Corn Husk Waste Valorisation: Synthesis and Characterization of High-Performance Carbon for Supercapacitor

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***Abstract*—Corn is known to be the Queen of cereals. It is used as a basic raw material of various industrial products. As a result, a lot of corn husk is been wasted which creates a lot of biomass pollution. This CH can be utilized to make carbon. After the collection of CH from the vendors, it was cleaned and dried at room temperature. Moisture removal was carried out at 110°C. The biomass was further crushed into fine powder to undergo the process of torrefaction and carbonization during which CHBC was formed. CHBC/$NiCo_2O_4$ was formed by hydrothermal method. Characterization of the carbon was done using SEM, XRD, CV and EIS to study its surface morphology and electrochemical performance. The highest specific capacitance of CHBC was at 228 Fg^{-1} with current density $1Ag^{-1}$. The highest power density was at 1800 Wkg^{-1} with energy density of $5Whkg^{-1}$. The highest specific capacitance of $NiCo_2O_4$/CHBC was at 294 Fg^{-1} with current density $1Ag^{-1}$. The highest power density was at 2000 Wkg^{-1} with energy density of 15 $Whkg^{-1}$. Thus, these result show that $NiCo_2O_4$/CHBC could be used to make efficient electrodes for supercapacitors.**

***Index Terms*—corn husk; biomass; carbonization; torrefaction; supercapacitors**

I. INTRODUCTION

Corn is grown in more than 170 regions globally. It is one of the most widely-planted crops in the world [1]. Being rich in carbohydrates and fibres, corn has become a staple food in the diets of people living in tropical regions and is the main grain used for animal feed in temperate regions. [2] Corn crops produce huge amounts of biomass typically consisting of 15% husk, 35% leaves, and 50% cobs.[3] Thus, increase in the amount of corn production results in the increase in corn husk waste. Corn husk (CH) is a lignocellulosic biomass which is renewable and sustainable. The chemical composition of corn husk consists of cellulose, lignin, hemicellulose, and other impurities. When not treated well, this organic biomass is regarded as an agricultural waste. Converting these wastes optimally into value added end applications such as biodegradable pots, organic fertilizers, corn husk fibre [4], activated carbon could solve environmental problems. This research focuses on converting cornhusk into active carbon. Being rich in carbon content of lignin, such a lignocellulosic biomass is a good option to be used as precursor for producing activated carbon.

Energy storage devices like supercapacitors, battery and fuel cells are mainly focusing on the eco-friendly carbon materials. Use of biomass derived carbon can solve this problem to a greater extent [5]. In this article CHBC was derived by torrefaction and it was further coupled with $NiCo_2O_4$ to form a binary composite material for supercapacitor.

II. METHODOLOGY

2.1 PREPARATION OF CORN HUSK BIOCARBON (CHBC)

Torrefaction was performed at 220°C. Hemicellulose is the first constituent of the biomass to start decomposing. It is chemically most active and its major degradation starts at 220°C. [6] By the end of this stage, almost all hemicellulose is decomposed, and small fractions of the cellulose start decomposing. Cellulose degrades at higher temperature (>275°C), but its major degradation occurs within a narrow temperature band of 270–350°C. Lignin starts softening. Fig. 1 shows the various products formed during torrefaction. [7]

