Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cobalt Phosphide (Co_2P) Encapsulated in Nitrogen-rich Hollow Carbon Nanocages with Fast Rate Potassium Ion Storage

Characterization Techniques

Morphology, structure and composition of electrode materials were investigated using transmission electron microscopy (TEM, FEI TECNAI G2 TF20ST), high-resolution TEM (HRTEM), electron energy loss spectroscopy (EELS), X-ray Diffraction (XRD, PANalytical Empyrean X-ray Diffractometer) and Raman spectroscopy (WITec, Nd:YAG laser with λ = 532 nm). The chemical states of different ionic species within the samples were further analyzed using X-ray photo-electron spectroscopy (XPS, AXIS ULTRA) technique.

Electrochemical tests were carried out using CR-2032 coin cells. The working electrodes were prepared by casting the slurry of active material (Co_2P@NCC), carbon black and polyvinylidene difluoride binder (8:1:1 in weight ratio) on a copper foil and drying out the solvent in vacuum oven at 80 °C. The mass loading of the active material was about 1 mg cm^{-2}. An electrolyte of 0.8 M KPF_6 in ethylene carbonate (EC) / diethyl carbonate (DEC) / propylene carbonate (PC) (2:1:2 vol/vol/vol) without any additives was used, along with a potassium metal foil as a counter electrode. The galvanostatic charge-discharge tests were tested on Abrin battery cycler. The CV curves were recorded on a Princeton electrochemical workstation. All tests were conducted at room temperature.

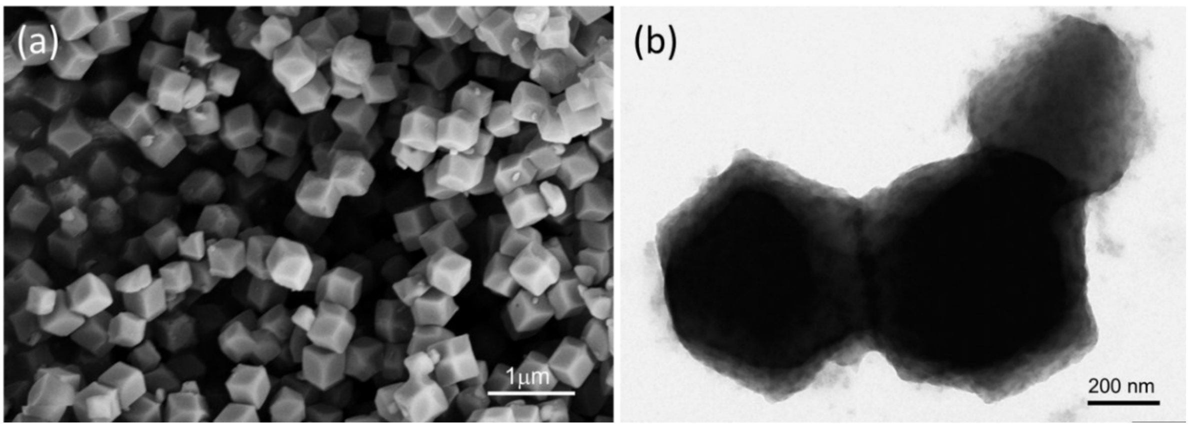

Fig. S1 Morphological characterization of as-synthesized ZIF-67 precursors. (a) shows the Field Emission Scanning Electron Microscope (FESEM) image and (b) shows corresponding TEM image of rhombic dodecahedral shaped microstructures.

