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Cold Emission Properties of Solvo-thermally Synthesized Carbon Spheres

Abstract

Amorphous carbon spheres with varying diameters have been prepared by a low temperature solvothermal route. The structure of the as prepared sample has been investigated by several sophisticate electron microscopic techniques like TEM and FESEM. X-ray diffraction studies show the amorphousness of the sample. The atomic force microscopy gives detail about the topology of the sample. It has been shown that the carbon materials have the potential to be used as cold cathode emitter with a turn on field 4.99 V/□m. The cold cathode characteristics of the sample with different cathode to anode distance have been studied in detail.

Keywords: Carbon, Electron microscopy, Electron emission, Work function.

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Introduction

It is an established fact that the different carbon structures find its extensive applications in various fields of science and technology. With the discovery of CNTs by Iijima (Iijima S.1991) and even before that the extensive uses of carbon fibers and diamond like carbon films in various fields like field emission devices, bio-medical applications, coating industry, magnetic storage device etc. (Salgueiredo E.et.al.2008; May PW et.al.1999) have accelerated researchers to explore more and more carbon structures and their applications, especially with the advent of nanotechnology. Different carbon nanostructures like carbon flakes, onion, carbon tree as well as carbon spheres and their different applications have been reported by many workers (Kinoshita H.et.al2008, Mehraban Z.et.al.2009). Although numbers of reports are available in field of synthesis of spherical carbon, its different properties still now have not been studied rigorously. Being propelled with this fact we have reported here a very simple low temperature solvothermal route for synthesizing the carbon spheres. The sample thus prepared was characterized by XRD, SEM, transmission electron microscopy TEM and AFM. Carbon spheres showed good field emission properties. Cold emission properties of the sample with cathode to anode distance have been investigated.

Experimental

The synthesis involves taking ferrocene and sulfur in 1 : 2 ratio and mixing it in a mortar. The mixture was then shifted to 1 Teflon coated stainless steel autoclave of 100 ml in volume that was already 90 % filled with benzene. The whole system was then isolated for 72 hours in an air oven kept at 573 K temperature. A blackish powder was obtained after letting the mixture be cooled normally and was collected through filtration process. The residue was washed several times with alcohol and distilled water and dried over night at 330 K overnight. The sample, thus prepared with characterized by XRD (Bruker D8 Advance), SEM (JEOL-JSM-6360), HRTEM (JEOL-JEM 2100) and AFM (NT-MDT, Solver Pro). The cold cathode characteristics of the as prepared material were examined in high vacuum cold emission set up system.

Results and Discussions

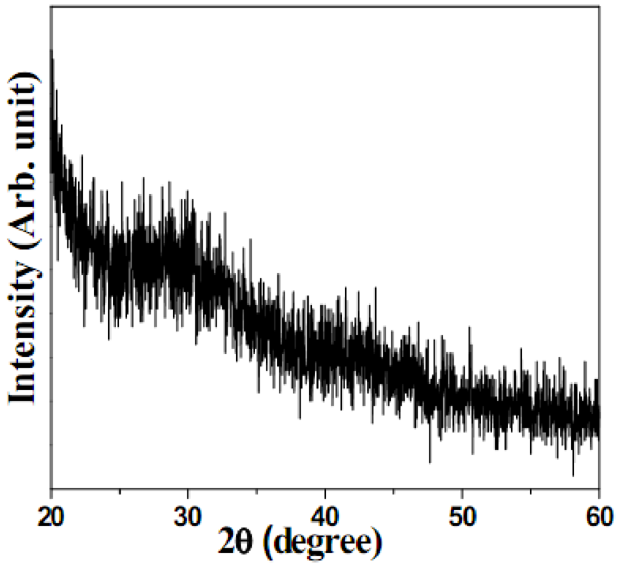

Fig.1: XRD patterns of the amorphous carbon spheres prepared at 200 ^{0}C.

