

Graphitization induced Structural Transformation of Candle Soot Carbon into Carbon Nano Onion as a Functional Anode for Metal-ion Batteries

Anil D. Pathak^{#*}, Darshna Potphode[#], Chandra S. Sharma

Creative & Advanced Research Based On Nanomaterials (CARBON) Laboratory,

Department of Chemical Engineering,

Indian Institute of Technology Hyderabad, Kandi-502285, Telangana, India

**Corresponding author email: anildaliprasad@iith.ac.in*

[#] Equal contribution

Section S1

The interlayer spacing (d_{002}) (eq.S1) is calculated by Bragg's law, crystallite height (L_c) along c-axis (eq.S2) and crystallite size (L_a) along a-axis (eq.S3) were evaluated by Debye-Scherrer formula.

$$d_{(002)} = \frac{\lambda}{2 \sin \theta_{(002)}} \quad (\text{S1})$$

$$L_c = \frac{K_1 \lambda}{\beta_{(002)} \cos \theta_{(002)}} \quad (\text{S2})$$

$$L_a = \frac{K_2 \lambda}{\beta_{(100)} \cos \theta_{(100)}} \quad (\text{S3})$$

where, λ is a wavelength of 0.154059 nm for Cu K α radiation. $\theta_{(002)}$ and $\theta_{(100)}$ are the Bragg angles corresponding to the diffraction peaks at 25° and 43°, respectively. k_1 (0.94) and k_2 (1.84) are Scherrer parameter for L_c and L_a , respectively. $\beta_{(002)}$ and $\beta_{(100)}$ is the full width at half maximum (FWHM) for corresponding diffraction peak.

Section S2

We used Gaussian suite of computer programs with B3LYP functional and 6-31+G(d,p) basis sets to calculate the highest occupied molecule orbital (HOMO) energy and the lowest unoccupied molecule orbital (LUMO) energy [1]. Here, we have modelled graphitic structure by taking four layers of graphene with interlayer distance of graphitized candle soot carbon calculated from XRD pattern (i.e. d_{200}) at each graphitization temperature and energy gap evaluated based on difference in HOMO and LUMO energy.

Section S3

To determine the appropriate kinetic for the given transformation reaction is relatively straightforward with the use of classical Arrhenius equation [2] as follow:

$$\frac{dL_c}{dt} = k_o \exp\left(-\frac{E_A}{RT}\right) \quad (\text{S4})$$

where L_c is the crystallite size along c axis, k_o is the pre-exponent kinetic constant, E_A is the activation energy of the process, R is the gas constant, T is the absolute temperature and t is the time. The above equation can be modified as:

$$\ln\left(\frac{dL_c}{dt}\right) = \ln(k_o) - \frac{E_A}{RT} \quad (\text{S5})$$

By plotting, $\ln(dL_c/dt)$ versus $(1/T)$, the activation energy during graphitization process, can be estimated from the slope of the graph and pre-exponent kinetic constant from the intersection value on y axis.

Section S4

Therefore, we used the diffraction patterns of graphitized candle soot carbon to evaluate the average crystallite size (d_{XRD}) and microstrain (ε) at each graphitization temperature using the Williamson-Hall relation eq. (6) [3,4].

$$\beta_{(Total)} = \beta_{(size)} + \beta_{(strain)} = \frac{K_1 \lambda}{d_{(XRD)} \cos \theta} + 4\varepsilon \tan \theta \quad (\text{S6})$$

where, $\beta_{(total)}$ is the sum of the full-width at half-maximum (FWHM) of the XRD peak due to FWHM of micro-strain ($\beta_{(strain)}$) and FWHM of crystallite size ($\beta_{(size)}$). K_1 the Debye-Scherrer

constant (0.94), λ the incident X-ray wavelength, and θ the diffraction angle.

By plotting $\frac{\beta_{(total)} \cos \theta}{k_1 \lambda}$ along x-axis and $\frac{4\varepsilon \sin \theta}{k_1 \lambda}$ along y-axis, the micro-strain (ε) and crystallite size (d_{XRD}) may be estimated from the slope of the line and the intersection with the vertical axis, respectively [5,6]

References

- 1] J. Tirado-Rives, W.L. Jorgensen, Performance of B3LYP density functional methods for a large set of organic molecules, *Journal of Chemical Theory and Computation*. 4 (2008) 297–306. <https://doi.org/10.1021/ct700248k>.
- 2] J.A. Newell, D.D. Edie, E.L. Fuller, Kinetics of carbonization and graphitization of PBO fiber, *Journal of Applied Polymer Science*. 60 (1996) 825–832. [https://doi.org/10.1002/\(SICI\)1097-4628\(19960509\)60:6<825::AID-APP5>3.0.CO;2-L](https://doi.org/10.1002/(SICI)1097-4628(19960509)60:6<825::AID-APP5>3.0.CO;2-L).
- 3] G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminium and wolfram, *Acta Metallurgica*. 1 (1953) 22–31. [https://doi.org/10.1016/0001-6160\(53\)90006-6](https://doi.org/10.1016/0001-6160(53)90006-6).
- 4] I.F. Cruz, C. Freire, J.P. Araújo, C. Pereira, A.M. Pereira, Multifunctional Ferrite Nanoparticles: From Current Trends Toward the Future, 2018. <https://doi.org/10.1016/B978-0-12-813904-2.00003-6>.
- 5] M.P. Proenca, C.T. Sousa, A.M. Pereira, P.B. Tavares, J. Ventura, M. Vazquez, J.P. Araujo, Size and surface effects on the magnetic properties of NiO nanoparticles, *Physical Chemistry Chemical Physics*. 13 (2011) 9561–9567. <https://doi.org/10.1039/c1cp00036e>.
- 6] C. Fernandes, C. Pereira, M.P. Fernández-García, A.M. Pereira, A. Guedes, R. Fernández-Pacheco, A. Ibarra, M.R. Ibarra, J.P. Araújo, C. Freire, Tailored design of $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ nanoferrites: A new route for dual control of size and magnetic properties, *Journal of Materials Chemistry C*. 2 (2014) 5818–5828. <https://doi.org/10.1039/c4tc00429a>.