

## The morphological study of FePO<sub>4</sub>/plasma treated bamboo charcoal composite act as cathode material in energy storage devices

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The capacity of energy storage devices to be based on the cathode material with best morphology. The FePO<sub>4</sub> nanoparticles were synthesized by hydrothermal method and Bamboo charcoal (BCC) was synthesized and activated by pyrolysis method. The cold Plasma was used to magnify the surface behaviour of activated Bamboo Charcoal. The hybrid composite of FePO<sub>4</sub>/Plasma exposed BCC and pure FePO<sub>4</sub> nano materials morphological and structural properties were analysed through XRD, FTIR and SEM characterization studies. This research reveals that the Plasma exposed BCC nanoparticles were well incorporate with FePO<sub>4</sub> nanoparticles and delivered embedded FePO<sub>4</sub> nanoparticles. The result shows that the FePO<sub>4</sub>/plasma exposed BCC particle size was decreased when compare to pure FePO<sub>4</sub>, which in turn increase the energy storage capacity of the material.

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### 1. Introduction

Once it comes to cathode material synthesis we are facing the problem of lower abundance of Li and poor charge capacity of Na for secondary manufacturing applications like batteries and also Maricite LiFePO<sub>4</sub> and NaFePO<sub>4</sub> having various integration with Fe and Na which shows the electrochemical inactive unlike Olivine LiFePO<sub>4</sub>. These drawbacks are overcome by one of the best iron-based FePO<sub>4</sub> cathode material because these having single-phase reaction with large number of charge carriers to attain best kinetics and three dimensional ion migration [1-7]. The main aspects in energy storage devices are to improve the Charge-discharge capacity and which are achieved by reducing the particle size [8-10] adding some conductive agents like carbon based materials and doping of ions [11,12]. Among the mentioned conditions, the adding of carbon based materials have been given the enhanced conductivity of active materials and the possibilities of carbon supplements are carbon nanotubes, activated carbon nanoparticles and graphene etc., and among them activated carbon nanoparticles are given best conductivity, stability in both physical and chemical, high surface area and low density of particles [13-17]. In this work the activated carbon as Bamboo charcoal (BCC) prepared by Pyrolysis method and also the surface area, porosity was magnified by the treatment of Low temperature Plasma without disturbing the whole properties of BCC to achieve the best conductivity [18]. Here as prepared FePO<sub>4</sub> nanoparticles are added with DC glow discharge Plasma exposed BCC and compared the characteristics studies of both Pure FePO<sub>4</sub> and FePO<sub>4</sub>/ Plasma exposed BCC.

### 2. Experimental

#### 2.1. Preparation of FePO<sub>4</sub> nanoparticles

FePO<sub>4</sub> nanoparticles were synthesised by hydrothermal method with precursors of Ferrous Sulphate and di ammonium hydrogen phosphate and taken in stoichiometric ratio then these samples were added one by one with 50ml of Distilled water and stirred with strenuous manner about 30 minutes after that NaOH solution were added drop by drop to obtain the Ph value of 9.

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The solution was subjected to stirring for 4 hours to get the homogenous solution then the solution is poured in to Teflon container and placed in hot air oven with the temperature of 140°C for 16 hours for hydrothermal process. As prepared solution is cleaned with distilled water and ethanol, dried in hot air oven for overnight and grinded by mortar to obtain nanoparticles. This sample was pre sintered with the temp of 750 °C for 12 hours and sintered with 600 °C for 6 hours.

## 2.2. Preparation of Bamboo Charcoal

The BCC was prepared and activated by using pyrolysis method. The charcoal was prepared with the optimising annealing temperature of 600°C for 6-7 hours then charcoals are fine-grained and activated at 1000°C for half an hour [18-20].

## 2.3. Preparation of FePO<sub>4</sub>/Plasma exposed BCC hybrid composites

As prepared FePO<sub>4</sub> nanoparticles were mixed with plasma exposed BCC in the ratio of 1:1 based on stoichiometric ratio and grained in pestle mortar for one hour to obtain fine nano composites.

## 2.4. Plasma Treatment

The Plasma reactor contains two electrodes made up of Aluminium, Pirani gauge power supply and gas valve with the features of 50\*30 diameters (Figure.1). The whole chamber was cleansed by distilled water and acetone. The activated BCC was taken in the sample holder which is placed between two electrodes with the separation of 6cm. The atmospheric air Plasma was produced with the parameters of DC power 450 V and 0.03mbar pressure[18].