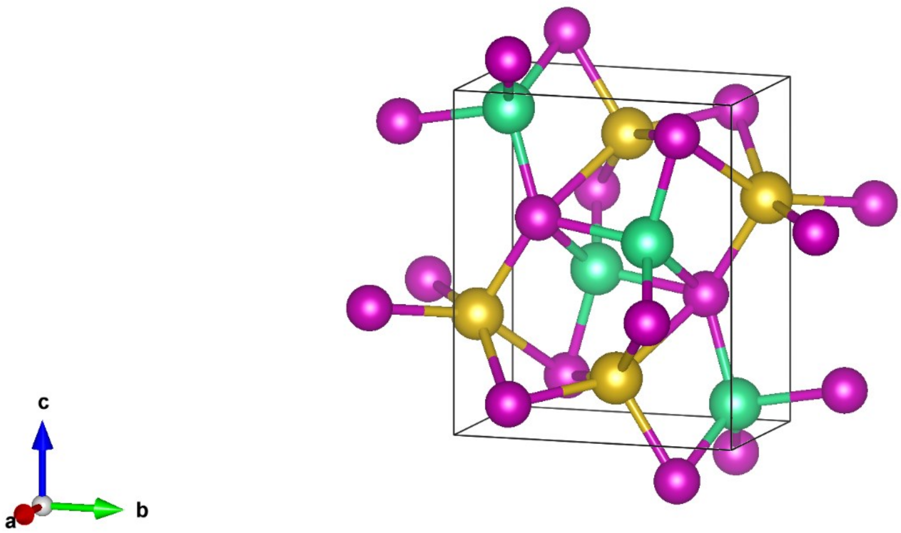

Fig. S2 A ball-stick model of the primitive unit cell of orthorhombic Co_2P which contains edge-sharing CoP_4 tetrahedra and CoP_5 pentahedra, resulting in nine-coordinate P atoms.[1] In the Figure, tera- and penta- co-ordinated Co atoms are labelled with different colors. (Gold Co atoms → CoP_5, Green Co atoms → CoP_4), whereas Pink atoms represent P.

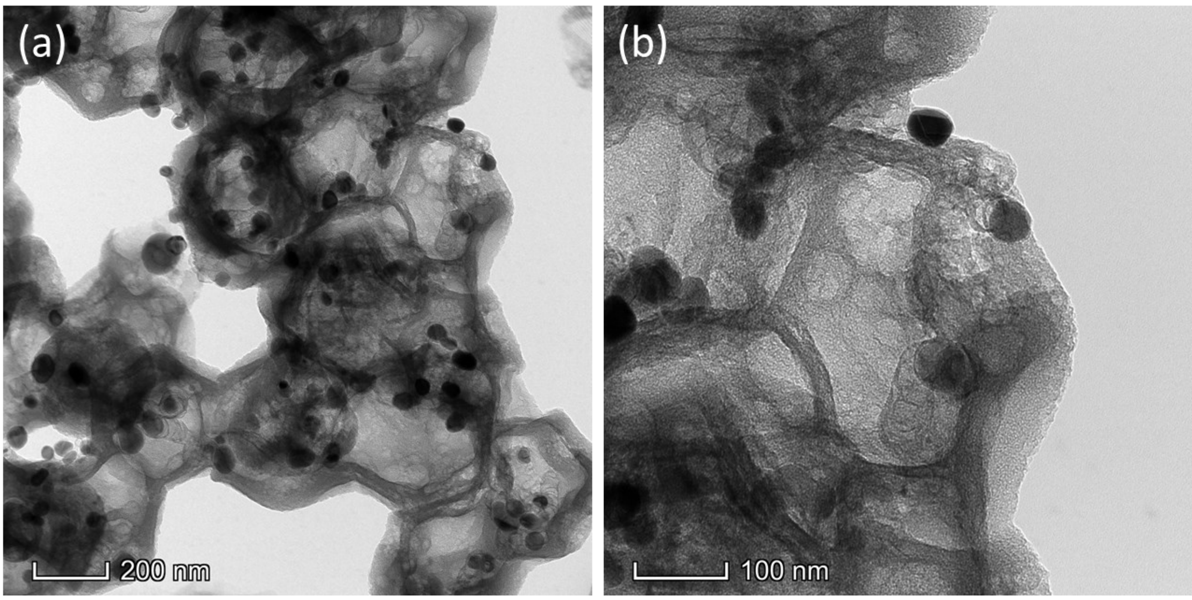

Fig. S3 (a) and (b) TEM images of the Co_2P@NCC nanocomposite. The dark and spheroidal-shaped Co_2P nanoparticles are encapsulated inside the hollow carbon nanocages, forming a 'rattle-like' structure.