X-Ray Diffraction Analysis:The crystalline behavior of our samples has been investigated with the help of an x-ray diffractometer by Cu Kα radiation. The XRD pattern is shown in **Fig.1**. From the XRD pattern it

of the sample has also been confirmed from the SAED pattern, obtained from the microscopic study (discussed later.)

Microscopic Study

It can be seen that no distinct peak appeared indicated the amorphousness of our sample. The amorphousness

Fig. 2 shows the SEM images of the samples taken with different magnification. It can be seen that there are mainly two kind of distinct features. One is spherical in shape and other is sponge like. The diameters of the spheres are not uniform and vary from 2-3 µm to 600-700 nm. The structure of the sponge like region was not clearly resolved in the SEM image. Hence TEM study was performed as discussed in the next section. The reason of appearance of such region may be due to the incompleteness of the reaction due to either of the insufficient time or reaction temperature. The growth mechanism of such a structure may be a topic of further research.

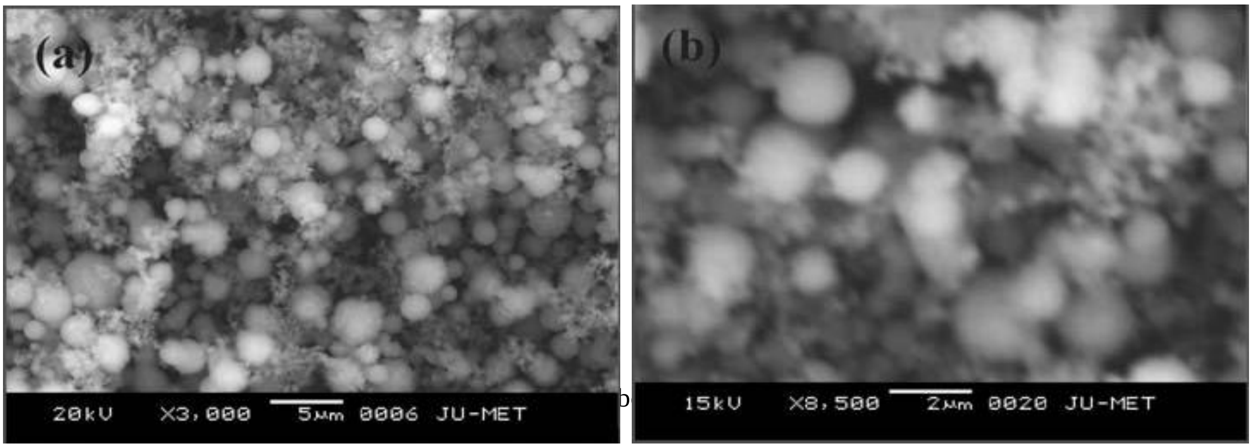

Fig. 2: SEM micrograph of the prepared sample with different magnification.

spherical in shapes having diameter from 5 to 25 nm. The observed particle size does not match with that obtained from SEM image. These lead us to conclusion that the TEM results indicate the spongy region of the SEM picture. Although the exact growth mechanism is not clear but it can be speculated that probably these small spheres with the completion of the reaction grows up to form the bigger spherical particles. The AFM histogram (discussed later) data also supports the presence of small particles. The SAED pattern shown inset of fig.3b shows that the samples are completely amorphous supporting the XRD result.