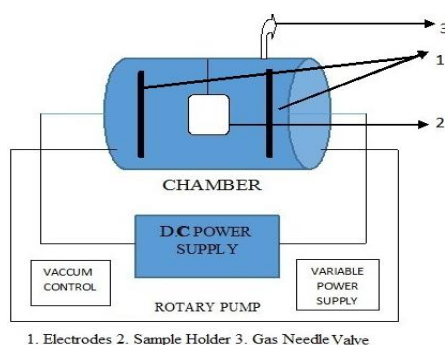


Fig. 1. Over view of Plasma Chamber.

## 2.5 Characterization

The crystalline structure formation was studied XRD (XPRT-PRO with radiation of CuK<sub>α</sub>). By the instrument of FT-IR Spectroscopy (Shimadu 8400S) the exist functional groups of pure FePO<sub>4</sub> and FePO<sub>4</sub>/Plasma exposed BCC was observed. The morphological character of surface of nanoparticles was concluded with best resolution by Scanning Electron Microscope (SEM: S-800).

## 3. Results and Discussions

### 3.1. XRD Investigation

Fig. 2 gives the result about XRD crystalline pattern for pure FePO<sub>4</sub> shows the peaks at  $2\theta = 25.80, 20.44$  and  $29.12^\circ$  for the miller indices of (102) (100) and (103) respectively in the crystal structure of trigonal with JCPDS (96-901-2513). The particle size of pure FePO<sub>4</sub> nanoparticles are calculated by Debye- Scherer formula [21], and the value is 52nm. The FePO<sub>4</sub>/Plasma exposed BCC composite pattern shows the same peaks as like FePO<sub>4</sub>, but one additional extra peak is observed with the  $2\theta$  value of  $28.02^\circ$  corresponding miller indices of (420) <sup>20</sup>. This result confirmed that the plasma exposed activated BCC is incorporate with FePO<sub>4</sub> crystal

structure. The calculated particle size was in the range of 49.25nm which reveals that the composite of plasma exposed activated BCC should reduce the size of the nanoparticles and increased the surface area; hence the energy storage capacity was increased. This result shown that the plasma exposed BCC added with  $\text{FePO}_4$  intensity is enhanced than the pure  $\text{FePO}_4$  and it does not alter the original crystalline nature of pure  $\text{FePO}_4$ .

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

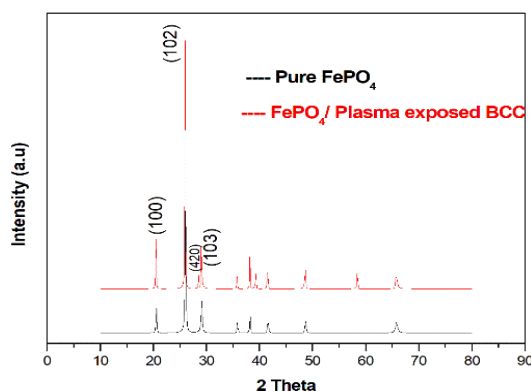


Fig. 2. XRD pattern of Pure  $\text{FePO}_4$  and  $\text{FePO}_4$ / Plasma exposed BCC

### 3.2. Functional group analysis

FTIR analysis revealed possible functional groups in  $\text{FePO}_4$  and also it has been used to identify the changes in crystal structure after the addition of plasma exposed BCC. In Fig. 3 the spectrum of FTIR for pure  $\text{FePO}_4$  gives the certain absorption peaks at the wavelength range of 1020, 582, 630 and 432  $\text{cm}^{-1}$  corresponds to (P-O) vibrational mode, (Fe-O) vibrational mode, weak peaks of symmetric stretching vibrations of  $\text{PO}_4^{3-}$  and (O-P-O) bending modes respectively [22-24].

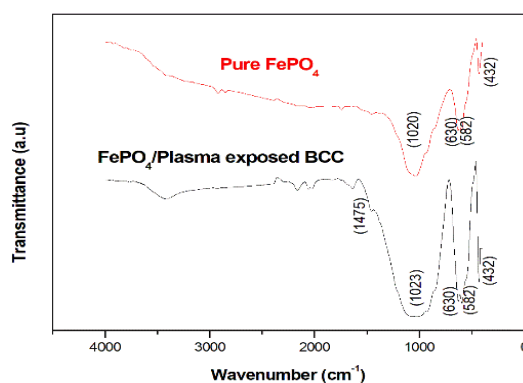


Fig. 3. FTIR pattern of Pure  $\text{FePO}_4$  and  $\text{FePO}_4$ / Plasma exposed BCC.

