Physica Status Solidi (b) 244(11):3916-3919, 2007

Nanocarbons: efficient synthesis using natural lava as supported catalyst

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PACS 68.37.Hk, 68.37.Lp, 68.43.–h, 81.05.Uw, 81.07.De, 81.15.Gh

Low-cost mass production of CNTs becomes prerequisite for their applications in chemistry and catalysis in which the availability of large amounts of material with well-defined surface, chemical and mechanical properties is required. Natural occurring iron oxides in volcanic lavas are used as catalysts for CNT synthesis in the well-established CVD (chemical vapor deposition) process while the lava itself acts as support. As in a common CVD process, the quality of the CNTs can be controlled by the synthesis parameters such as flow rate, hydrocarbon to hydrogen ratio and growth temperature.

1 Introduction

Carbon nanotubes and carbon nanofibers – tiny structures made of pure carbon – have been used in a nanotechnology. However, because their production on an industrial scale remains expensive, their commercial use areas as in such catalysis has remained inconceivable. In addition to the carbon source, the main cost factors are the preparation of supports (silicate, aluminates) and the impregnation of high dispersed metal particles on them.
Mount Etna is the highest and most active volcano in Europe. The eruptions in 2002–2003 were the most explosive eruptions in recent years. November 2002 edition of the local newspaper “La Sicilia” reported that volcanologists of the Instituto Nazionale di Geofisica (Catania section) estimated the volume of emitted lava to be about 10–11 million cubic meters, while the volume of tephra exceeded 20 million cubic meters. The Mount Etna lavas are slightly evolved forms of an alkaline series (trachybasalts and alkali basalts) exhibiting a porphyritic texture with abundant phenocrysts of plagiocalase as well as fewer clinopyroxene and olivines [1]. The main components are Si (SiO_2 48 wt%), Al (Al_2O_3 19.2 wt%), Mn (MnO 0.2 wt%), Mg, Ca, Na and Fe (Fe_2O_3 11 wt%). The Fe_2O_3 is distributed among silicate phases and Fe–Ti oxides [1]. The presence of iron oxide particles in Etna lava makes it to an ideal material to grow and immobilize nanocarbons. Metal particles such as Fe are necessary for the catalytic growth of CNTs/CNFs [2]. These particles catalyze the decomposition of the carbon source and control the growth kinetics of the tubes/fibers [3]. In an earlier brief report, it has been shown that nanocarbons, mainly CNTs/CNFs, can be successfully grown on Mount Etna lava in a CVD process using ethylene as carbon source [4]. However, due to the broad size-distribution (from a few nanometer to several micrometers) and the heterogeneity of the chemical environment of Fe it is a challenge to obtain CNTs with uniform morphology and microstructure with this material. In the present work, the influence of reaction temperature and carbon concentration on the type of nanocarbon deposits grown on lava’s surface were investigated. The relative carbon concentration in the gas phase is taken as a key parameter based on the previous work by Alstrup as the driving force of the CNT growth [5]. Baker and co workers also stated the importance to reach an over saturation of carbon in the catalyst particle prior to nucleation of carbon filament [6]. Hence, varying the temperature and the H_2/C_2H_4 ratio will vary the rate of atomic carbon supplied into the catalyst. It is expected that only catalyst particles with highest activity to produce atomic carbon will reach the carbon supersaturation to nucleate and further grow CNTs under specific conditions.

Table1 Experimental conditions for carbon deposition on Lava samples

Sample	Reduction temperature C	Growth temperature C	C_2H_4 ml/min	H_2 ml/min	He ml/min
Lava2	700	700	20	50	35
Lava3	650	650	20	50	35
Lava4	700	700	20	20	65

2 Experimental

The Mount Etna lava used in the present work was collected in the north flank of Etna on the 23rd November 2003. For the CVD growth, the crushed powder (1 g) was put into a horizontal quartz reactor and reduced with hydrogen at a flow rate of 50 ml/min at 600–700 °C for 2 h. A mixture of helium, ethylene and hydrogen with a total flow rate of 105 ml/min, was introduced into the reactor for 1 h. The H_2/C_2H_4 ratio was set to 1 and 2.5 with helium flow rate of 65 ml/min and 35 ml/min respectively to compensate the total flow. The product was cooled down to room temperature in helium. The experimental details are shown in Table 1.

3 Results and discussion

The synthesis parameters change and control the morphology of CNTs/CNFs on natural lava stone. As depicted in Fig. 1, the SEM images for the first two samples (Lava2 and Lava3) contain carbon materials with irregular morphology (Fig. 1b and c respectively). The SEM image of the original lava is shown in Fig. 1a. The irregular carbon produced in Lava2 and Lava3 are graphitic as shown in Fig. 1b and c. There is an indication that the catalyst is still too active under this condition, as such high amount of irregular carbon materials resulted from these two samples. Even as the growth temperature is reduced to 650 °C which means a lower rate of C_2H_4 decomposition, the irregular shaped carbon material is still observed.

