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Synthesis of Carbon Nanobeads from Plant base Precursor for Electrode Material of Supercapacitor

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Abstract: Supercapacitors are an important energy storage devices due to their capability of higher energy density and higher power density. Carbon materials such as graphene, carbon nanotubes, active carbon and graphite with high surface area have been widely investigated as electrode materials in electrical double layer capacitors. In present work the activated carbon nanobeads have been synthesized by chemical vapor deposition technique using cold pressed Safflower seed oil (Kardai oil) and Fe nanoparticles as catalyst. TEM analysis shows the size of carbon nanobeads are around 82 nm. XRD study shows the graphitic crystalline nature of carbon nanobeads. The surface area of carbon nanobeads by BET measurement is 879 m^2/g. Specific capacitance measured by cyclic voltammetry, shows maximum value 425 F/g at scan rate 5mV/s in 6M KOH electrolyte solution.

Keywords- *carbon nanobeads; specific capacitance, pyrolysis, chemical vapor deposition, Fe nanoparticles, safflower seed oil*

I. INTRODUCTION

Supercapacitors are used as energy storage devices because of their capability of higher energy density and higher power density. Supercapacitor can offer many desirable properties compared to conventional batteries such as super long cycle life, short charging time and high power density [1-7, 30]. The properties of the electrode materials and the electrode/electrolyte interface affect directly the performance of supercapacitors [8-10, 30]. Carbon is the most naturally occurring abundant material exhibiting a variety of molecular and structural forms such as graphite, diamond, nanotubes, nanobeads, graphene, fullerene, nanodiamonds, amorphous carbon, porous carbon, etc. with various applications [11-17, 30]. Carbon-based electrodes for supercapacitor applications have been widely investigated because of its chemical and thermal stability and excellent electrical properties [18-22, 30]. Also carbon-based materials shows high power and cycling performances and they are of interest because of their properties like high specific surface area [18-20, 30]. Currently, carbon materials, such as graphene, carbon nanotubes, activated carbon, porous carbon, have been successfully applied in energy storage area by taking advantage of their structural and functional diversity. Among these graphene or carbon nanotube, as a promising and rising star in carbon materials, exhibits specific structure and exceptional physicochemical properties [23–26], nevertheless, their preparation process is usually complicated [27, 28]. The high quality graphene is commonly prepared through chemical vapor deposition using fossil fuel-based molecules as precursors (such as methane, acetylene, ethylene), which suffers from high cost and very low yield [26, 27, 29]. Plant based-derived carbon, as a type of electrode materials, has attracted much attention because of its structural diversities, adjustable physical/chemical properties, environmental friendliness and considerable economic value. Sharon M. research group have been able to synthesize various types of Carbon Nano Materials from different plant based precursors [30].

In this work, Carbon nanobeads are synthesised by optimizing the temperature by chemical vapor deposition. The plant based precursor-Safflower oil obtained from seeds is used. The obtained carbon nanobeads are activated chemically and its viability as electrode material for supercapacitor is investigated.

II. MATERIAL AND METHODS

Materials:

Safflower oil: The Safflower plant (Carthamus tinctorius) has yellow and orange flowers. The cold pressed safflower oil (Kardai oil) obtained from seeds of this plant.

Metal catalyst: Fe nanomaterial,

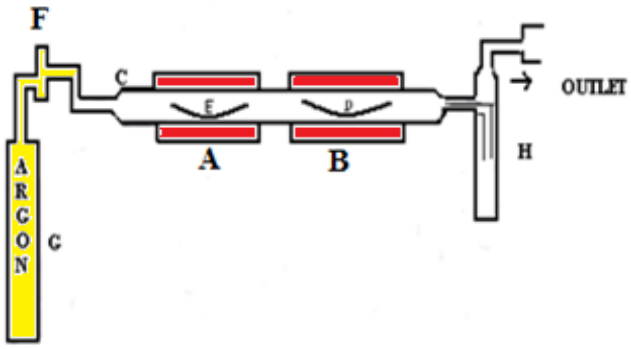
Chemicals: KOH, $ZnCl_2$, HCl, HNO_3

Synthesis of Carbon nanobeads from Safflower oil

Pyrolysis unit in the form of Chemical Vapor Deposition (CVD) furnace is used in the synthesis of carbon nanobeads from Safflower oil.

