

Supporting Information

Elucidating the role of Cobalt Nanoparticles and Mn-phosphate in Etched ZIF-67/Phthalimide-NC and Phthalimene Oxide for Supercapacitor and Electrochemical Oxygen Evolution Reaction

Tapan Dey^a, Nitish Kumar^b, Rahul Patil^a, Prakash Kumar Pathak^b; Sudip Bhattacharjee^c, Praveen Yadav^d, Asim Bhaumik^c, Rahul R. Salunkhe^{b*}, Saikat Dutta^{a*}

^aElectrochemical Energy & Sensor Research Laboratory,
Amity Institute of click chemistry Research and studies,
Amity University Noida, Uttar Pradesh 201313, India
E-mail: sdutta2@amity.edu

^bMaterials Research Laboratory,
Department of Physics,
Indian Institute of technology Jammu,
Jammu and Kashmir, India
E-mail: rahul.salunkhe@iitjammu.ac.in

^cSchool of Materials Science,
Indian association for cultivation of science,
Jadavpur Kolkata, India

^dRaja Ramanna Centre for Advanced Technology (RRCAT),

Dept. of Atomic Energy,

Indore 452013, MP, India

Experimental Procedures

Chemicals:

Potassium-Phthalimide, ands U.S. Standard testing sieve are directly purchased from sigma Aldrich. These all are used without further purification. **Preparation of K-Ph-NC:**

Potassium phthalimide salt was pyrolyzed in an argon (Ar) atmosphere at different temperatures, followed by an acid wash to prepare large-size carbon nanosheets (LCNs). K-Ph- NC was prepared by direct pyrolysis of commercially available K-phthalimide at 700 °C for 2 h under an Argon atmosphere with a heating rate of 5 °C min⁻¹. After cooling down to room temperature, the carbon was washed with 1 M HCl solution, DI water, and ethanol, respectively.

Preparation of e-ZIF-67/K-Ph-NC

According to the previous publication, polystyrene (PS) nanospheres having carboxylic acid modifications on their external surface were synthesized. After that, ZIF-67 nanoparticles were put together on the PS nanosphere's surface to create a composite called PS/ZIF-67. The PS core was then removed from the composite by soaking it in N, N-dimethyl formamide, giving an itched-ZIF-67 (denoted as e-ZIF-67). The e-ZIF-67 spheres were pyrolyzed at 800°C under an Ar environment. The supercapacitor results of e-ZIF-67/K-Ph-NC (containing Co atoms) is compared with potassium phthalimide carbon nanosheet.

Preparation K-Ph-Oxide (K-Ph-O) from K-Ph-NC

Briefly, K-Ph-NC (3.0 g) was suspended in a mixture of concentrated H_2SO_4 (360 mL) and H_3PO_4 (40 mL) under continuous stirring for 0.5 h. The mixture was placed in an ice bath to keep the temperature below 10 °C and KMnO_4 (18 g) was slowly added by stirring. Subsequently, the mixture was transferred to a 500 mL round bottom flask and heated at 50 °C under constant stirring for 12 h. After cooling to room temperature, the resulting dark solution containing the product was poured onto ice (~450 mL) containing 30% H_2O_2 (3 mL). The resulting mixture (yellowish-brown color) was then passed through a U.S. Standard testing sieve (Sigma Aldrich, 300 μm) and then filtered through a polyester fiber to separate larger particles (unconverted graphite). The collected filtrate containing KPO was centrifuged (8500 rpm, 10 min), and the supernatant was decanted away. The collected KPO was washed in succession with water (200 mL), dilute HCl (30%, 200 mL), and ethanol (200 mL). After each wash, KPO was collected by centrifugation (8500 rpm, 10 min), followed by coagulation with 200 mL of diethyl ether. The resulting suspension was centrifuged to obtain pure KPO which was dried at room temperature under a vacuum.

Electrochemical Analysis

Electrode preparation, electrochemical analysis, device construction, including calculations were carried out according to our recent report.¹ For three-electrode measurements, the graphite electrode was coated with active material (mass loading of 0.8 mg). The platinum wire was used as the counter electrode, while a standard Ag/AgCl electrode was used as the reference electrode. All three electrode measurements were carried out in a 3 M KOH aqueous electrolyte. The stainless-steel circular electrodes with active material (mass loading of 2.4 mg) were utilized for two-electrode measurements.

