

Synthesis of uniform carbon mesospheres by arc discharge method

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In this paper, carbon mesospheres (CMs) with uniform shape were successfully synthesized by arc discharge method using Fe_3O_4 as catalytic material. Morphology of CMs was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) technique. The obtained results showed that the synthesized CMs have an average diameter of 246 nm and were formed with different structures including solid structure and core-shell structure. Graphitic structure of CMs is characterized and confirmed by using both X-ray diffraction (XRD) and Raman spectroscopy. The prepared CMs with uniform size could be used for many potential applications for various industrial fields such as batteries, capacitors, fuel cells and especially in the commercial lubricants.

(Received April 24, 2017; accepted August 9, 2018)

Keywords: Carbon mesospheres, Graphitic structure, Arc discharge

1. Introduction

Recently, many different carbon nanostructures have been discovered including graphene, nanotubes (CNTs) and fibers, onions, spheres, horns, calabashes, flasks, etc [1-2]. Beside of CNTs and graphene, carbon spheres (CSs) have also been received a great attention to scientists due to their unique properties and high potential application in various fields [3]. CSs have been using for many studies in lithium batteries, drug delivery, tissue regeneration, heterogeneous catalysis and as lubricants, etc. [3-7].

Up to now, CSs could be synthesized via two main routes; the first one includes the chemical vapor deposition (CVD), arc-discharge and laser ablation processes that require a high temperature to decompose the carbon-containing materials. The second route with lower temperature process consists of the pyrolysis and catalytic decomposition of organic compounds. Qui et al. reported that a narrow range of 10–20 μm ball-like carbon material could be prepared from coal using nickel as catalyst by arc plasma method [8]. Large-scale production of CSs had also been achieved via direct pyrolysis of hydrocarbons by a simple CVD method for 60 min and the spheres that formed varied in size between 50 and 100 nm [9]. Mohammed and coworkers also reported on using CVD method to prepare 130 nm CNs with deoil asphalt used as a source of carbon [10]. In other report, Mi and coworkers synthesized the carbon microspheres with a regular and perfect shape, high yield and narrow-range distributions from 1 to 2 μm in diameter by a glucose hydrothermal

method at 500 °C for 12 h [11]. In addition, CSs were also found for the first time in metallurgical coke by Gornostayev et al. [12] and from coal by chemical solid synthesis as reported by Fathabadi and coworkers [13]. Recently, Chen and coworkers reported the preparation of different sized CNs using a new and environmentally friendly route from wheat straw via hydrothermal carbonization at 180°C for 8 h, the obtained results are quite good but the CNs seem to aggregate together [14]. According to the reported results, the proposed approaches have shown quite good for obtaining the uniform CSs, but still could be found at least one of problems needing to be improved such as long-time process, larger size, toxic materials or non-uniform shape distribution. In the context of the studies, new approaches needing to develop in order to overcome all above problems are indispensable.

Thus, this paper, we proposed an approach to synthesize the uniform carbon mesospheres by using arc discharge method and Fe_3O_4 catalytic material. Morphology and microstructure of CMs are also investigated and presented.

2. Experimental

2.1. Materials

A pure graphite rod with a purity of 99.99 % and dimensions of 6 mm (\varnothing) \times 80 mm (length) purchased from Sigma Aldrich, was used for both an anode and a cathode.

Iron (III) chloride (FeCl_3), iron (II) chloride (FeCl_2) supplied by Sigma Aldrich with high purity were used to prepare Fe_3O_4 nanoparticle catalytic material.