The CVD furnace has two heating zones; (i) Oil vaporizing zone and (ii) Pyrolyzing zone of furnace for carbonization. In oil vaporizing zone a quartz boat containing 50 ml safflower oil was and placed at the centre of heating zone. In pyrolyzing zone, an

extremely small quantity of acetone mixed with the 1 mg of catalyst is spread throughout the quartz boat and kept exactly middle of heating zone.



A –Vaporizing furnace
B– Pyrolyzing furnace
C-Stainless steel tube
D-Quartz boat with catalyst
E-Quartz boat with precursor
F-Gas flow regulator
G-Gas cylinder
H-Gas bubbler

Fig. 1 Schematic diagram of the CVD setup

Before switching on the power supply, the Stainless steel tube was flushed with carrier gas-Argon for 15 minutes. After flushing the temperature of vaporizing furnace was adjusted to 400^0C. By adjusting different reaction temperatures 800^0C, 850^0C, 900^0C, 950^0C, 1000^0C, 1050^0C and 1100^0C of pyrolyzing furnace, the possibility of synthesis of carbon nanobeads is investigated. It is observed that at reaction temperature 950^0C of heating zone, nanobeads were get synthesized. The optimum temperature which initiate the formation of carbon beads is 950^0C. At this temperature Fe nanoparticles give catalytic reaction than all other temperature under investigation and triggers the formation of nanobeads. The time parameter kept constant i.e., 3 hours and argon gas flow rate 100 sccm. After completion of process, the furnace was allowed to cool down to the room temperature. The carbon samples accumulated on the quartz boat was collected and purified by acid treatment.

Purification of Carbon nanobeads and chemical activation

The collected soot contains impurities like amorphous carbon, metal catalyst etc. To remove these impurities obtained carbon sample was first soaked in 1:1 HCl for 24 hrs and then 3 hours in HNO_3. The filtered carbon sample was thoroughly washed with distilled water five times. For chemical activation, obtained carbon sample in soaked in 60% $ZnCl_2$ for one hour then filtered and washed with distilled water until filtrate water pH obtained approximately 7. Finally it was rinsed with acetone to remove the traces of water and then dried in oven at 60^0C for 24 hours.

Characterization and specific capacitance measurement

The morphological observations of as-synthesized and purified activated CNBs were carried out by TEM. EDAX to find wt% of elements and X-ray diffraction (XRD) witjh CuK_α source to identity structure of obtained material. Surface area of material by BET. Specific capacitance of CNBs in 6M KOH electrolyte solution obtained by cyclic voltammetry study using Gamry Reference 3000 Potentiostat/Galvanostat.