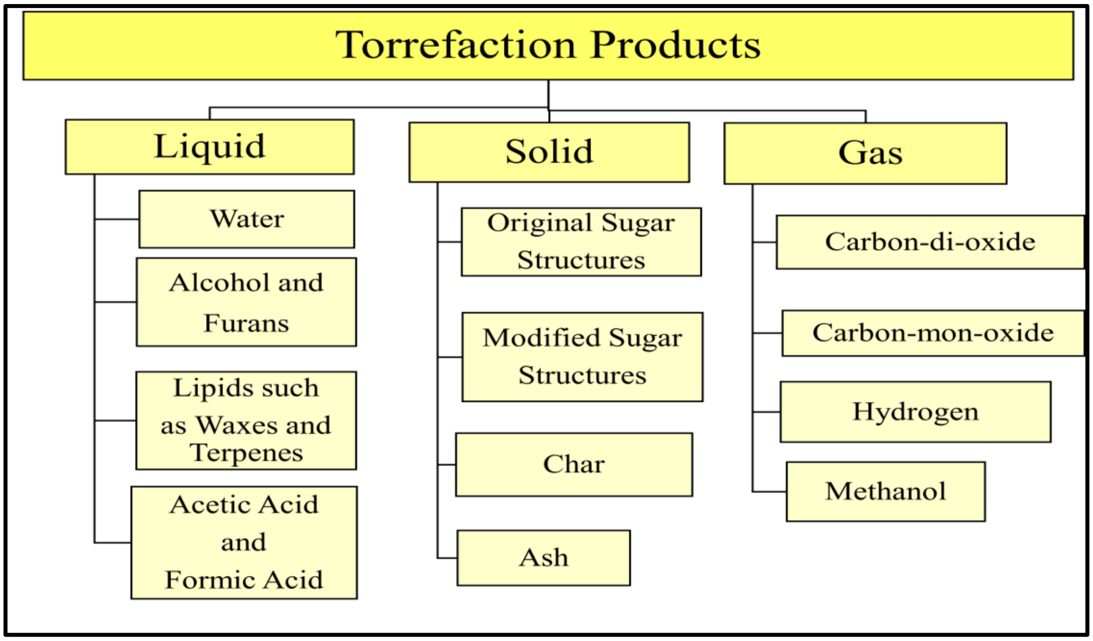

FIG. 1 - PRODUCTS OF TORREFACTION OF BIOMASS

Approximately 10 grams of CH fine powder and 9 grams of CH residue powder were weighed and put in the crucibles and filled till neck level. The crucibles were wrapped with 6 layers of aluminium foil and put into the torrefaction reactor. The temperature was set at 220°C for 2h.

Carbonization process is a phase to enrich carbon content in carbonaceous material by eliminating non-carbon species using thermal decomposition.[8] Carbonization was done at 400°C for 2 hours. The schematics of CHBC is shown in Fig. 2. The CH structure, mainly lignin and cellulose, keeps breaking and decomposing to produce slightly richer fixed carbon content compared to torrefaction.

2.2 PREPARATION OF $NICO_2O_4$/CHBC

$NiCo_2O_4$/CHBC was prepared by hydrothermal process. Nickel and Cobalt Nitrate hexahydrate were mixed in a stoichiometric ratio of 1:2 in 50 ml of distilled water and stirred magnetically. Later, CHBC was added to the mixture and magnetically stirred. It was then sonicated for 30 minutes. Further the mixture solution was transferred in autoclave for 18 hours at 180˚C. [9] After that, the autoclave was cooled down at room temperature naturally and the solution was filtered. The precipitate was dried at 110˚C and thus $NiCo_2O_4$/CHBC was prepared.

FIG. 1 SHOWS THE SCHEMATIC REPRESENTATION OF PREPARING CARBON FROM CORN HUSK.

III. RESULTS AND DISCUSSION

3.1 SCANNING ELECTRON MICROSCOPY (SEM)

The structural morphology of CHBC and $NiCo_2O_4$/CHBC was studied using SEM. Fig. 3 (a) reveals the rough surface of CHBC with excellent interconnectivity. On the surface of CHBC some pores are observed which are ideal for ion transfer in the material [10]. These pores allow deep penetration of the electrolyte. Fig. 3 (b) shows the SEM image of $NiCo_2O_4$/CHBC which reveals $NiCo_2O_4$ nanoparticles being distributed all over the surface of CHBC. The distribution of $NiCo_2O_4$ on the surface of CHBC increases the ionic conductivity of the binary composite. Since, there is direct exchange of ions between pseudocapacitive material and electrolyte it always results in the enhanced electrochemical results which are truly due to this type of surface morphology.

3.2 X-RAY DIFFRACTION (XRD)

The crystal structure of the samples is studied by XRD. Fig. 3 (c) shows the XRD graph for CHBC which reveals some sharp peaks in the XRD curve because the lignin and cellulose present in the sample have not completely broken down into carbon. This can be eliminated by performing carbonization at higher temperatures. No impurity is present while synthesizing the CHBC. Fig. 3 (d) shows the XRD curve for $NiCo_2O_4$/CHBC which reveals diffraction peaks related to $NiCo_2O_4$. All peaks are well indexed to $NiCo_2O_4$ cubic phase with (JCPDS card no. 20-0781) [11-12]. The peaks observed in XRD curve are in good agreement with the JCPDS data. The most prominent peak that matched are 111 and 220 at 2θ values 19 and 30. The unindexed peaks in the XRD curve are associated with the CHBC and lignin and cellulose present in the sample with shift in higher values of 2θ.