2.2. Preparation of carbon mesospheres

Carbon mesospheres were synthesized by using the arc discharge apparatus as described in Fig. 1. The reaction chamber was connected to the vacuum pumps, to H_2 and Ar gas supply. A hole with dimension of 4 mm (Φ) x 5 mm (length) is drilled on the anode, then the hole is filled with catalyst material which consisted of a mixture of a graphite powder and Fe_3O_4 nanoparticles with an average size of 20 nm (Fig. 2). In which, Fe_3O_4 nanoparticles prepared by the chemical co-precipitation method by adding the solution of NaOH into an aqueous solution of FeCl_3 , FeCl_2 salt with a molar ratio of $\text{Fe}^{2+}/\text{Fe}^{3+} = 1/2$ under vigorous mechanical stirring for 60 minutes at the temperature of 50°C . The gap between the graphite electrodes was initially set up of 0.3 mm and manually controlled. Arc plasma was generated for 5 min at currents from 70 to 100 A under voltages from 10 to 13 V. The pressure of the chamber was maintained at approximately 500 Torr in a mixture of continuous flow gases consisting of Ar and H_2 gas. The apparatus was cooled by a cold water line. After arc discharge process, the samples inside wall of quartz tube were collected for the characterizations.

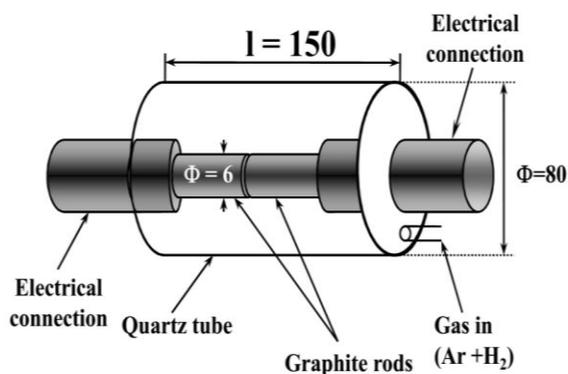


Fig. 1. Schematic diagram of the arc discharge apparatus used for growing the carbon mesospheres

2.3. Characterization

The morphology of CMs was observed by a Hitachi S-4800 field emission scanning electron microscopy (FE-SEM) with a voltage of 10 kV. Chemical elements of the products were analyzed by SEM energy dispersive spectroscopy (SEM-EDS, Hitachi S-4800). Transmission electron microscopy (TEM) measurements were carried out using a JEM 1010 JEOL, Japan operating at a voltage of 80 kV. X-ray pattern of samples were recorded on a Bruker D8 Endeavor X-ray diffractometer using $\text{CuK}\alpha$ radiation. The Raman spectra of CMs were performed at room temperature, using a Microscopie confocal RAMAN

Labram -1B Yvon Jobin spectrometer using a 514 nm laser excitation.

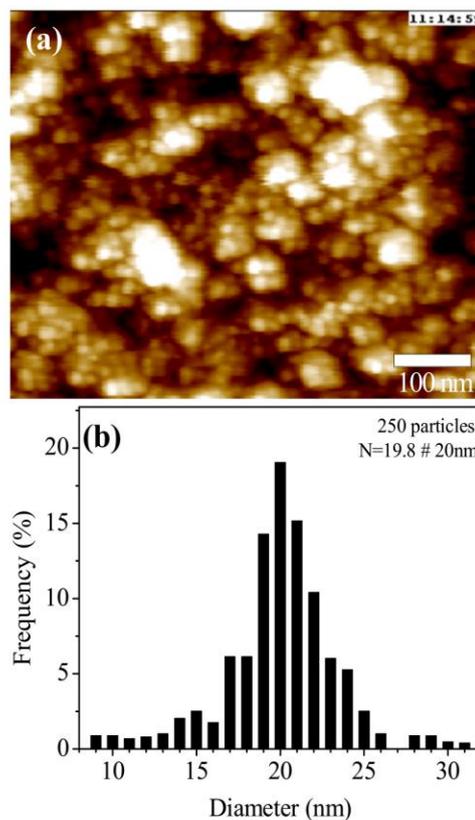


Fig. 2. a) AFM image and b) histogram of diameter distribution of Fe_3O_4 nanoparticles