In  $\text{FePO}_4$ / plasma exposed BCC composite graph the peaks at 1020, 582, 630 and 432  $\text{cm}^{-1}$  shows that the presence of  $\text{FePO}_4$  and also found a new absorption peak at 1475  $\text{cm}^{-1}$  with C=C stretching mode which confirms that the plasma exposed BCC interact with internal lattices of  $\text{FePO}_4$ . From this FT-IR spectrum result reveals that the sample is a group of Phosphate.

### 3.3. SEM analysis

The SEM image shows that the structure of  $\text{FePO}_4$  Nano clusters made up of many nanoparticles are arranged in the sponge-like shape, in Figure.4 the BCC- $\text{FePO}_4$  composite reveals that the CNT is formed with sponge- like  $\text{FePO}_4$  structure which distinctly appeared and declares that the  $\text{FePO}_4$  nanoparticles well dispersed with plasma exposed BCC and delivered embedded  $\text{FePO}_4$  nanoparticles with carbon nanotubes. The presence of main compounds such as Fe, P, O and C in the spectra of EDAX result gives the BCC nanoparticles incorporate with  $\text{FePO}_4$  in well manner.

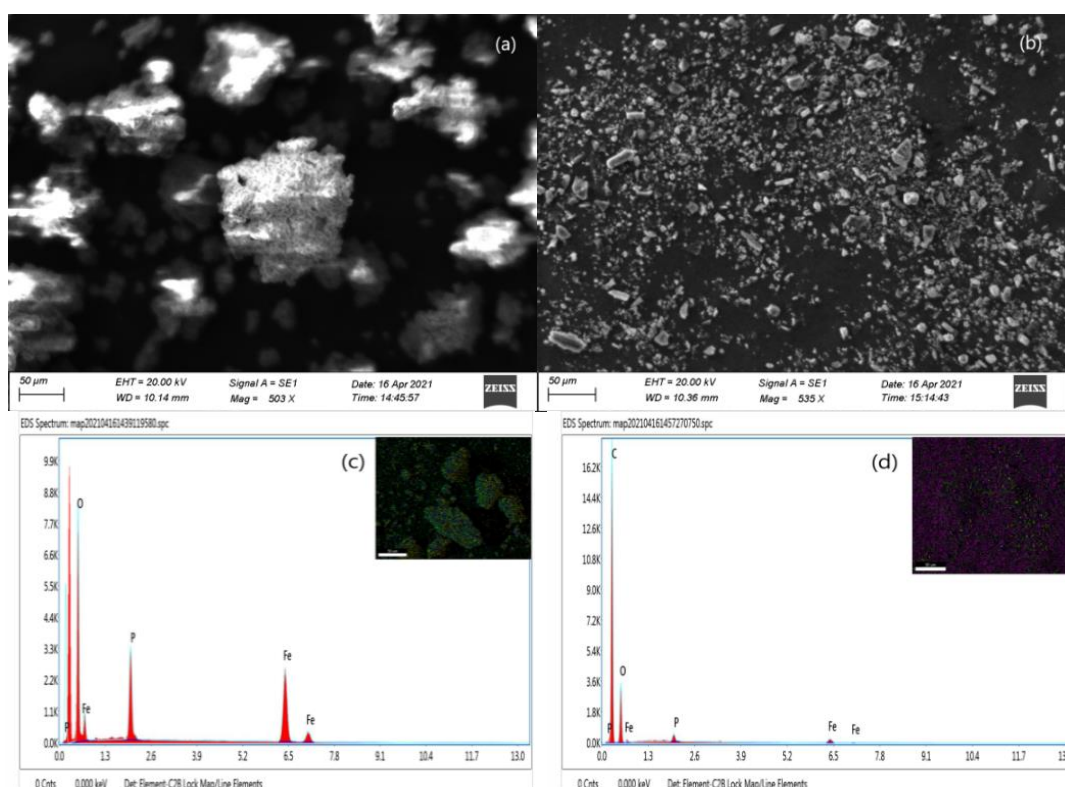


Fig . 4. SEM Images of (a) Pure  $\text{FePO}_4$  (b)  $\text{FePO}_4$ /Plasma exposed BCC  
EDAX Images of (c) Pure  $\text{FePO}_4$  (d)  $\text{FePO}_4$ /Plasma exposed BCC.