In the study, graphite electrodes served as the current collector in the three-electrode setup, while carbon cloth electrodes were used for two-electrode measurements. The graphite substrate with an area of 1 cm^2 was polished using zero-size polish paper and rinsed with ultrapure water. The substrates were then ultrasonicated in a 0.5 M HCl solution for 15 minutes, followed by ultrapure water for 30 minutes, then dried overnight at $80 \text{ }^\circ\text{C}$. The ultra-micro balance (Mettler Toledo) was used to determine the mass of each electrode. To create the slurry, 85% active material, 10% carbon black and 5% PVDF were mixed in an NMP solution, and the resulting mixture was drop cast onto the electrodes and dried at $80 \text{ }^\circ\text{C}$ for 5 hours. For the two-electrode measurements, disk-shaped carbon cloth electrodes with a diameter of 15 mm were cutted using disk cutter. The active mass loading for two electrode measurements was approximately 1.5 mg per electrode was used.

The electrochemical measurements were carried out in both a three-electrode and symmetric two-electrode setup. The drop-cast NPC on the graphite electrode served as the working electrode in the three-electrode cell, while platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively. A 3M KOH aqueous solution was used as the electrolyte for the measurement, and an electrochemical workstation (CHI 1150C, CH Instruments, USA) was used to conduct all the electrochemical measurements. Cyclic voltammetry (CV) results were examined within the potential range of -1 V to 0 V. In addition, the symmetric two-electrode setup was constructed using the HS flat test cell (Hohsen Corp.) with carbon cloth electrodes. CV and galvanostatic charge-discharge (GCD) measurements analyzed the material's performance.

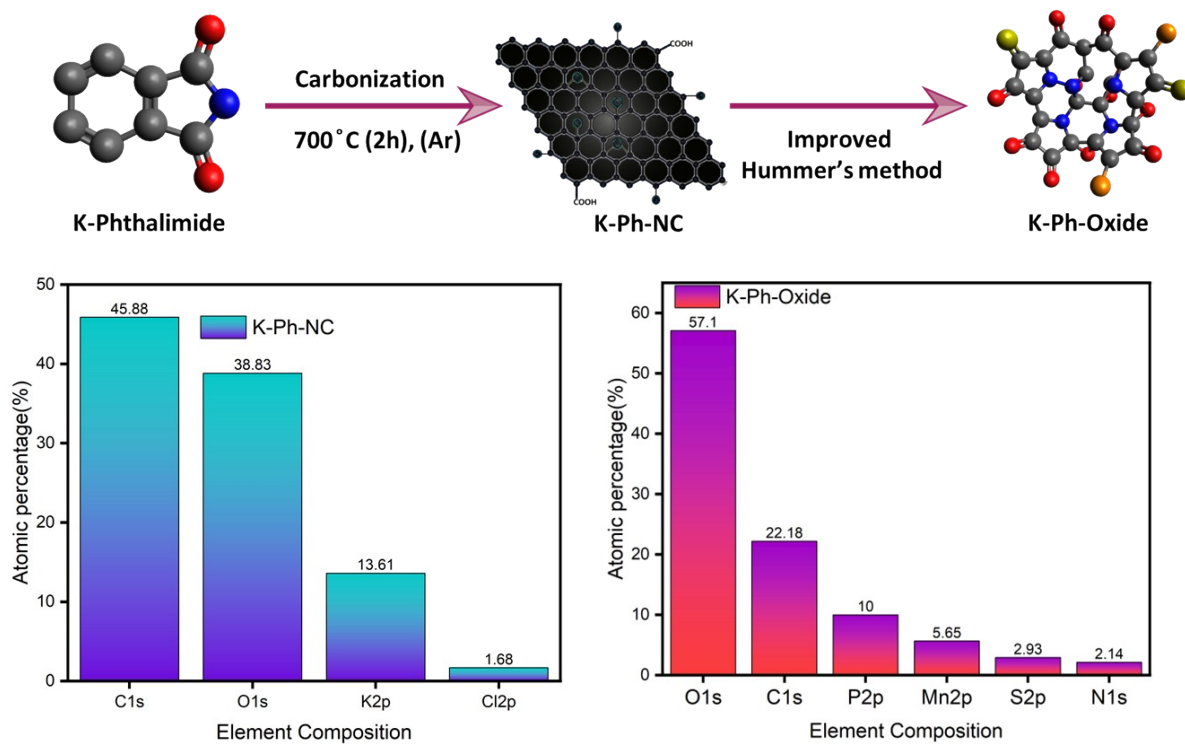


Figure S1. Percentage elemental composition of (b) K-Ph-NC and (c) K-Ph-Oxide showing graphene oxide like phthalimene oxide formation with rise in surface oxygen functional groups.

