs [24]. The work done for the synthesis of CNTs from coal using mainly arc discharge technique is summarized in Table 1.

Graphene is the important and most recent member of carbon nanostructure family recently investigated experimentally has been known from the long time theoretically. Zhou et al. synthesized chemically derived graphene with anthracite coal as the starting material by means of catalytic graphitization, chemical oxidation, and dielectric barrier discharge (DBD) plasma-assisted deoxygenation [25]. Here, we report the formation of CNTs with emphasis on the formation of SWCNTs from Indian coal using arc discharge method. It may be pointed out that most of the investigations on the synthesis of CNTs from coal carried out so far have used anthracite coal. In contrast to this, in the present case, bituminous coal having lower carbon content (<65%) which is the type of coal generally available in India, has been used in the present study for the synthesis of CNT. The bituminous coal rod has been subjected to coking process, before it is used for CNT synthesis. Thus, we have used annealed coal rod as anode electrode for the synthesis of CNTs as well as graphene. A feasible scheme for transformation of coke to CNT through arc discharge has been put forward. In the present investigation, efforts have also been carried out to synthesized graphene in a cost effective way using bituminous coal. It may be pointed out that the present study on the synthesis of few layer graphene using coal as anode by arc discharge method is first of its type.

2. Methods

2.1. Preparation of coal based electrode

In the present investigation, bituminous coal rod obtained from Jharia, Dhanbad (India) has been used for the synthesis of single and multi-walled CNTs and graphene. A rectangular rod was cut out from a coal piece of dimension $(30 \times 8 \times 8)$ mm and was placed inside the quartz tube (outer diameter ~2.5 cm) and flushed with argon (Ar) gas in order to remove air from the quartz tube. The rod was then heated slowly from room temperature to 900 °C under an Ar atmosphere at a heating rate of 40 °C/min. and was kept at 900 °C for four hours. The flow rate of argon was ~80 sccm. After carbonization, the furnace was put off and allowed to cool down to room temperature under Ar gas flow. After cooling, the annealed coal rod becomes lighter due to extraction of coal gases such as: hydrogen, carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), various hydrocarbons and other volatile matters [26]. Also, the electrical resistance of the coal rod on annealing changes from $\sim 10^6\ \Omega$ to $\sim 14\ \Omega$. These characteristics of the annealed coal rod made it suitable for its use as starting material for CNTs and graphene formation. The proximate and ultimate analysis of the coal samples are shown in Table 2. It is seen from Table 1 that the different process

Table 1
Summary and comparison of work done on CNTs production from coal using arc discharge method.

Coal type	Catalyst	Anode electrode	Atmosphere	Products	Refs.
Bituminous (Eastern Kentucky)	Ni–Y	Rod of coal powder + coal tar + Ni–Y (4.25:1)	He	SWCNTs (dia.: ~1.2–1.7 nm) deposited on the walls of the chamber	[9]
Anthracite Sinkiang Uighur Autonomous, China	Fe	Hollow carbon rod of coal and coal tar (20%) filled with Fe + carbon powder (1:1)	He	Bamboo shaped CNTs (dia.: ~40–60 nm) deposited on around the cathode	[10]
Three kinds of Chinese coals: natural coke (Huaibei coal mine, anhui province) Long-flame coal (Lingwu coal mine) anthracite (Taixi coal mine, Ningxia Hui autonomous region)	No catalysts	Rod of coal powder + coal tar (67:33)	He	MWCNTs (dia.: ~2–15 nm)	[15]
Samla (Raniganj mines, India) organorefining with N-methyl-2-pyrrolidone + ethylenediamine (15:1)	No catalyst	High purity graphite rod filled with super clean coal	He	MWCNTs and SWCNTs	[16]
Anthracite (China)	Fe	Hollow carbon rod of coal and coal tar (80:20) filled with Fe + carbon powder (2:1)	He	Film like SWCNTs (dia.: ~1.24 and 2.19 nm) deposited on Fe wire cage	[17]
Anthracite (Shanxi province, China)	Fe	Fe + coal powder + coal tar (3:1:1)	He	Bundle of DWCNTs (dia.:~1–5 nm) deposited on Fe wire cage	[18]
Anthracite (Yunnan province, China)	CuO	High purity graphite rod filled with CuO + coal powder (3:7)	He	Branched CNTs deposited on around the edge of cathode	[20]
Anthracite (Yunnan province, China)	CuO	High purity graphite rod filled with CuO + coal powder (1:9)	Ar	Long Cu wires inside CNTs deposited on cathode	[21]

Table 2
Analysis of coal sample from XIth seam of Jamadoba colliery, Jharia, Dhanbad, India.

Samples	Proximate analysis (wt.%)				Ultimate analysis (daf, wt.%)				
	M_{ad}	A_d	V_{daf}	FC_{ad}	C	H	N	S	CO_2
Coal	1.4	22.9	23.0	52.7	65.5	3.9	1.8	0.6	0.65
Float	1.5	7.8	29.2	61.5	79.6	4.8	2.4	0.8	0.35
Coke	1.4	13.5	1.9	83.2	82.2	0.6	1.7	0.8	0.44

M–Moisture, A–Ash, V–Volatile matter, FC–Fixed Carbon.