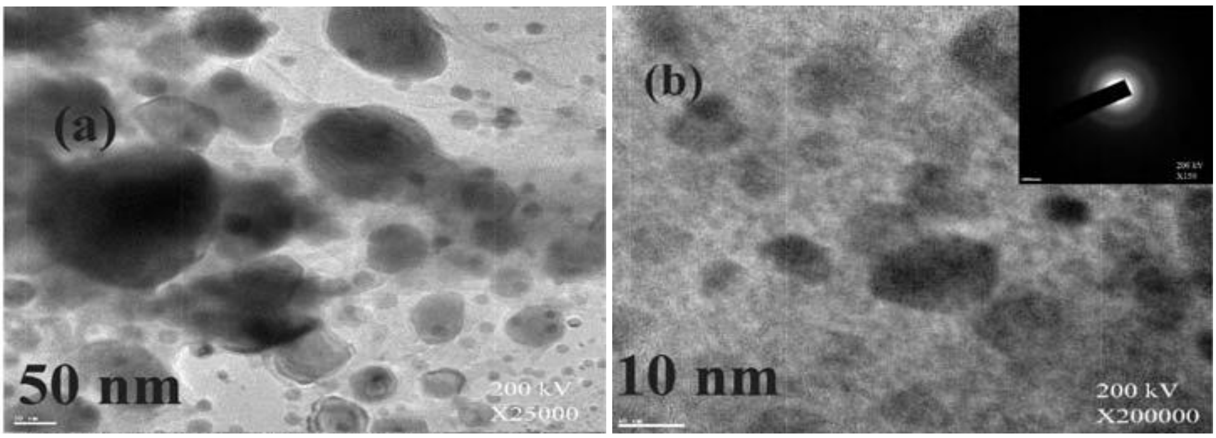

Fig.3: TEM micrograph of the prepared sample with different magnification (3a-3b) and inset 3b the SAED patterns of carbon sphere

For AFM study the sample was dispersed in ethanol and a thin film has been prepared on glass substrate by dip coating technique. When the alcohol gets evaporated the film became ready for AFM study. The corresponding 3D picture with histogram is shown in **Fig. 4**. It can be seen in **fig. 4a** that the surface is a rough one with rms roughness 50 nm.

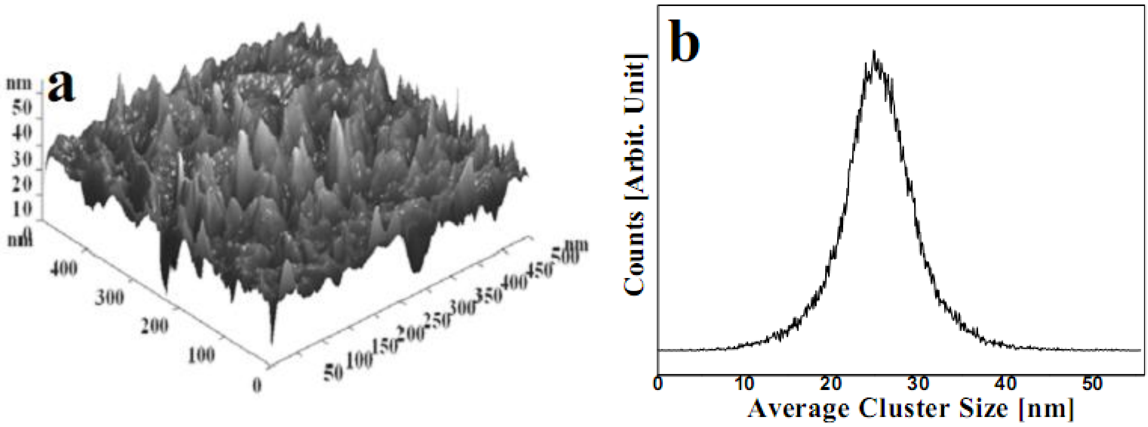

Fig. 4: (a) 3D AFM image of dispersed carbon film (b) corresponding histogram.

Field Emission Study

Cold emission experiment has been done at room temperature. The emission ccurrent with applied electric field has been related to each other by well-known Fowler Nordheim equation (Fowler RH, Nordheim L. 1928) given below:

$$I = Aat_F^{-2}\phi^{-1}(\beta E)^2 \exp\{-bv_F\phi^{3/2}/\beta E\} \qquad (1)$$

Here the meaning of different constants may be found in the previous report [7].