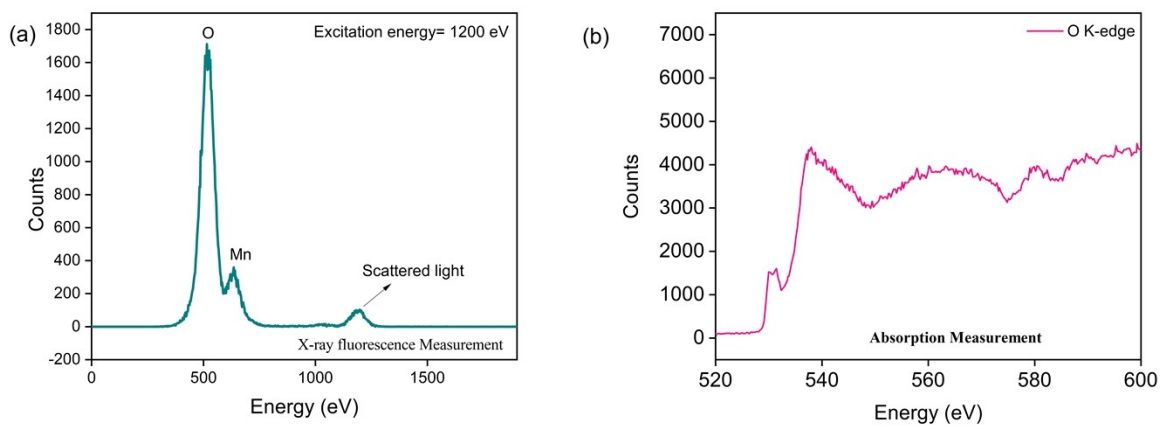


Figure S2. (a) Soft X-ray fluorescence spectra for K-Ph-Oxide. (b) X-ray fluorescence measurement of O K-edge spectra for K-Ph-Oxide.