The sample Lava4 contains more CNTs. The SEM image in Fig. 1d show good uniformity of the CNTs, indicating a selective activation of Fe particles of uniform size. The sample shows carbon nanotubes with well-defined morphology. With smaller hydrogen to ethylene ratio more selective carbon material can be produced in the Lava4 sample. The presence of hydrogen during CNT synthesis is considered to keep the metals in an active state to avoid total encapsulation which leads to deactivation. Having a lower hydrogen concentration in the system, the thermodynamic equilibrium of carbon precipitation and carbon dissolution in the metal particles will be changed. The condition used in Lava4 decreases the activity of various active sites in the lava sample. The condition suppresses the formation of irregular carbon material, and a more defined growth of carbon nanotubes can be seen. We believe that decreasing the hydrogen content will decrease the number of metals active to precipitate carbon. In the case of sample Lava3 we also observed a small amount of well defined CNTs. However, due to the presence of a large amount of the irregular carbon material the well defined growth is difficult to observe with SEM. The rate of carbon decomposition decreases with decreasing hydrogen content in the Fe/SiO_2 system as reported by McCaldin [7].

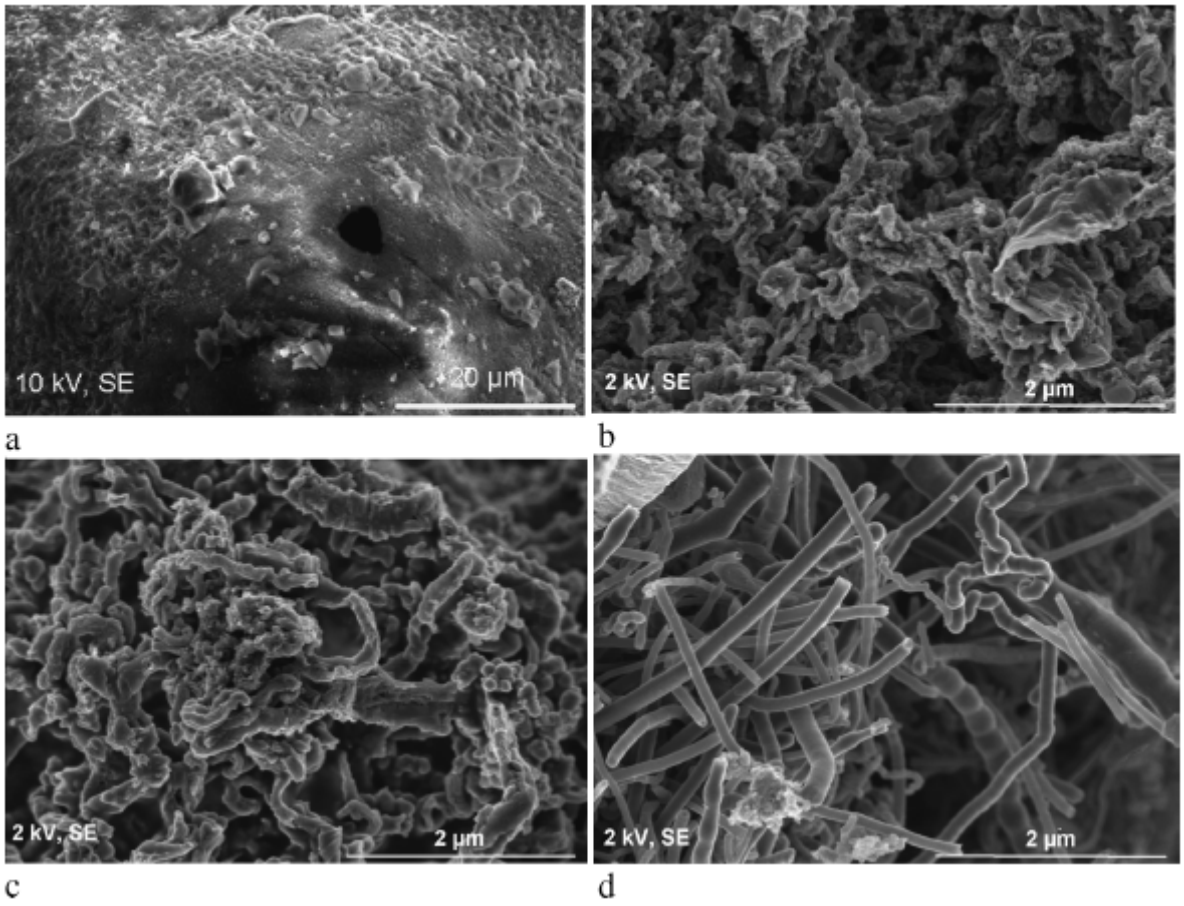

Fig. 1 SEM images of a) fresh lava; b) Lava2, c) Lava3 and d) Lava4 after the exposure of reduced lava to a C_2H_4 and H_2 mixture for 1 hour under different conditions.