The values of F-N constants are respectively

$a=1.541434\times10^{-6}$ AeV V^{-2} and $b= 6.830890\times10^{9}$ $eV^{-3/2}$ Vm^{-1}.

Equation (1) when simplifies takes the form

$$I= AC\beta^2E^2/\varphi)\exp[-B\varphi^{3/2}(\beta E^{-1}) \qquad (2)$$

Where A, B, C are the constants.

The experimental voltage current plots of our sample taken for various cathodes to anode distances are summarized in **Fig.5**. The turn on field (E_{TO}) defined as the field required obtaining an emission current of 0.6 μA, decreases from 12 to 5 V/μm as cathodes to anode distances was increased from 120 to 300 μm. The variation of E_{TO} with inter-electrode distance has been summarized in **Table 1**. F-N plots, which is a plot of ln (I/E^2) with 1/E have been shown in **Fig.6** and can be seen that it has three different linear region for high, medium and low field domain. Separate calculation of enhancement factors β and effective work function (Banerjee D, Jha A, Chattopadhyay KK. 2009 has been done for each region. The result is summarized in **Table-2.**

It is evident that β varied from one region to other. This is indeed a different result as compared to the other results reported previously [8]. This can arise from the tip geometry of our field emission set up. The above mentioned findings clearly prove that if we can synthesis the structure by a controlled manner it would be a material of potential for using in cold emission display.

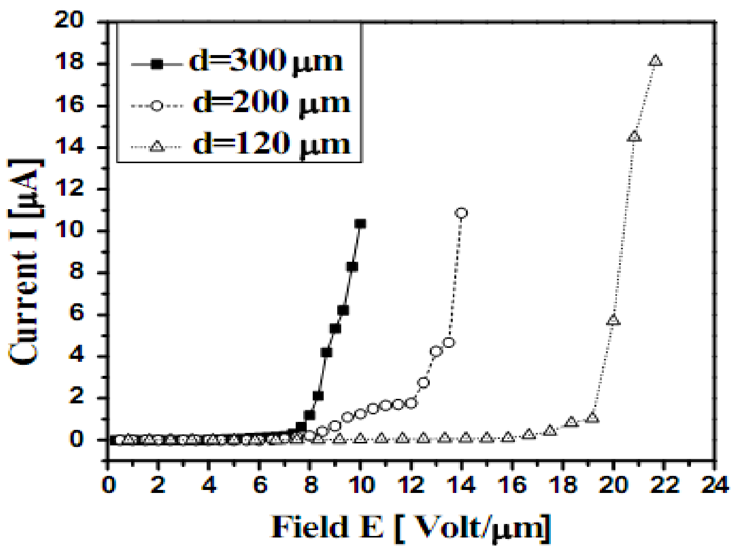

Fig. 5: cold cathode characteristics of carbon nano/micro structures with different inter electrode distances.