3. Results and discussion

FESEM images of CMs at various magnifications are shown in Fig. 3a and 3b, confirmed that the CMs have a narrow size distribution with diameter ranging from 150 to 350 nm. The CMs seem to be separates with each other without any agglomeration. High-magnification SEM image shown in Fig. 3b indicates that the smoothly spherical morphology of CMs were obtained, which is believed to highly beneficial for the tribology applications [6]. EDS spectra of CMs was shown in Fig. 3c. As can be seen in the spectra, the carbon content was measured to be 96.43 wt.%. The result indicated that the structure of CMs is mainly carbon element. The Fe content was also measured with the content of 2.48 wt.%. The presence of Fe content in the synthesized product could be a remaining catalytic material after arc discharge process. Besides, small quantity about 1.09 wt.% of Tm element also detected. This was attributed to the impurities of either graphite rods or Fe source.

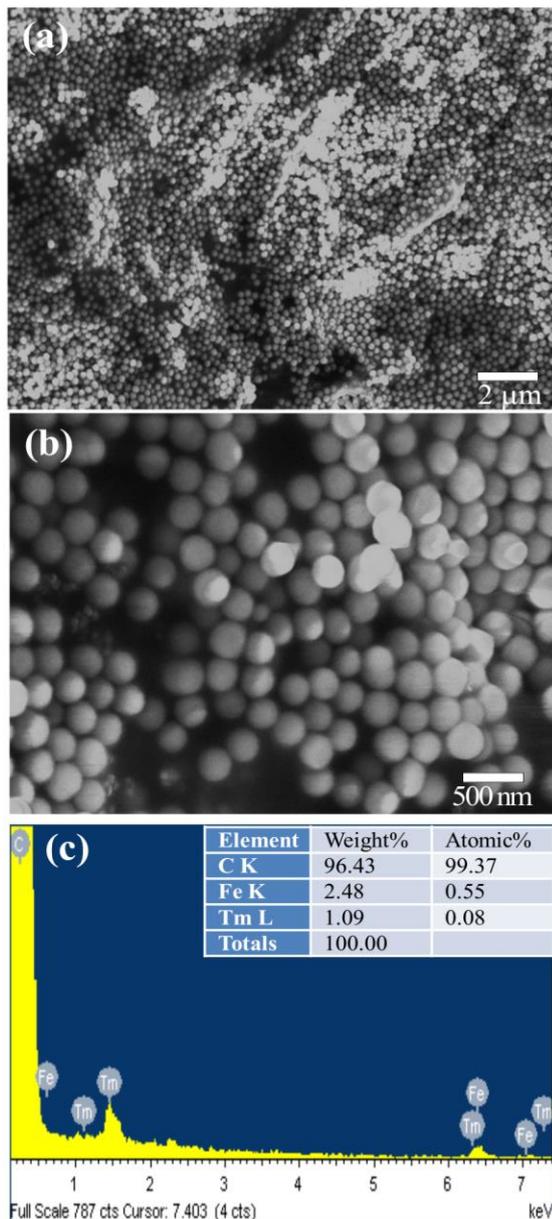


Fig. 3. SEM image (a) at low magnification (b) higher magnification and (c) EDS spectra of carbon mesospheres collected inside wall of quartz tube

Transmission electron microscopy (TEM) was used to further investigating the morphology and microstructure of the CMs. Fig. 4 shows the TEM images the synthesized CMs. As can be seen, CMs have two different types including solid structure and core-shell structure. For solid structure, some CMs have uniform structure (Fig. 4a) and others have black regions decorated (Fig. 4b). These black regions could be either defect points or leftover catalytic materials. For core-shell structure, a black point located center of the spheres was covered by carbon shell. This black point could be Fe nanoparticle. More analysis is needed to confirm the hypothesis. Future characterizations such as high resolution TEM, EDX mapping are planned to shed light on that matter to rule out the local formation. Fig. 5 shows the histogram of diameter distribution of the

CMs. Average diameter of CMs calculated from 350 spheres is about 246 nm.