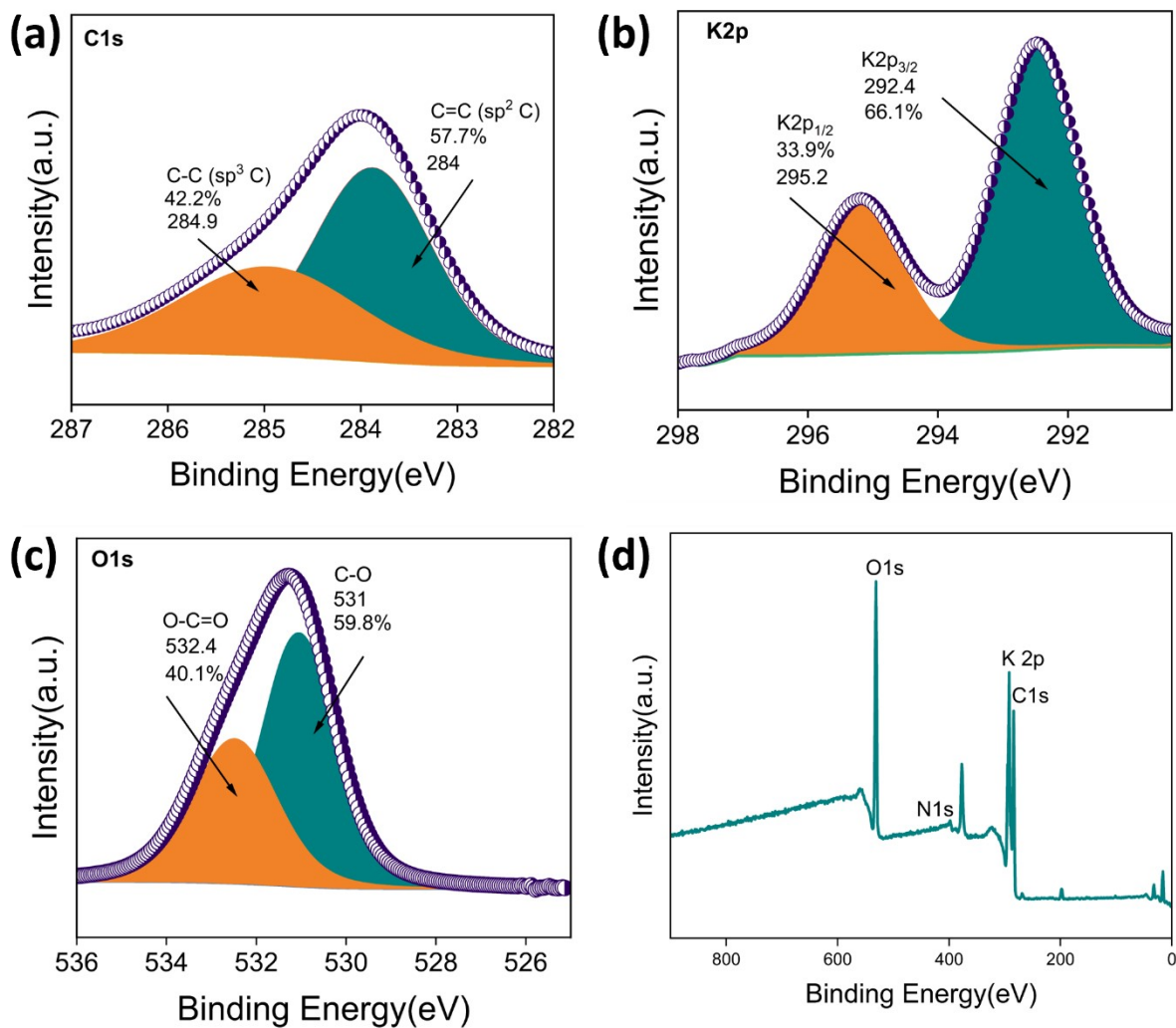


Figure S3. Deconvoluted XPS spectral peak of (a) C1s, (b) K2p, (c) O1s and (d) XPS survey peaks for K-Ph-NC.