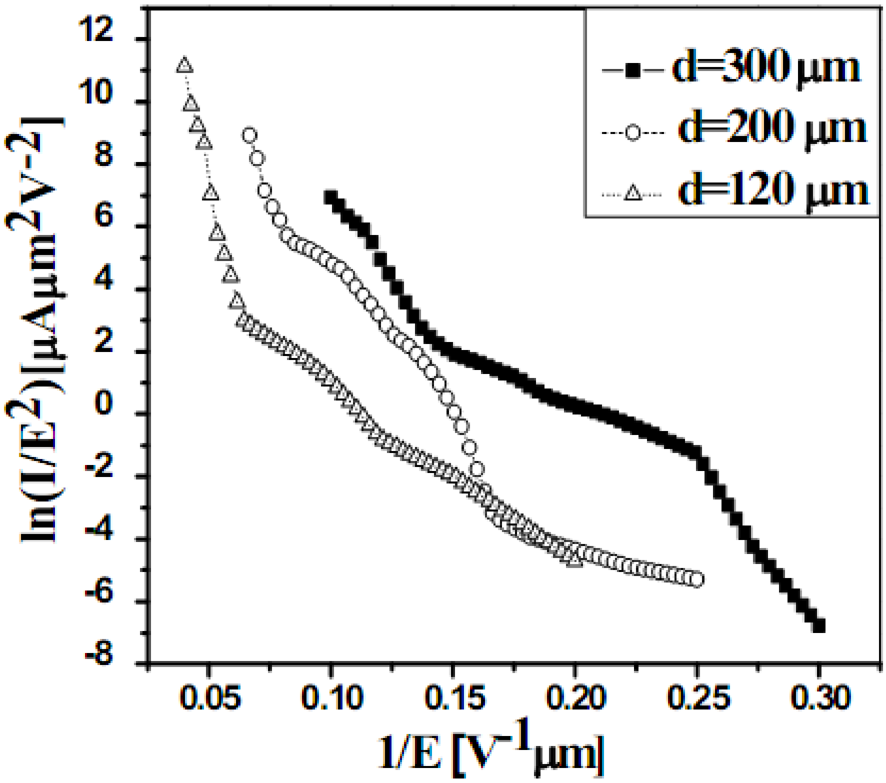

Fig. 6: F-N plot of voltage current response of **Fig.5**

Table 1: Change of E_{TO} with inter-electrode distance

Electrode Distance (µm)	Turn on Field (V/µm)
120	12
200	6.9
300	5

Table 2: Values of effective work functions and enhancement factors of carbon spheres for different inter-electrode distance

	Distance (mm)	Enhancement Factor (β)	Effective work function
High Field region	120	644	0.066
	200	410	0.09
	300	237	0.13
Medium Field region	120	2386	0.028
	200	821	0.057
	300	1174	0.045
Low Field region	120	701	0.063
	200	3636	0.021
	300	1488	0.038

Conclusion

Amorphous carbon micro/nano spheres were synthesized by an easy solvothermal process. The as prepared sample has been studied with XRD, SEM, TEM and AFM.

The microscopic study revealed the fact that there are spheres with different diameter from micro to nano range. XRD as well as SAED pattern obtained from TEM proves the amorphousness of the sample. The sample thus developed shows promises towards being used as cold emitter with turn on field 4.99 V/mm for an inter-electrode distance as high as 300 µm

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References

Banerjee D, Jha A, Chattopadhyay KK. 2009. Low-temperature synthesis of amorphous carbon nanoneedle and study on its field emission property Emission. *Physica E* 41: . 1174-1178.

Fowler RH, Nordheim L. 1928.Electron Emission in intense Electric Fields. *Proc. R. Soc. Lond*. A, 119: 173-181.

Iijima S.1991. Helical microtubules of graphitic carbon. *Nature.* 354: 56-58

Kinoshita H, Vacher B, Belin M, Montagna G, Martin JM, Ohmae N.2008. Diamond-derived carbon onions as lubricant additives. *Tribology.* 41: 69-78.

May PW, Kuo MT, Ashfold MNR.1999.Field emission conduction mechanisms in chemical-vapour-deposited diamond and diamond-like carbon films. *Diamond and related Materials.* 8: 1490-1495.

Mehraban Z, Farzaneh F, Dadmehr V. 2009.Catalytic chemical vapour deposition synthesis of carbon spheres. *Materials Letters*. 63: 1653-1655.

Murphy EL, Good Jr. LH. 1956. Thermionic Emission, field Emission, and the Transition Region. *Phys.Rev.* 102: 1464-1473.

. Salgueiredo E, Vila M, Silva MA, Lopes MA, Santos LD, Costa FM, Silva RF, Gomes PS, Fernandes MH.2008. Biocompatibility evaluation of DLC-coated Si_3N_4 substrates for biomedical applications. *Diamond and related Materials.* 17: 878-881.