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Microwave irradiation on carbon black: Studies on the transformation of particles into nano-balls, nano-sticks and nano-onion like structures

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ABSTRACT

The solid-state transformation behavior of carbon black (CB) nanoparticles after irradiated with microwave energy was studied with and without influence of a metal catalyst. The CB sample was exposed to microwave radiation at power of 900 W from the oven and collected after 15 min and after 30 min and 45 min of irradiation. The samples were characterized using X-ray diffraction measurements, Raman spectroscopy, scanning electron microscopy, high-resolution transmission electron microscopy (HRTEM) and thermogravimetric analysis. Characterization of the samples prepared without catalyst shows that microwave irradiation can transform CB nanoparticles into nano–balls and nano–stick like structures. While nanoballs of almost 300–500 nm diameter are visible in all the samples irrespective of microwave irradiation time, amorphous nano-stick like structure are present only in the sample collected after 30 min of microwave irradiation. CB irradiated together with a metal catalyst resulted in metal-encapsulated onion like structures with perfectly arranged graphene layers.

1. Introduction

Carbon black (CB) is nanoscale particles with quasi-spherical nature, produced from incomplete combustion of hydrocarbons [1]. The size of CB particles vary from 10 to 1000 nm depending on the production processes [1,2]. Due to nanoscale effects, CB particles usually appear in the form of aggregates. CB is semi-amorphous and consists of many individual graphite layers that are only roughly parallel to one another and it shows a notably larger spacing between the layers compared to that of graphite [3,4]. Although CB does not have the three-dimensional repetition of graphite, there are finite two-dimensional repetitions within each layer and hence CB is termed as 'turbostratic' as its structure is between amorphous and graphitic [5]. Transformation of amorphous carbon into graphitized carbons was studied by many researchers and the carbons were even classified in terms of graphitization, graphitizable, non-graphitizable and intermediate, i.e. partially graphitized carbons [6–10]. Studies of the structural transformation process of CB particles is carried out in the quest of obtaining further insight into the carbon structures [11]. Marsh et al. [12] carried out X-ray diffraction studies on CB to investigate the structure and reported that many bent and faceted layer planes and few closed shell structures would be formed when CB is heat treated to high temperatures. However, CB cannot be fully graphitized by high temperature heat treatment alone as it does not possess any crystal nucleus for pentagons and hexagons to grow around [2]. Formation of fullerene-like structures within CB particles during heat treatments is possible, nevertheless they grow in a random and disordered fashion as reported elsewhere [13–16].

In this project, transformation behavior of CB when exposed to microwave radiation is studied with and without the presence of catalyst to explore the transformation process of CB nanoparticles into other carbon nanostructures under varying experimental procedures. Heating the samples with the use of microwaves is efficient and energy saving process due to rapid, and volumetric heating [17,18]. In addition, technologically important novel materials have been developed so far which cannot be synthesized through conventional methods [18–21]. Considering these advantages, microwave-assisted solid phase transformations of CB with and without catalyst processes are studied in the present work.

2. Experiments

The CB used in the following experiments was ENSACO 350 G provided by Timcal Graphite & Carbon and referred hereafter

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Timcal 350 G. For each experiment, a small quantity of CB (few mg) was placed in a glass beaker of 200 ml, toluene (few ml) was added and the mixture was heated on a hot plate. Initially, temperature was raised from room temperature to 120 °C and kept at the same temperature for 30 min. Next, the temperature was increased to 200 °C at a rate of approximately 5 °C for each 15 min, and maintained at 200 °C for 30 min. Then heating was continued to 300 °C at an average rate of 5 °C/min and then the rate was increased to 20 °C/min until the temperature of 500 °C was reached. 500 °C was maintained for 6 h and finally the sample was allowed to cool. The sample named CBT500. The pretreated carbon sample was then placed in a ceramic crucible and exposed to microwave radiation at power of 900 W in oven. The microwave oven was set to run continuously but was stopped every 15 min for sample collection. The collected samples were named CT500-1, CT500-2, and CT500-3, for 15 min, 30 min and 45 min microwave irradiation respectively. A similar experiment was performed with the addition of ferrocene (few grams) to CB and toluene. For the ferrocene experiment a sample was collected only after 30 min of continuous microwave irradiation and named CFT500.