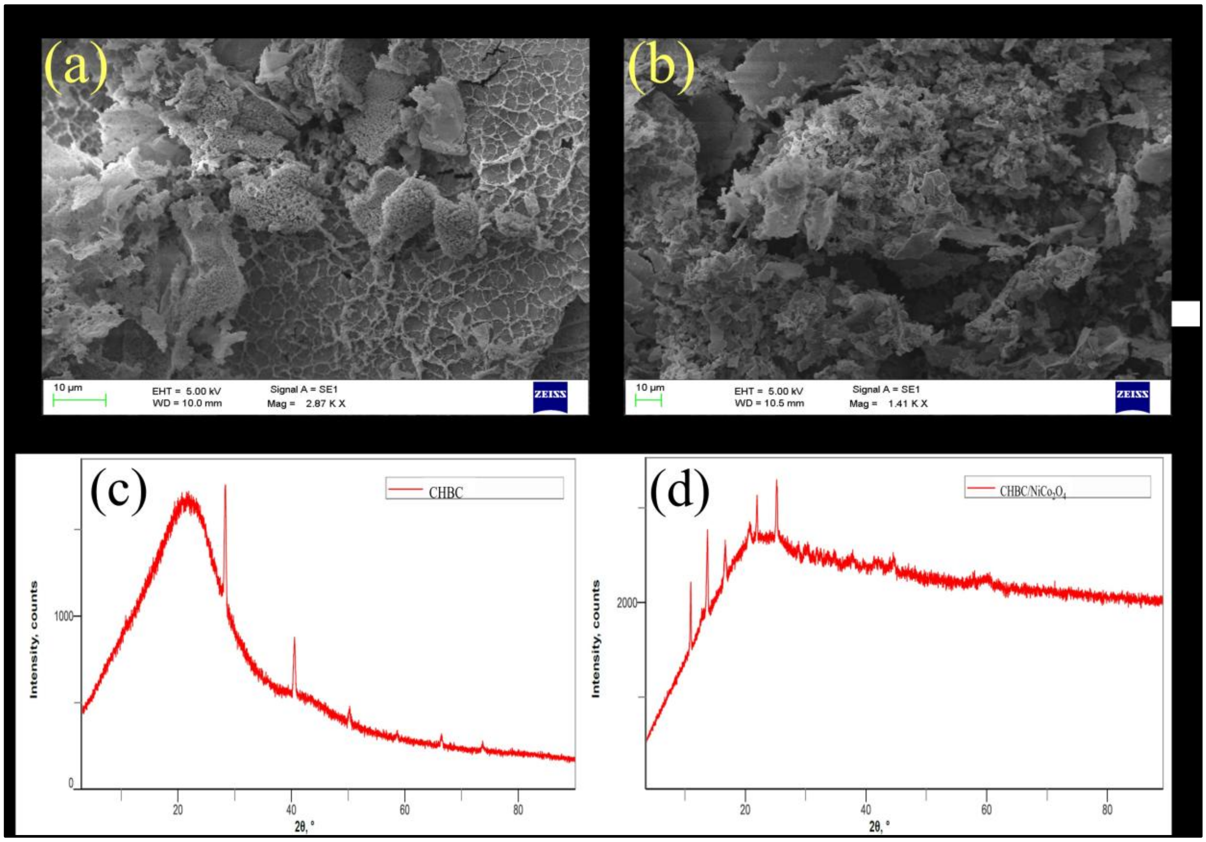

FIG. 3 SCANNING ELECTRON MICROSCOPY OF (A) CHBC; (B) NICO$_2$O$_4$/CHBC, XRD CURVE OF (C) CHBC AND (D) NICO$_2$O$_4$/CHBC