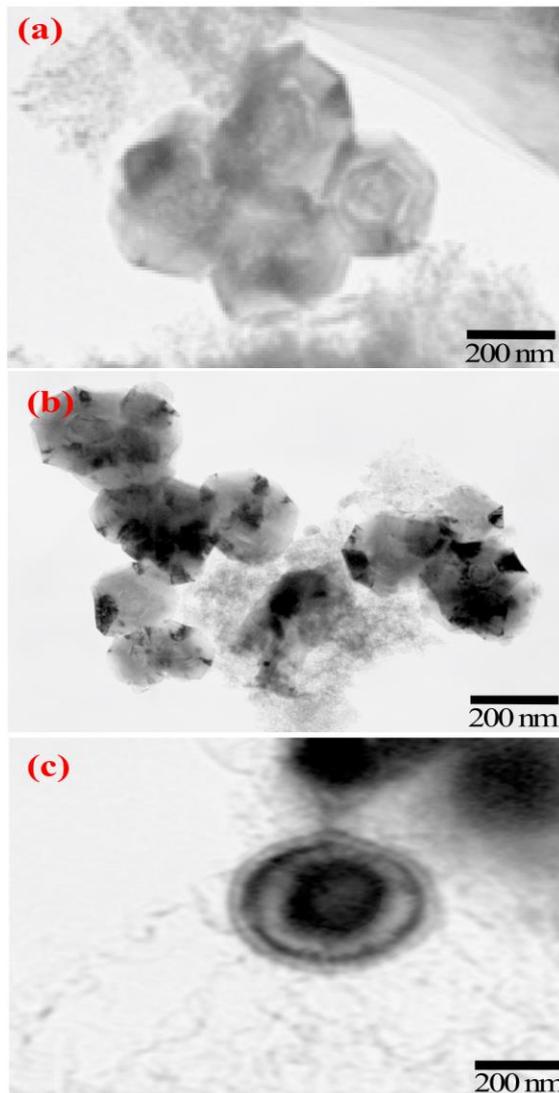


Fig. 4. TEM images of carbon mesospheres with different structure (a-b) solid structure and (c) core-shell structure

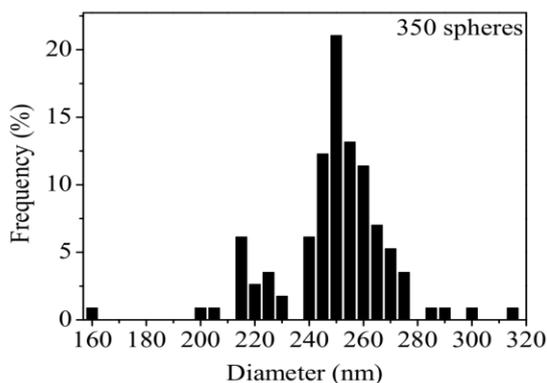


Fig. 5. (a-b) Histogram of diameter distribution of carbon mesospheres

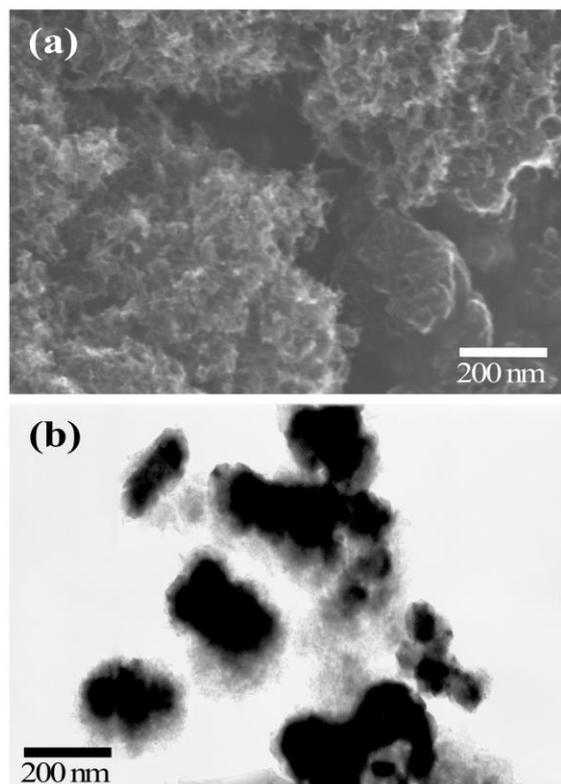


Fig. 6. a) SEM and b) TEM image of sample collected inside wall of quartz tube after arc discharge without using Fe_3O_4 catalytic material