## 4. Conclusion

The nano composite cathode material  $\text{FePO}_4$ /Plasma exposed BCC was synthesized by hydrothermal method with suitable annealing procedure, BCC prepared and activated by pyrolysis method. The hybrid  $\text{FePO}_4$ /Plasma exposed BCC cathode material shown the enhanced intensity and surface properties since the particle size was reduced and increased surface area. From the SEM image the Plasma exposed activated BCC incorporate with  $\text{FePO}_4$  and formed carbon nano tubes which gives the enhanced surface area and utilized in energy storage devices.

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## References

- [1] Sang Won Woo, UNIST, 1 (2014).
- [2] Hirokazu Okawa, Junpei Yabuki, Youhei Kawamura, Ichiro Arise, Mineo Sato, *Journal of Materials Research Bulletin* **43**, 1203 (2008).
- [3] M. Sato, S. Tajimi, H. Okawa, K. Uematsu, K. Toda, *J. Solid state Ionics* **152**, 247 (2002).
- [4] K. S. Nanjundaswamy, A. K. Padhi, J. B. Goodenough, *J. Electrochemical Society* **144**, 1188 (1997).
- [5] K. S. Nanjundaswamy, A. K. Padhi, J. B. Goodenough, C. Masquelier, *J. Solid state Chemistry* **135**, 228 (1998).
- [6] Shu-Yi Duan, Jun-Yu Piao, Tian-Qi Zhang, Yong-Gang Sun, *J. NPG Asia materials* **9**, 1 (2017).
- [7] R. Cai, H. Liu, W. Zhang, H. Tan, D. Yang, Y. Huang, *Small* **9**, 1036 (2013).
- [8] Zhongyu Wang, Yangcheng Lu, *J. ACS Omega* **4**, 14790.
- [9] M. Gaberscek, R. Dominko, J. Jamnik, *J. Electrochem. Commun.* **9**, 2778 (2007).
- [10] S. M. Zhang, J. X. Zhang, S. J. Xu, X. J. Yuan, B. C. He, *J. Electrochim. Acta*, **88**, 287 (2013).
- [11] W. X. Wang, P. Y. Gao, S. M. Zhang, J. X. Zhang, *J. Alloys Compd.* **692**, 908 (2017).
- [12] L. Chen, P. Wu, K. W. Xie, J. P. Li, B. Xu, G. P. Cao, Y. Chen, Y. W. Tang, Y. M. Zhou, T. H. Lu, Y. S. Yang, *J. Electrochim. Acta* **92**, 433 (2013).
- [13] C. L. Gong, Z. G. Xue, S. Wen, Y. S. Ye, X. L. Xie, *J. Power Sources* **318**, 93 (2016).
- [14] Y. G. Guo, J. S. Hu, L. Wan, *Adv. Mater.* **20**, 2878 (2008).
- [15] H. Dou, P. Nie, D. R. MacFarlane, *J. Mater. Chem. A* **2**, 19536 (2014).
- [16] Y. L. Liu, Y. H. Xu, X. G. Han, C. Pellegrinelli, Y. J. Zhu, H. L. Zhu, J. Y. Wan, A. C. Chung, O. Vaaland, C. S. Wang, L. B. Hu, *J. Nano Lett.* **12**, 5664 (2012).
- [17] A. Varzi, C. Ramirez-Castro, A. Balducci, S. Passerini, *J. Power Sources* **273**, 1016 (2015).
- [18] K. A. Vijayalakshmi, S. Saveetha, *J. Materials today: Proceedings* **43**, 1456 (2021).
- [19] G. Mingjie, Bamboo Engineering Research Center, E. Nanjing Forestry University, 1 (2004).
- [20] K. A. Vijayalakshmi, K. Vignesh, N. Karthikeyan, *J. Materials Technology: Advanced Functional Materials* **30**, A99 (2015).
- [21] M. Karthik, S. Sathish Kumar, R. Boopathiraja, K. L. Meganathan, T. Sumathi, *J. Mater Sci: Mater Electron*, 1 (2020).
- [22] Zhiyu Wang, Miao Shen, Tiancheng Liu, Chuming Yang, Junhua Li, Dong Qian, *J. Chemical Engineering* **361**, 342 (2019).
- [23] S. Kobayashi, C. A. J. Fisher, A. Kuwabara, Y. Ukyo, Y. Ikuhara, *J. Microscopy* **66**, 1 (2017).
- [24] V. Priyanka, R. Subadevi, M. Siva Kumar, *J. Advanced Engineering and Research Development* **4**, 1 (2017).