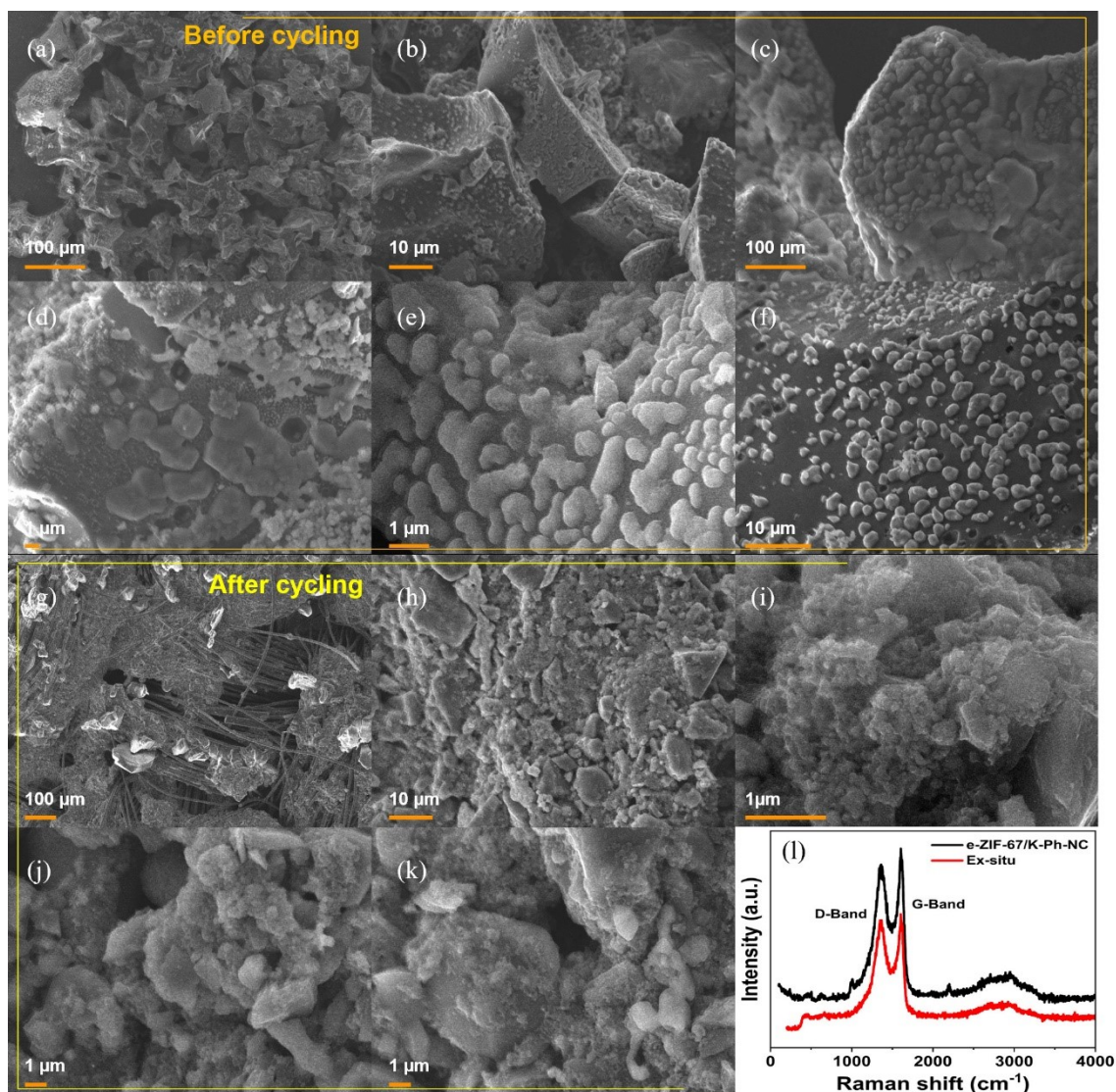


Figure S4. SEM images of e-ZIF-67/K-Ph-NC before cycling at (a) 100 μm , (b) 10 μm , (c) 100 μm , (d) 1 μm , (e) 1 μm and (f) 10 μm . Ex-situ SEM images of e-ZIF-67/K-Ph-NC after 250 cycles of CV at (g) 100 μm , (h) 10 μm , and (i-k) 1 μm . (l) Raman shifts of e-ZIF-67/K-Ph-NC before (black) and after (red) 250 cycles of galvanometric charge -discharge.