III. RESULTS AND DISCUSSION

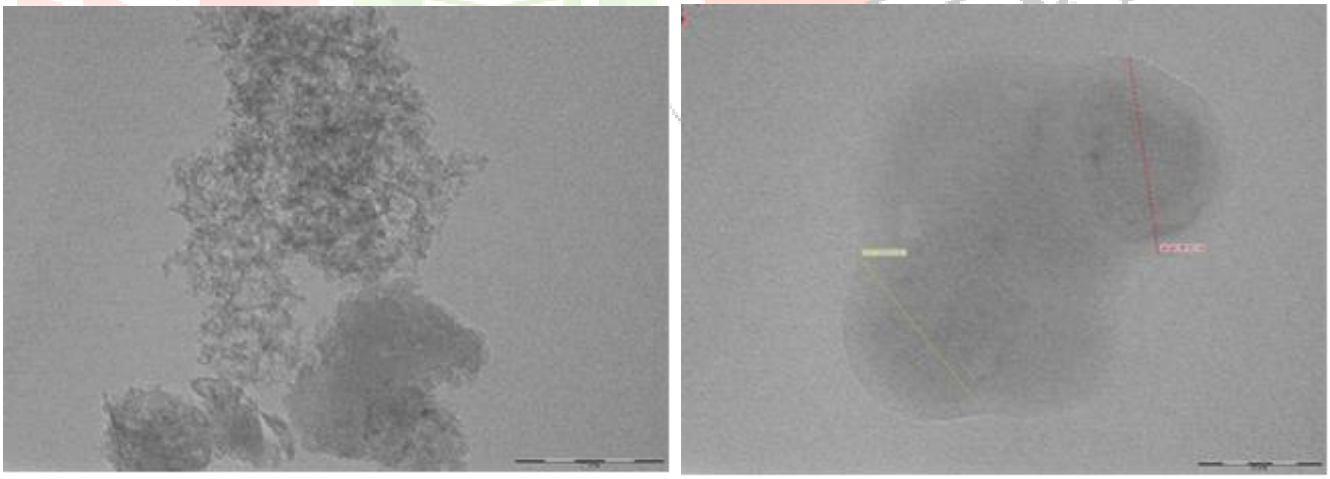
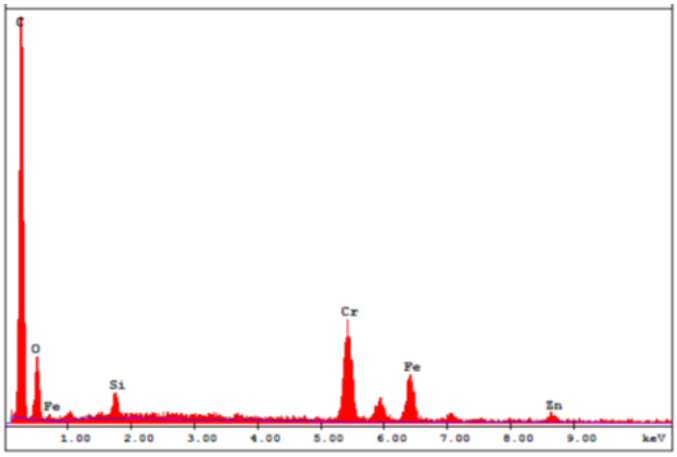


Fig. 2 TEM images of carbon nanobeads synthesized at reaction temperature 950^0C

TEM images of CNMs synthesized at 950^0C, using Fe nanoparticles as catalyst, in presence of Ar gas and Safflower oil as precursor showed carbon structure in form of nanobeads. A large number of homogenous nanobeads of about 80-83 nm diameter are obtained. The carbon beads grow like a chain during pyrolysis which clearly shows the graphitic nature of the beads. The oxygen present oxidizes the amorphous carbon in situ which is responsible for getting the carbon nanobeads of uniform diameter.



Element	C	O	Si	Cr	Fe	Zn
Wt %	97.03	0.74	0.07	0.95	1.20	0.01

Fig. 3 EDAX of CNBs

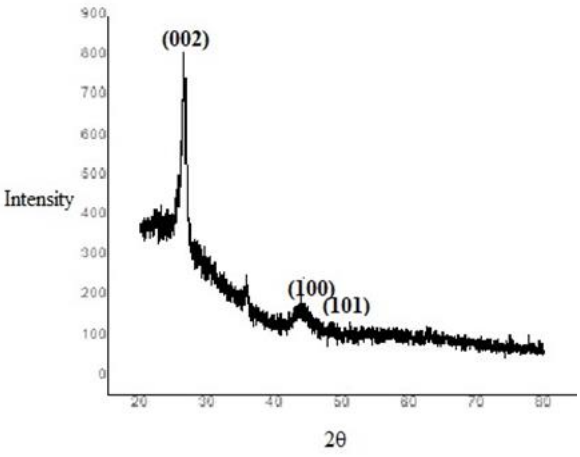
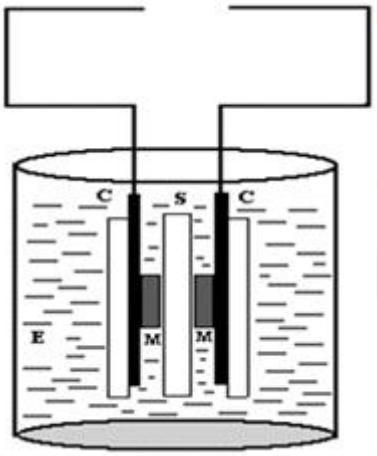


Fig. 4 XRD of CNBs

EDAX of CNBs shows the presence 97.03 wt % of Carbon and 1.20 wt % of catalyst Fe. Some trace amount of impurities of Fe, Cr due to use of 316L Stainless steel tube and Si may be due to use of quartz boat. Oxygen due to ingredient in cold pressed Oil or handling of carbon samples in open atmosphere.