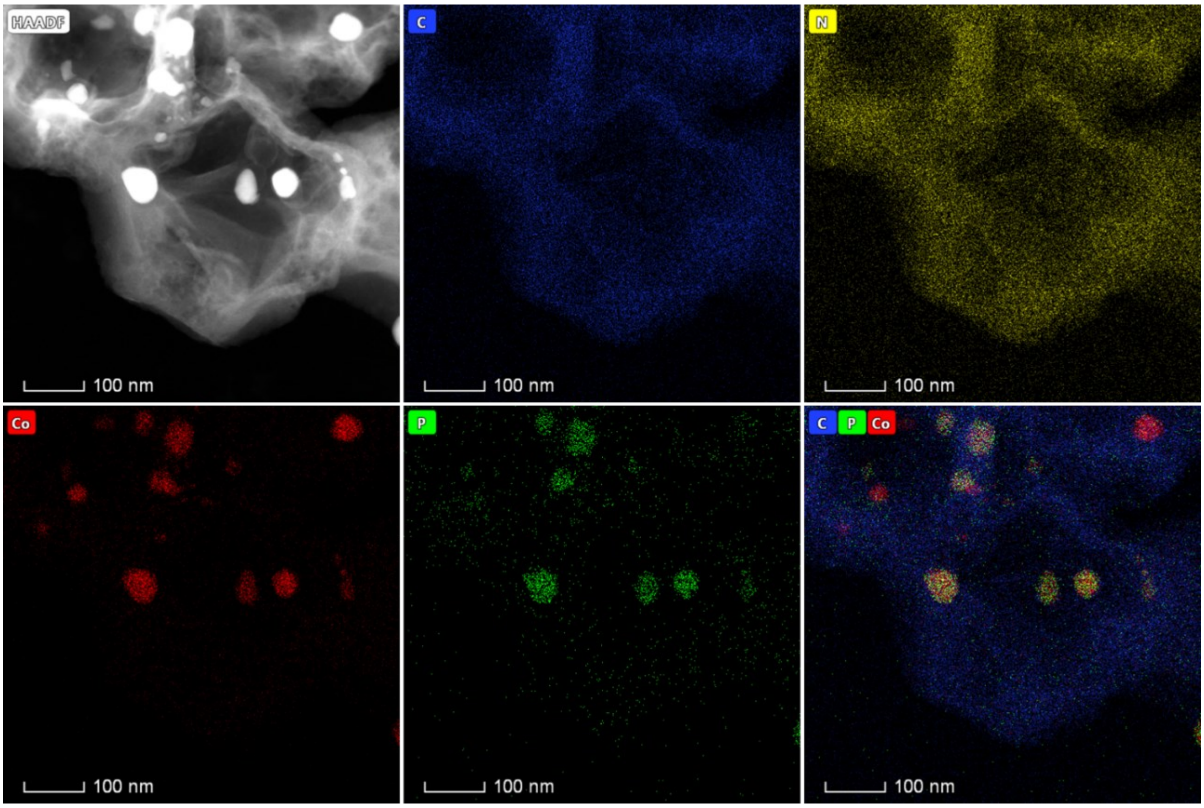

Fig. S4 EELS color mapping of various constituent elements like, C, N, Co, and P of the Co_2P/NCC nanocomposites. The study confirms uniform doping of N throughout the whole NCC matrix and presence of Co and P in constituting the Co_2P nanoparticles. One-to-one correspondence between Co and P elemental maps suggests absence of any metallic Co.