3.3 ELECTROCHEMICAL CHARACTERISATION

Electrochemical Performance of the composite materials were done using Galvanostatic Charge Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS). The GCD curves for CHBC and NiCo$_2$O$_4$/CHBC are shown in Fig. 4(a) and (b) respectively. The specific capacitance for the materials is calculated using GCD curves. The GCD curve for CHBC shows an IR drop at higher current density. CHBC has higher specific capacitance of 228 Fg^{-1} at current density of 1 Ag^{-1}. Specific capacitance for higher current density was calculated after excluding IR drop from GCD curve. The GCD curve for NiCo$_2$O$_4$/CHBC shows its highest specific capacitance at 294 Fg^{-1} at current density of 1 Ag^{-1}. NiCo$_2$O$_4$/CHBC also shows IR drop at higher current density. [13]

The interface between the surface electrode and electrolyte is studied using EIS. The Nyquist plot for (a) CHBC and (b) NiCo$_2$O$_4$/CHBC are shown in Fig. 4 (c) and (d) respectively. Nyquist plot is divided into three frequency regions of low, mid and high frequency. High frequency region is associated with surface resistance (R_s) of the electrode and mid frequency region with the charge transfer resistance (R_{ct}) which can be identified by the semicircle of Nyquist plot. CHBC and NiCo$_2$O$_4$/CHBC has surface resistance value of 1 Ω and 2.5Ω respectively. The charge transfer resistance (R_{ct}) for CHBC and NiCo$_2$O$_4$/CHBC is 3 Ω and 2.5 Ω respectively. From these results we can conclude that NiCo$_2$O$_4$/CHBC is more conductive and less resistive at it allows free exchange of electron between electrode and electrolyte.