To investigate the effect of Fe_3O_4 catalytic material on the formation of CMs, the same condition of arc discharge process was carried out with raw graphite rods and without Fe_3O_4 catalytic material inserted. SEM and TEM images of the sample collected inside of quartz tube were shown in Fig. 6. As can be seen, the products seem to be like an amorphous carbon without any clear structure. This demonstrated that Fe_3O_4 catalytic material has an important role in the formation of CMs during arc discharge process. The role of catalyst like Ni, Fe, Co in the formation of carbon nanomaterials like CNTs, graphene, carbon spheres and fullerenes, etc... have reported by many researchers [8, 15-17]. Most studies indicate that the catalyst activation concerns to the relationship between the melting temperature and the boiling temperature. In our experiment, the formation of CMs starts from the active individual carbon precursors in which the Fe_3O_4 nanoparticles act as catalyst. According to Kim et. al., to remain role as a catalyst, the used metals must have possibility to evaporate into the atmosphere and aggregate through the emission of its own thermal energy [15]. Because of the relatively higher temperature gradients at the region around the electrodes and cooling water line, the evaporated metal atoms could easily aggregate or turn into a liquid or solid phase. In this study, the Fe_3O_4 nanoparticles were used as catalyst and the arc discharge process was carried out under a mixture of gases (Ar , H_2). The presence of H_2 not only transforms Fe_3O_4 to Fe in order to help the active carbon atoms join together to

form bigger crystallites in the gas phase but also generates amount of water gas through reaction $4\text{H}_2 + \text{Fe}_3\text{O}_4 \Rightarrow 3\text{Fe} + 4\text{H}_2\text{O}$. The existence of water gas during arc discharge process could be a benefit for increasing the temperature gradients in reaction zone and therefore the formation of CMs with graphitic crystallite could be carried on rapidly. The aggregation of carbon atoms will start during arc discharge process until CM was formed due to it tends to become neutral and spherical in order to reduce surface energy [8]. The formed CM then will drop or stick on surface inside of quartz tube as shown in Fig. 3. It is noted that CMs are only found on surface inside of quartz tube. No such CMs are found on other positions like surface of cathode, anode, etc. in which mainly CNTs, or graphene flakes were found as shown in Fig. 7.

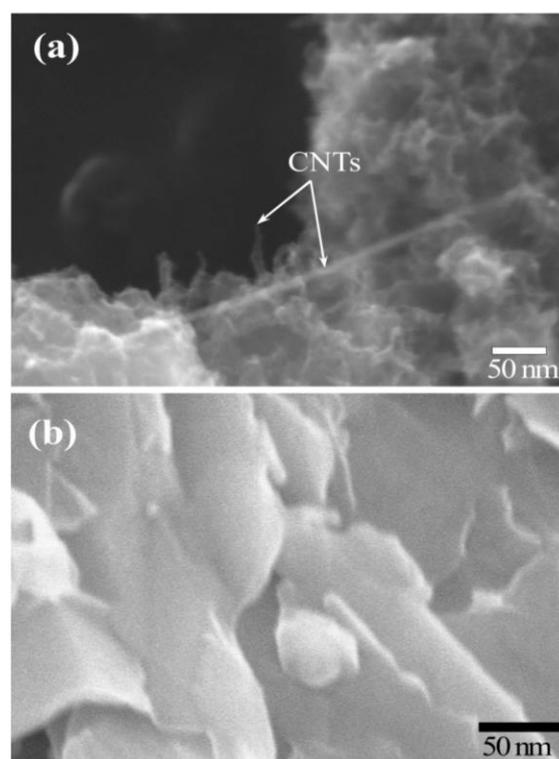


Fig. 7. SEM images of samples collected on cathode surface a) carbon nanotubes, b) graphene flake