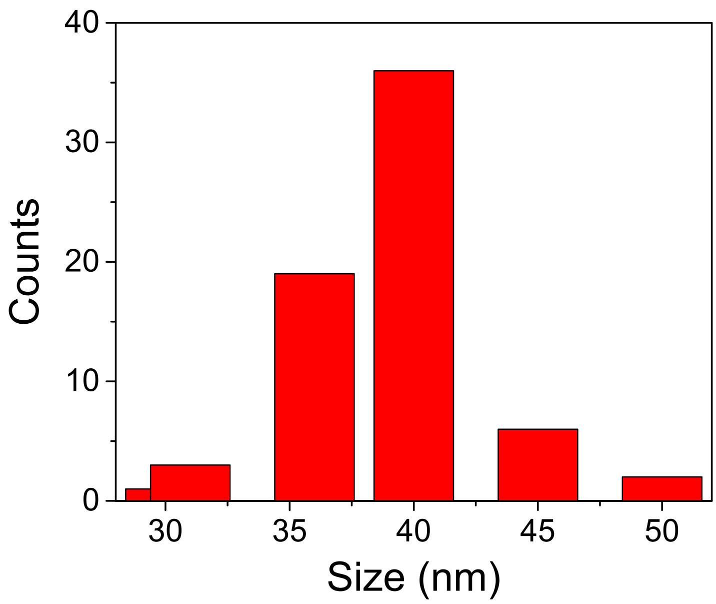

Fig. S5 Particle size distribution of Co_2P nanoparticles in NCC matrix.

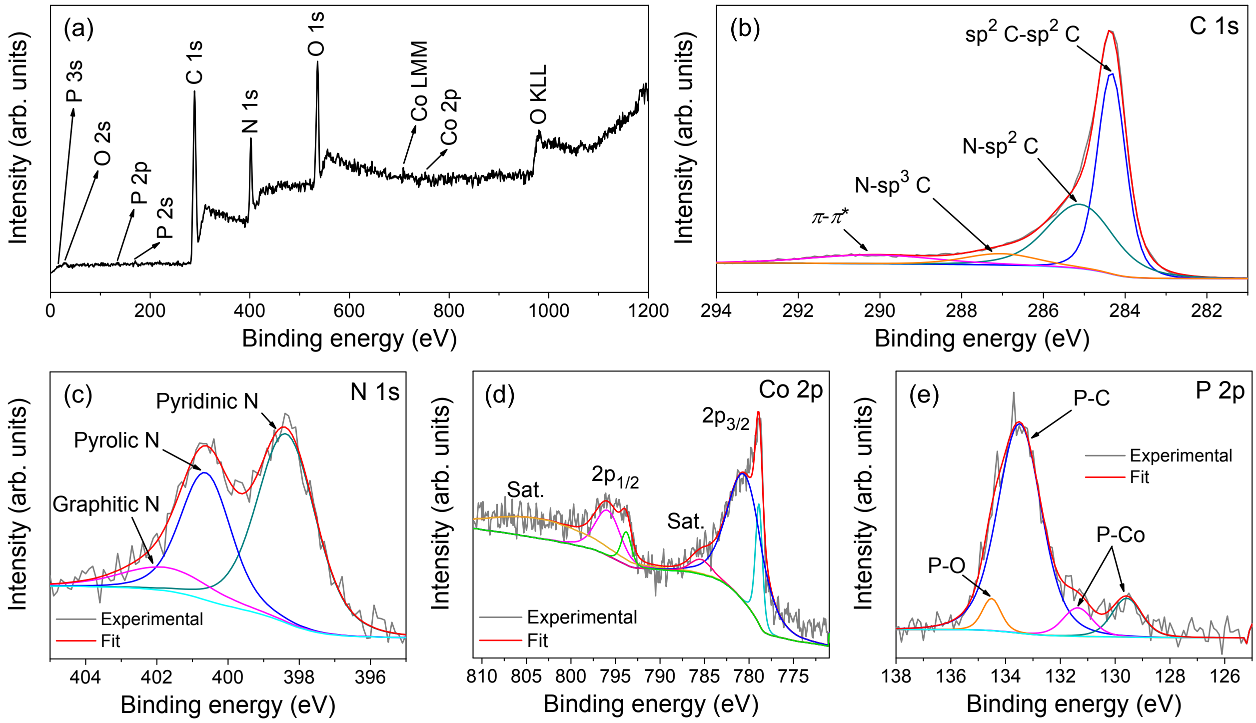

Fig. S6 Core-level XPS spectra of Co_2P@NCC. (a) Low resolution survey spectrum. (b) - (e) High resolution XPS spectra of C 1s, N 1s, Co 2p, and P 2p, respectively.