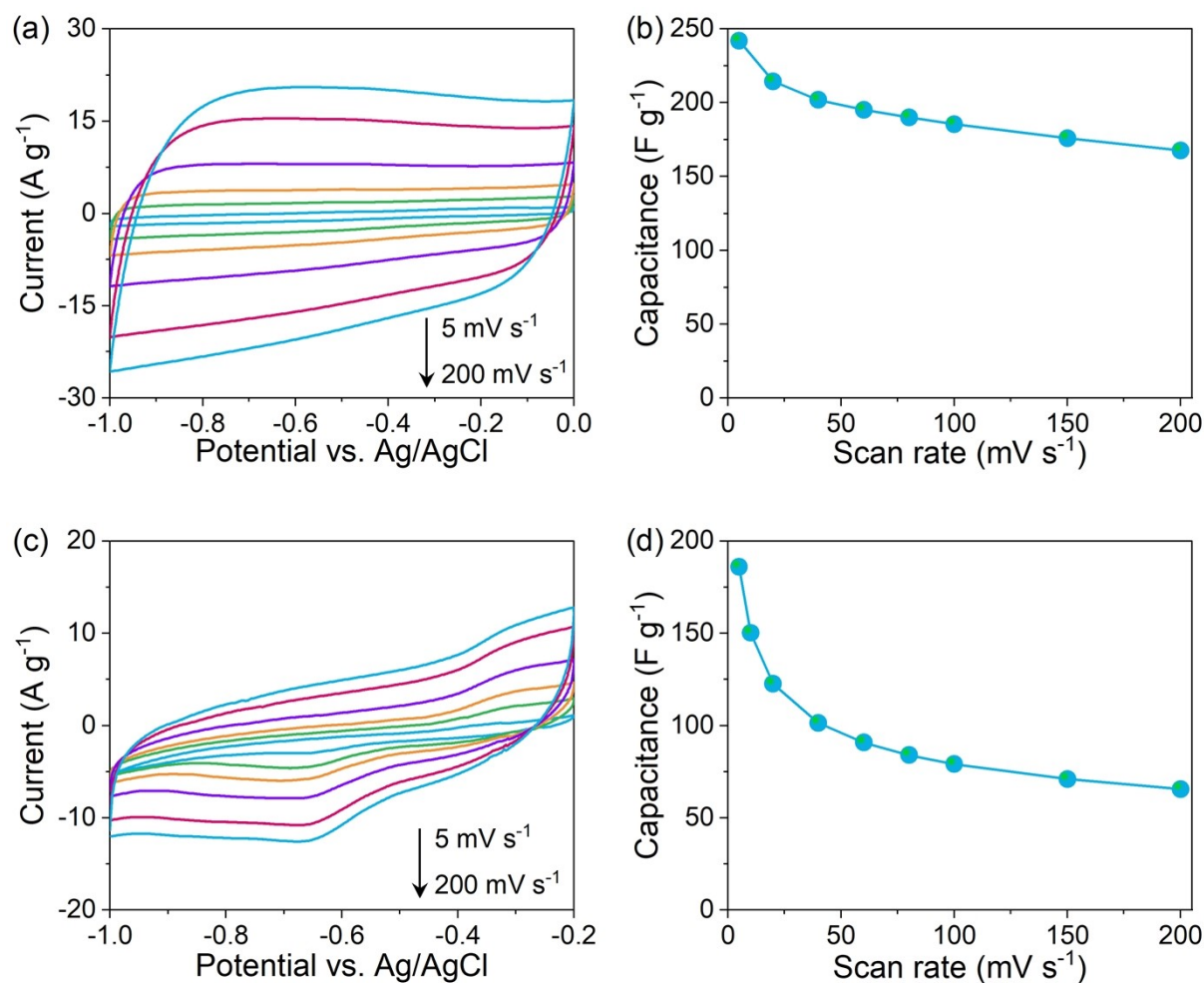


Figure S5. Three electrode performances for K-Ph-NC (a) CV curves at different scan rates varying from 5 to 200 mV s⁻¹. (b) capacitance retention curve with the scan rate. Three electrode performances for K-Ph-Oxide (c) CV curves at different scan rates varying from 5 to 200 mV s⁻¹ and (d) capacitance vs scan rate curve.

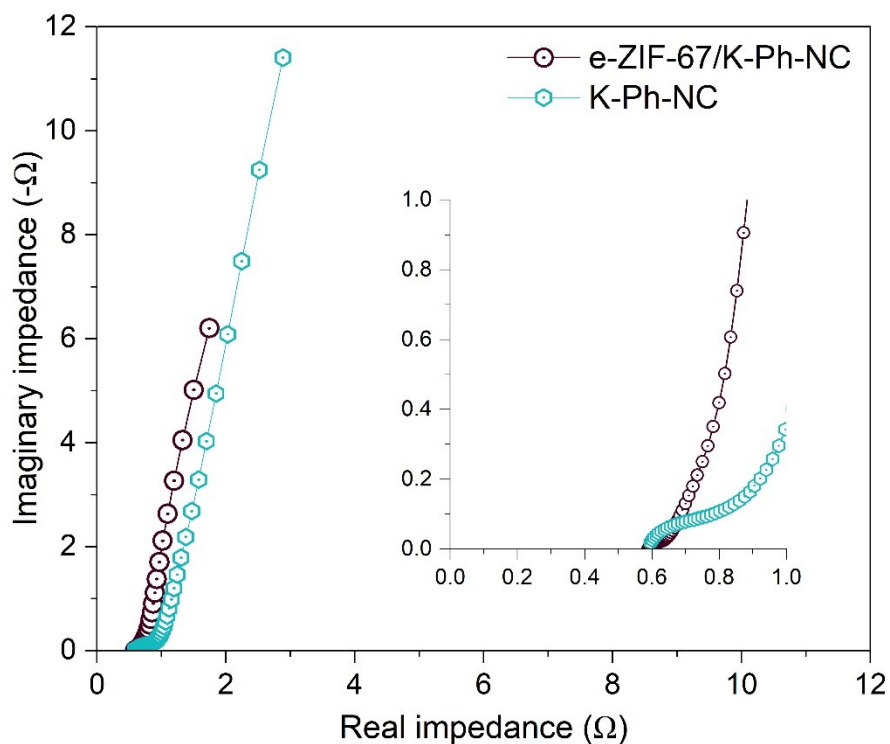


Figure S6. Comparative Nyquist plot for samples e-ZIF-67/K-Ph-NC and K-Ph-NC, inset shows zoomed-in view for impedance comparison.