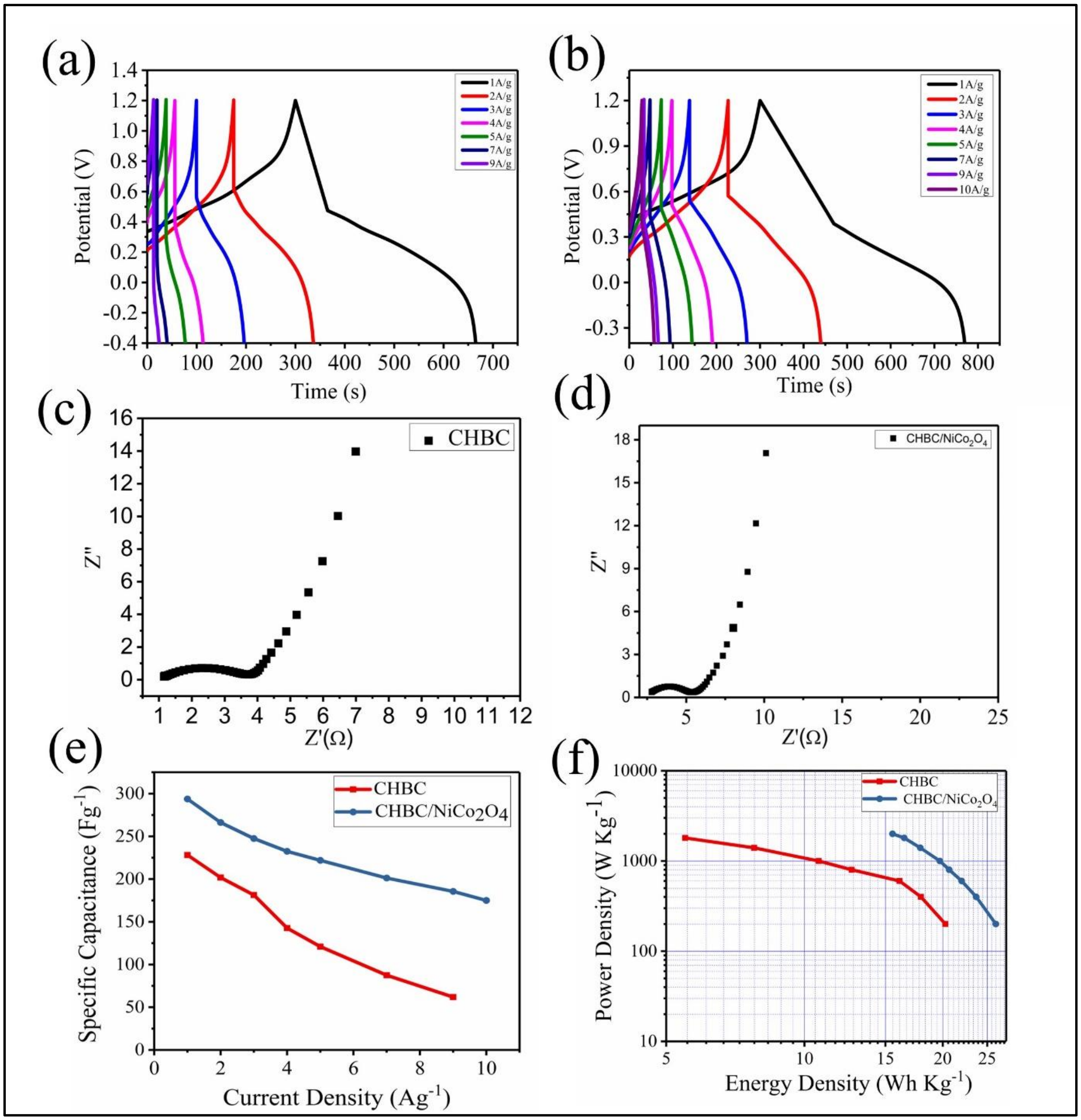

FIG. 4 GALVANOSTATIC CHARGE DISCHARGE (GCD) CURVES OF (A) CHBC AND (B) NICO$_2$O$_4$/CHBC, ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) OF (C) CHBC AND (D) NICO$_2$O$_4$/CHBC, CAPACITIVE CURVE OF CHBC AND NICO$_2$O$_4$/CHBC, RAGONE PLOT OF (E) CHBC AND (F) NICO$_2$O$_4$/CHBC

The relation between specific capacitance and current density is shown in Fig. 4 (e) for CHBC and NiCo$_2$O$_4$/CHBC. Capacitive curve reveals the electrochemical performance from which it can be clearly observed that NiCo$_2$O$_4$/CHBC outperforms the CHBC. NiCo$_2$O$_4$/CHBC has specific capacitance 294, 266, 247, 232, 221, 201, 186 and 175 Fg^{-1} at current densities of 1, 2, 3, 4, 5, 7 and 9 Ag^{-1}. CHBC has specific capacitance of 228, 202, 181, 142, 120, 87 and 61 Fg^{-1} at current densities of 1, 2, 3, 4, 5, 7 and 9 Ag^{-1}. All these results show NiCo$_2$O$_4$/CHBC is better electrode material than CHBC. [14]

The relation between energy density and power density can be well explained with the help of ragone plot. Fig. 4 (f) shows comparative ragone plot for CHBC and NiCo$_2$O$_4$/CHBC. The energy density for

CHBC is 20, 18, 16, 13, 11, 8 and 5 Wh kg^{-1} at power density of 200, 400, 600, 800, 1000, 1400 and 1800 W kg^{-1} respectively. Whereas, $NiCo_2O_4$/CHBC has energy density of 26, 24, 22, 20, 19, 17, 16 and 15 Wh kg^{-1} at power density of 200, 400, 600, 800, 1000, 1400, 1800 and 2000 W kg^{-1} respectively. Both the composite materials have faced gradual decrease in the energy density. But even at higher power density composite materials have higher energy density than the traditional capacitors.

IV. CONCLUSION

CHBC was prepared by two-step torrefaction and carbonization. $NiCo_2O_4$/CHBC was performed by hydrothermal method. Morphology revealed excellent fibre structure on the surface with compactness. Electrochemical results for $NiCo_2O_4$/CHBC and CHBC has higher specific capacitance of 294 Fg^{-1} and 228 at current density of 1 Ag^{-1} and energy density of 26 and 20 Wh kg^{-1} at power density of 200 W kg^{-1}. These results shows that $NiCo_2O_4$/CHBC is one of the potential electrode materials for supercapacitor.

ACKNOWLEDGEMENT

The authors would like to thank the Principal and the Head of the Department, Department of Physics, Bhavan's College, Andheri West, Mumbai (M.S), India, 400058- for their financial assistance and support.

Nainika Rajesh Dedhia, Shaikh Shaista Sharmuddin: Methodology, Conceptualization, Investigation, Data curation, Formal analysis, Writing- original draft.

Rounak R. Atram: Writing- review, editing, Conceptualization, Resources. Resources, Writing review & editing, Supervision.

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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