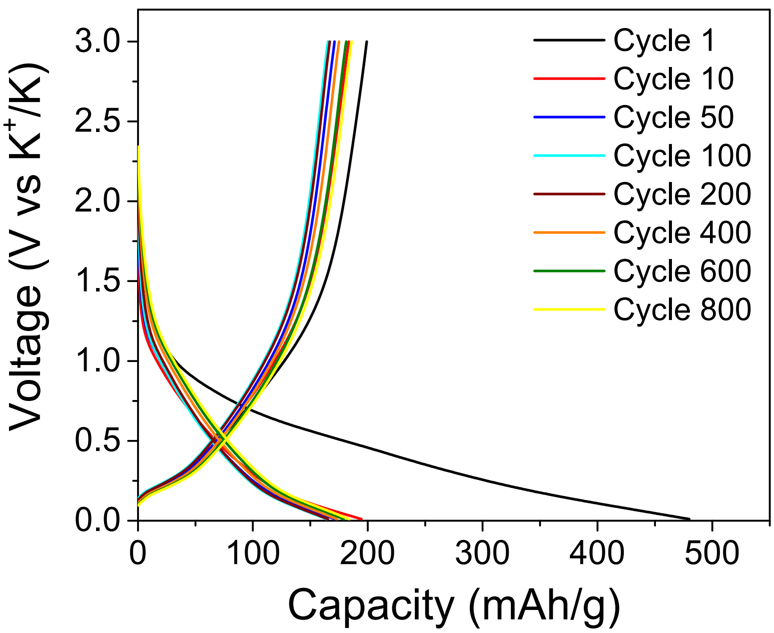

Fig. S7 Representative charge-discharge profiles recorded during the assessment of cycling performance of the Co_2P@NCC anode at a current density of 100 mA/g.

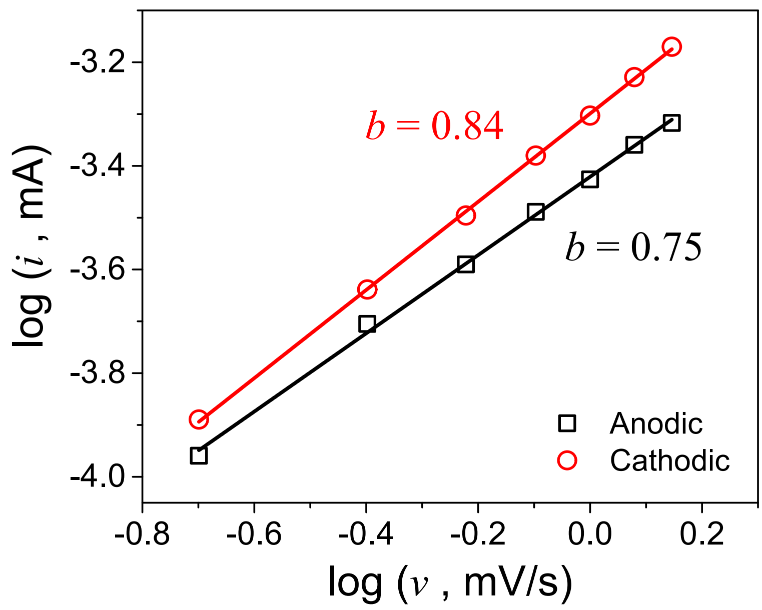

Fig. S8 Determination of *b*-values for selected cathodic and anodic processes during CV measurements.

Table S1 A comparison of rate capability of Co_2P/NCC nanocomposite versus state-of-the-art cobalt-based, phosphide-based, and carbon-based anodes from recently published literature, tested vs. K/K^+.