The XRD and Raman spectroscopy study were performed to determine the graphitic structure of CMs. As shown in Fig. 8, the XRD pattern of CMs shows some peaks at 26.18, 43.04, 54.38 and 77.48° corresponds to the (002), (100), (004) and (110) planes, respectively. The values of d-spacing of 0.34 nm and 0.21, calculated from the position of the (002) and (100) planes, are similar to that of representative graphite structure [18]. Besides, the broadening of the two peaks could be due to presence of amorphous carbon or the low graphitization degree with other hybrid orbitals of carbon such as sp^1 or sp^3 . It is interesting noted that there is no any typical peaks for Fe was detected in XRD pattern. This could be due to be below the detection limit in our XRD experimental conditions.

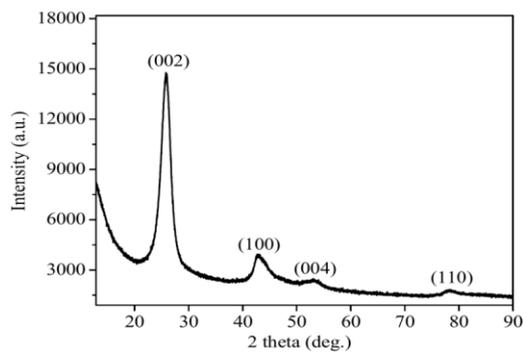


Fig. 8. XRD pattern of carbon mesospheres synthesized by arc discharge

Fig. 9 shows the Raman spectrum of CMs that recorded at ambient temperature. As seen, two main typical graphite bands at 1601.28 cm^{-1} and 1302.05 cm^{-1} correspond to an E_{2g} mode of graphite layer (G band) and presence of disordered graphite (G band), respectively [19]. The intensity ratio of D- and G-bands of CMs was estimated about $I_D/I_G = 1.7$. The intensity of D-band is higher than that of G-band indicated the highly disordered structure of CMs [6]. It could be due to the presence of the amorphous carbon content or defects. This result is consistent with the XRD study mentioned in previous section. The existence of disordered graphitic structure in products prepared by arc discharge method like carbon nanotube, fullerene also reported [20]. This is because of the difficulty in controlling the experimental parameters such as arc current, catalyst composition and its particle size, electrode shape and composition as well as atmospheric effects to obtaining the highly graphitic carbon nanomaterials.

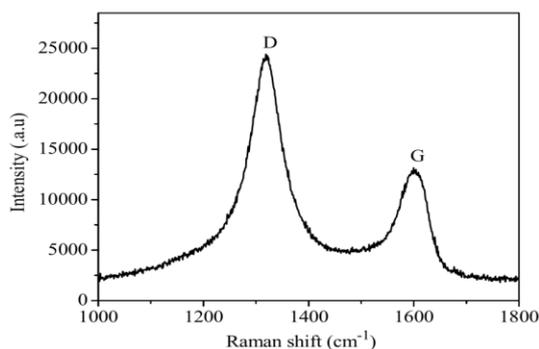


Fig. 9. Raman spectrum of carbon mesospheres synthesized by arc discharge

4. Conclusions

In conclusion, the CMs were successfully synthesized by arc discharge using Fe_3O_4 catalytic material. Results from the XRD and Raman studies confirmed that the CMs have a graphitic structure. The CMs shows a perfect shape and highly uniform with an average diameter of 246 nm. The synthesized CMs with narrow-distribution in diameter show high potential for various applications like batteries,

capacitors, fuel cells and especially in the commercial lubricants.

Acknowledgement

The research was financially supported by the Fostering Innovation through Research, Science and Technology (FIRST) under grant No. 16/FIRST/1a/IMS.

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