XRD of CNBs shows (002), which is designated to graphitic carbon and (100) and (101) associated with carbon. EDAX and XRD confirms the carbon with graphitic crystalline nature.

The specific capacitance of CNBs was measured using a fabricated cell, as shown in Fig. 5. Material was sandwiched between filter paper and flexible graphite sheet with stainless steel gauze inside (2mm thickness) working as one electrode. Same arrangement was made which would work as second electrode. Both the electrodes brought together and separated with thick filter paper. This assembly was held together by perspex plates and screwed to make a two electrode system. The fabricated cell was immersed in electrolyte KOH with concentration 6M.



C: Flexible graphite sheet with stainless steel gauze inside
M: Material whose specific capacitance to be measured
S: Separator (thick filter paper soaked with electrolyte
E: Electrolyte

Fig. 5 Schematic diagram of double layer capacitor cell

The specific capacitance was tested using cyclic voltammetry at different scan rates of 5, 10, 25 mV/s in the potential region between -0.4 V to +0.4 V. Capacitance is inversely proportional to scan rate. Lower the scan rate higher the capacitance. The decreasing trend of the specific capacitance can be related to parts of the surface of the electrode material are inaccessible at higher scan rates. Hence, the specific capacitance obtained at slow scan rates is thought to be closest to that of full utilization of the electrode material.

Formula used for calculating Specific Capacitance (Farad/g) is:
Capacitance (F) = Current (mA)/Scan Rate (mV) = X Farad
Specific Capacitance (F/g) = X Farads/Total mass of sample (g) = Y Farad/g.

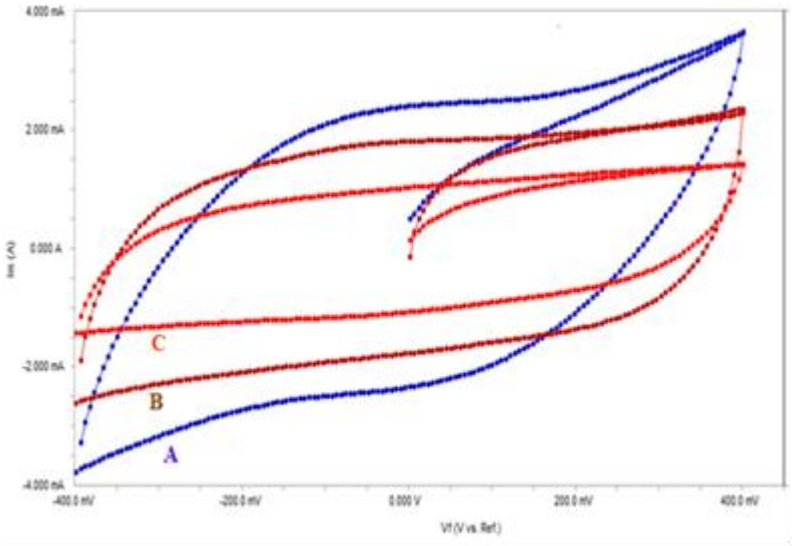


Fig. 6 Cyclic voltammograms of CNBs at different scan rate

Table I:Specific capacitance of CNBs		
Code	Scan Rate mV/s	Specific capacitance F/g
A	5	425
B	10	317
C	25	275

The specific capacitance at 5 mV/s, 10 mV/s and 25 mV/s was observed 425 F/g, 317 F/g and 275 F/g respectively. This high capacitance due to nano size of obtained activated carbon material i.e carbon nanobeads and high surface area 879 m^2/g.

IV. Conclusions

TEM and EDAX results confirm the synthesis of carbon nanobeads. XRD analysis confirms the graphitic crystalline nature of carbon nanobeads. The specific capacitance of synthesized activated carbon nano material i.e., carbon nanobeads is obtained 425 F/g at scan rate 5 mV/s in 6M KOH electrolyte solution. This high capacitance is due to high surface area 879 m^2/g. This study shows carbon nanobeads would be the promising material for the electrode of supercapacitor.

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