2.1. Characterization

X-ray diffraction (XRD) measurements were carried out using a XRD (Bruker D8 Advance diffractometer). The XRD patterns were recorded in the 2θ range of 10–80°, using a Cu Kα source (where λ was equal to 0.154 nm). Raman spectra of the collected samples were recorded using a Horiba-Jobin Labram 800 h Raman spectrometer. Raman analysis was carried out on powdered samples placed on glass slides which were directly mounted under an Olympus BX41 petrographic microscope. Measurements were performed with a 100 mW, 514 nm Argon ion Laser, focused to beam diameter of 1–2 μm through a 100× objective. The spectrometer was re-calibrated before each analytical session by 'zero-point' centering, and analysis of a Si-standard with a characteristic Si Raman band at 520.4 cm^{-1}. Spectra were obtained for 2 × 10 s in multi-window mode over a range of 800–3100 cm^{-1}, using an edge filter for 514 nm excitation wavelength with a 100 cm^{-1} cut-off, a 100 μm entrance slit, a 1800 lines/mm grating, and a Peltier-refrigerated (−70 °C) 1024 × 256 pixel CCD array detector. The effective laser power on the sample was nearly 0.5 mW. Thermogravimetric analysis (TGA) was performed to characterize the thermal properties of original and modified CB using thermogravimetric analyzer (TG500, TA Instruments). The samples were heated from ambient temperature to 800 °C at a heating rate of 10 °C/min with synthetic air as purging rate of 40 ml/min flow rate. The transformed carbon nanostructures were also characterized using field-emission scanning electron microscopy (FESEM) (Supra V55, Zeiss), and high-resolution transmission electron microscopy (HRTEM) in JEOL 2100. The samples were placed directly onto carbon tape in order to obtain FESEM images. For the HRTEM analysis, samples were mixed with ethanol, ultrasonicated and dropped on a carbon coated copper grid and bright field images were recorded using an acceleration voltage of 160 kV.

3. Results and discussions

3.1. Microwave irradiation effect without metal catalyst

3.1.1. XRD analysis

The measured XRD spectrum of Timcal 350G (as received) and different time of exposure of exposure of microwave irradiation CT500-1 (15 min), CT500-2 (30 min) and CT500-3 (45 min) respectively are shown in Fig. 1. The diffractograms of a parental carbon (Timcal 350G) shows two distinctive peaks at 2θ∼24.6° and 43.1° which are typical for the amorphous carbon. These peaks can be assigned to the (0 0 2) and (1 0 0/1 0 1) lines, respectively,

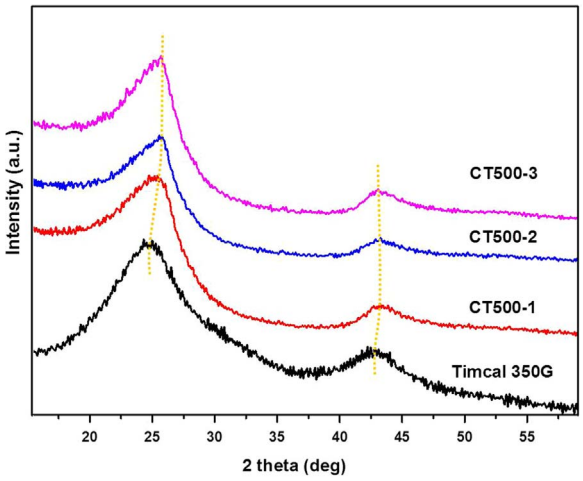

Fig. 1. XRD patterns of the samples, Timcal 350 G, CT500-1 (15 min), CT500-2 (30 min) andCT500-3 (45 min).

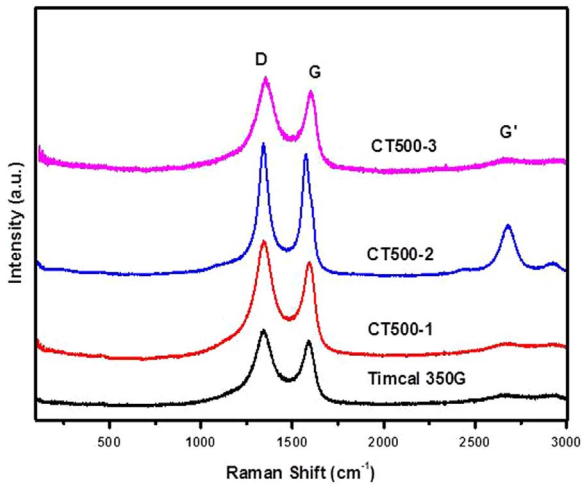

Fig. 2. Raman spectra of the samples, Timcal 350G, CT500-1 (15 min), CT500-2 (30 min) and CT500-3 (45 min).

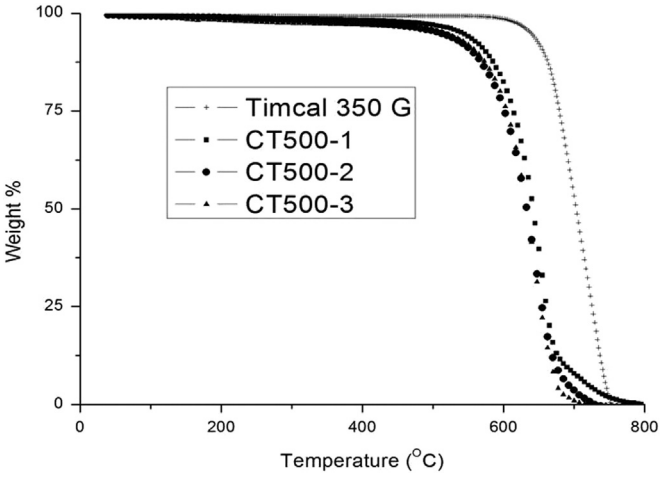

Fig. 3. Thermograms of Timcal 350G, CT500-1, CT500-2, and CT500-3 heated at a rate of 10°/C from 30 to 800 °C.