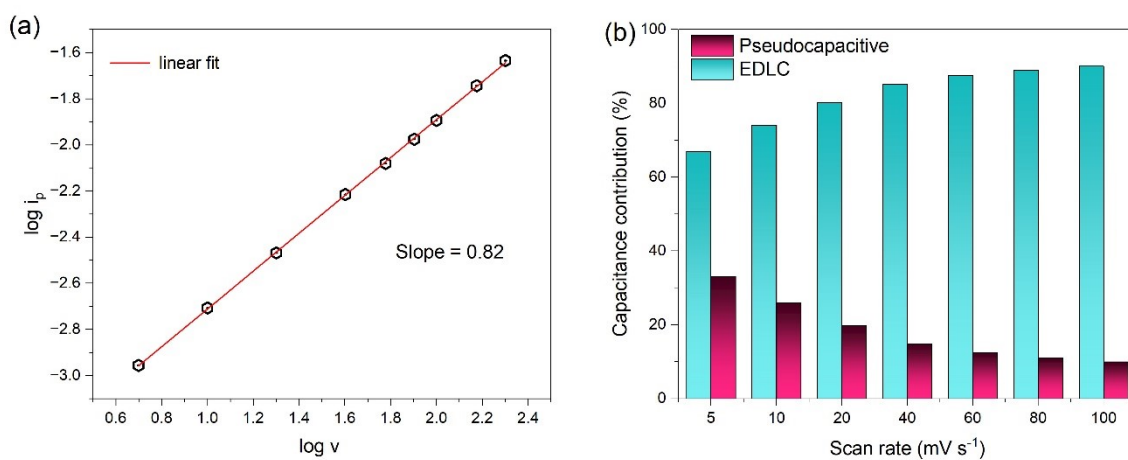


Figure S7. Charge storage mechanism study using power law and Dunn's method for sample e-ZIF-67/K-Ph-NC (a) "b" value plot, and (b) Pseudocapacitive and EDLC contribution and different scan rates.

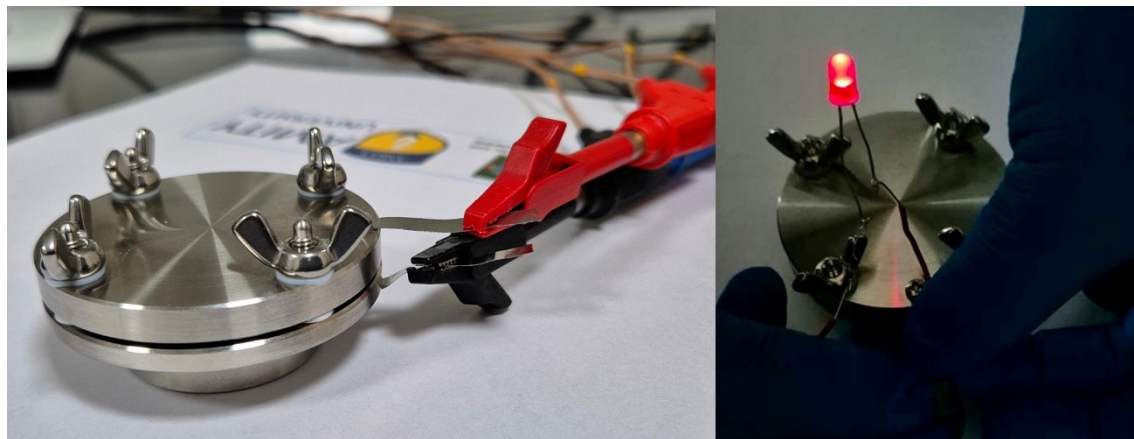


Figure S8. Photographs of (a) supercapacitor device and (b) lighting up of red LED of 1.5 V.