The TEM images of the carbon nanofibers reveal that the carbon materials produced in sample Lava2 and Lava3 are mainly thick fibers with irregular structure but highly graphitized. Whereas in the Lava4 sample the well-defined tubular carbons are observed. The distinction in morphology and microstructure of carbon in Fig. 2 is a result of varying carbon supply between the different conditions for the same lava sample and therefore varying the diffusion kinetic of carbon through catalyst. As demonstrated in Table 1 samples with lowest weight gain show better defined structure of CNTs. By lowering the temperature in Lava3 growth process the weight gain is less and thus better defined nanocarbon is observed compared with sample Lava2 (Fig. 2a and b). By decreasing the hydrogen content in Lava4 most of carbon material produced are CNTs. Lowering the temperature will decrease the rate of catalytic cracking of ethylene and decrease the degree of carbon super saturation in the catalyst. Decreasing the hydrogen content lowers the rate of catalyst regeneration to further adsorb and crack ethylene. Lowering the temperature and hydrogen content will decrease the amount of carbon supplied into the catalyst to some extent. Obviously, these parameters change the quality and quantity of carbon produced from the lava samples.

With respect to the intended applications it is desired to expose as much homogeneous carbon nanostructured material as possible to the application resulting a low cost and quite facile process of carbon nanotubes.

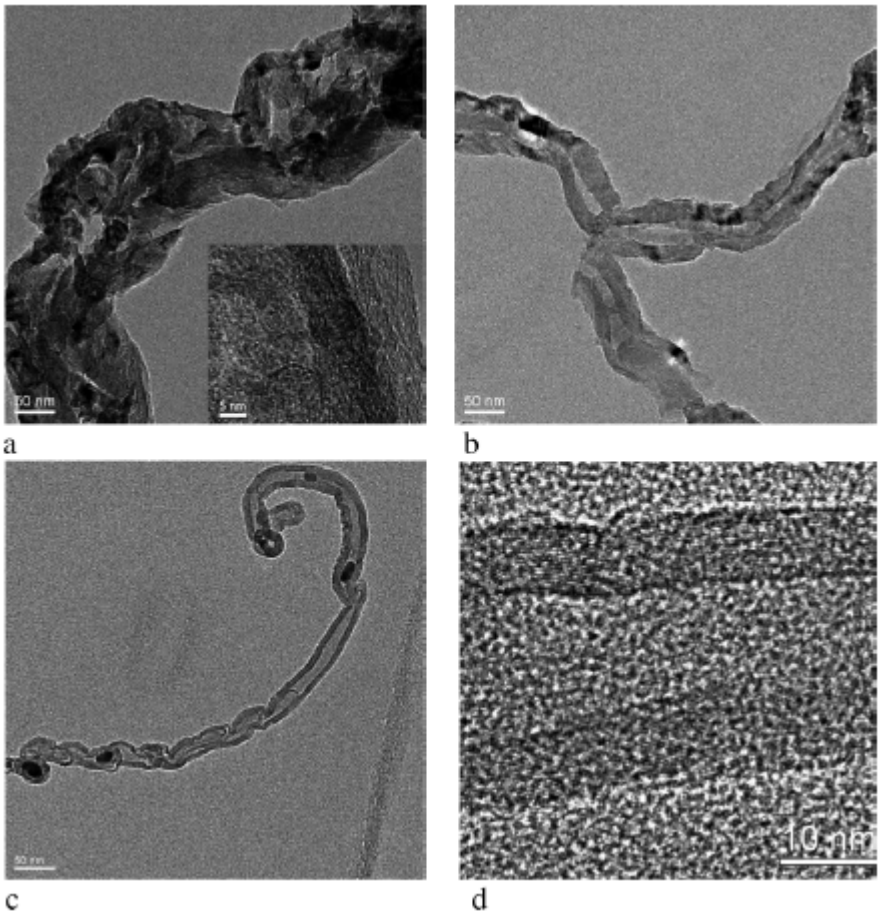

Fig. 2 TEM images of carbon material produced on Lava after exposure to C_2H_4 and H2 mixture for 1 hour: a) Lava2, b) Lava3, c) and d) Lava4.

4 Summary

Carbon nanomaterial was synthesized from ethylene on a highly heterogeneous lava sample. The lava contains 11% of atomic Fe but obviously with different local chemical environment throughout the bulk material. The rate of carbon supplied into the catalyst is taken as a focus to vary the quality of carbon material produced. Temperature and hydrogen concentration have been chosen as preliminary parameters to improve the quality of nanocarbon deposite. High gas phase carbon concentration can lead to the growth of carbon with ill-defined morphology on lava stone. Carbon nanotubes are synthesized on lava when the carbon concentration is reduced. The obtained results demonstrate that lowering the reaction temperature does not change the morphology of grown carbon deposits significantly, whereas decreasing the hydrogen concentration results in significant changes of structure and weight of the obtained carbon deposits from carbon fibers to multi-wall nanotubes.

Acknowledgment The work is partially supported by the Deutsche Forschungsgemeinschaft performed in frame of ELCASS.

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