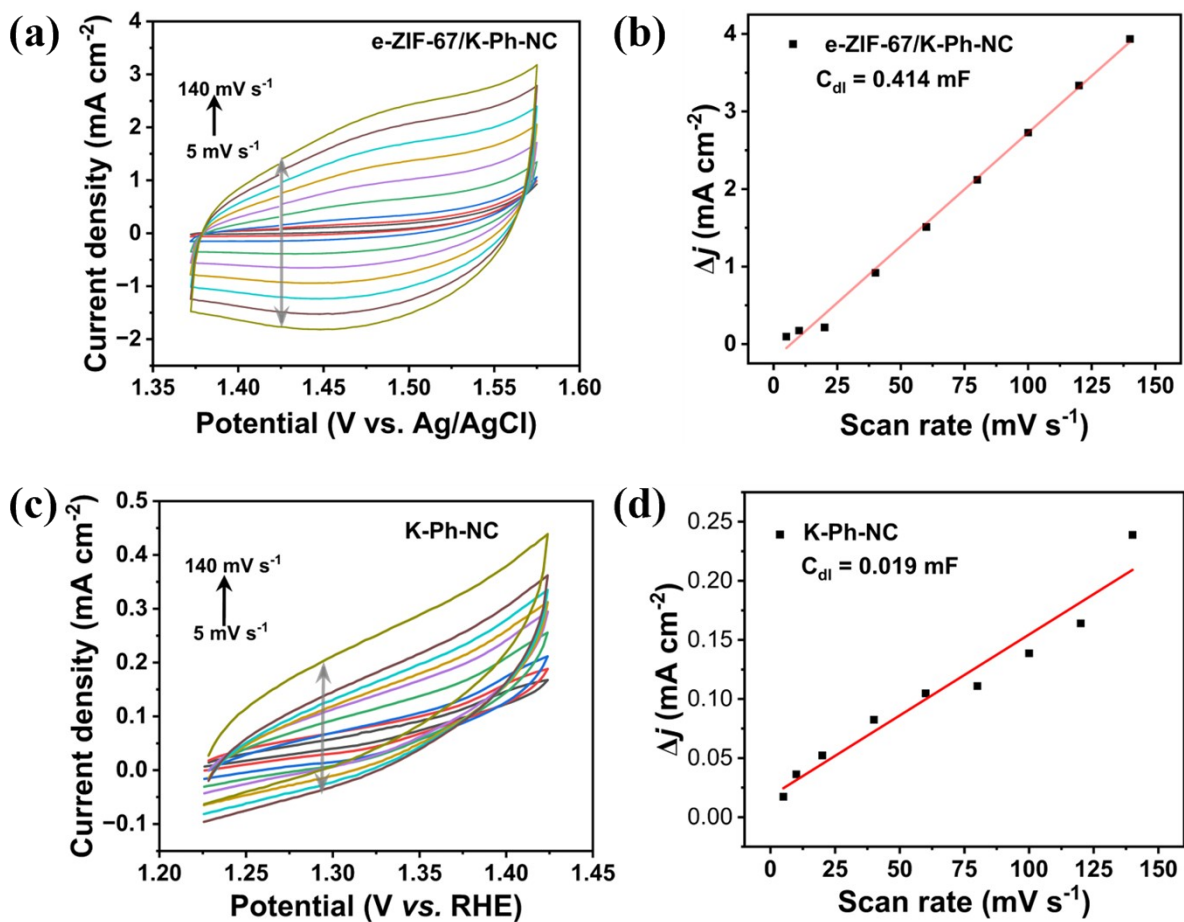


Figure S9. CV scans in a non-Faradaic potential range of (a) e-ZIF-67/K-Ph-NC and (c) K-Ph-NC in 1 M KOH at scan rate of 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} , 40 mV s^{-1} , 60 mV s^{-1} , 80 mV s^{-1} , 100 mV s^{-1} , 120 mV s^{-1} , 140 mV s^{-1} . Double layer capacitance (C_{dl}) for (b) e-ZIF-67/K-Ph-NC and (d) K-Ph-NC. Half of the differences in current density variation ($\Delta J = (J_{\text{cathodic}} - J_{\text{anodic}})/2$) at a potential of 0.94 V vs RHE plotted against scan rate fitted to a linear regression enables the determination of double-layer capacitance (C_{dl}). C_{dl} value calculated from the slopes of the linear fitting of Δj (mA cm^{-2}) vs. scan rate (mV s^{-1}).

Table 1. Comparative OER table of e-ZIF-67/K-Ph-NC with other Co-based system.

SL. No.	Active site	Overpotential at 10 mA cm ⁻²	Reference
1.	e-ZIF-67/K-Ph-NC	450 mV	This work
2.	Co-CoO@C	374 mV	2
3.	P,Mo,-O-Co/PNC	373 mV	3
4.	Mo@Co ₃ O ₄	490 mV	4
5.	RD-ZIF-67-RT	540 mV	5
6.	Co-Pi NA/Ti	450 mV	6
7.	Co ₃ (PO) ₄	590 mV	7

References

1. N. Kumar, T. A. Wani, P. K. Pathak, A. Bera and R. R. Salunkhe, *Sustain. Energy Fuels*, 2022, **6**, 1762-1769.
2. S. Fathima T.K, A. Ghosh and S. Ramaprabhu, *Int. J. Hydrogen Energy*, 2024, **49**, 780-793.
3. T. Dey, A. Rajput, G. Jhaa, B. M. Matsagar, N. C. R. Chen, N. Kumar, R. Salunkhe, K. C. W. Wu, B. Chakraborty and S. Dutta, *ChemNanoMat*, 2024, **10**, e202400089.
4. L. Sun, M. Feng, Y. Peng, X. Zhao, Y. Shao, X. Yue and S. Huang, *J. Mater. Chem. A*, 2024, **12**, 8796-8804.
5. J. Mor, J. Prakash, M. K. Thota, U. K. Goutam and S. K. Sharma, *J. Solid State Chem.*, 2024, **335**, 124638.
6. L. Xie, R. Zhang, L. Cui, D. Liu, S. Hao, Y. Ma, G. Du, A. M. Asiri and X. Sun, *Angew. Chem. Int.l Ed.*, 2017, **56**, 1064-1068.
7. H. S. Ahn and T. D. Tilley, *Adv. Funct. Mater.*, 2013, **23**, 227-233.