Sl. No.	Material	Voltage window	1st reversible discharge capacity (1st CE)	Rate performance	Ref. # Publish year
1.	**Co_2P/NCC**	**0.01-3 V**	**270 mA/g @ 50 mA/g (42.1%)**	**196 mAh/g @ 100 mA/g 137 mAh/g @ 500 mA/g 91 mAh/g @ 2 A/g**	**This work**
2.	N, P-Codoped Porous Carbon Sheets/CoP Hybrids	0.01-3 V	174 mAh/g @ 50 mA/g (19.6%)	134 mAh/g @ 100 mA/g 94 mAh/g @ 500 mA/g 54 mAh/g @ 2 A/g	[2] 2018
3.	C-Co_2P@rGO	0.01-3 V	143 mAh/g @ 20 mA/g (~35%)	~100 mAh/g @ 100 mA/g ~ 75mAh/g @ 500 mA/g 50 mAh/g @ 2 A/g	[3] 2019
4.	ZIF-8@ZIF-67-Derived Nitrogen-Doped Porous Carbon	0.01–2.5 V	~200 mAh/g @ 50 mA	150 mAh/g @ 500 mA/g ~175 mAh/g @ 100 mA/g ~115 mAh/g @ 2 A/g	[4] 2020
5.	Oxidizing-acid treated melamine foam	0.01-3 V	~200 mAh/g @ 50 mA/g (26.7%)	170 mAh/g @ 100 mA/g 110 mAh/g @ 500 mA/g 80 mAh/g @ 1 A/g	[5] 2019

	carbons (OMFCs)-60				
6.	CoSe-S@Carbon	0.01-3 V	~225 mAh/g@ 100 mA/g	~225 mAh/g@ 100 mA/g 3.3 mAh/g @ 2 A/g	[6] 2020
7.	Pristine $Co_{0.85}Se$ hollow cubes	0.01-2.5V	233 mAh/g @ 50 mA/g	173 mAh/g @ 100 mA/g 138 mAh/g @ 500 mA/g 110 mAh/g @ 1 A/g	[7] 2020
8.	Co@graphitic nanotubes	0.01-3 V	200 mAh/g @ 50 mA/g	121 mAh/g @ 100 mA/g 49 mAh/g @ 500 mA/g 21 mAh/g @ 1 A/g	[8] 2020
9.	Cobalt terephthalate (CoTP)/Super P composite	0.1-2 V	216 mAh/g @ 60 mA/g	100 mAh/g @ 120 mA/g 27 mAh/g @ 480 mA/g	[9] 2017
10.	$Co_{0.85}Se$-QDs/C-2	0.01-2.5 V	~180 mAh/g @ 50 mA/g	~110 mAh/g @ 100 mA/g ~75 mAh/g @ 500 mA/g	[10] 2019
11.	FeP@C nano-boxes	0.01-2.5 V	201 mAh/g @ 100 mA/g (47%)	101 mAh/g @ 500 mA/g 65 mAh/g @ 1 A/g 37 mAh/g @ 2 A/g	[11] 2019
12.	FeP nanocubes	0.01-2.5 V	160 mAh/g @ 100 mA/g	75 mAh/g @ 500 mA/g 50 mAh/g @ 1 A/g 35 mAh/g @ 2 A/g	[11] 2019
13.	FeP/C composite	0.01-3 V	218 mAh/g @ 50 mA/g (45.1%)	186 mAh/g @ 100 mA/g 113 mAh/g @ 500 mA/g 79 mAh/g @ 1 A/g	[12, 13] 2020, 2019
14.	N–CNF@FeP	0.01-3 V	222 mAh/g @ 50 mA/g (57%)	195 mAh/g @ 100 mA/g 140 mAh/g @ 400 mA/g 103 mAh/g @ 800 mA/g	[14] 2020
15.	Bimetallic Fe-Ni phosphide	0.01-2.5 V	168 mAh/g @ 50mA/g	107 mAh/g @ 100 mA/g 64 mAh/g @ 500 mA/g 46 mAh/g @ 2 A/g	[15] 2020
16.	Sn_4P_3@Carbon Fiber	0.01-2 V	~200 mAh/g @ 50 mA/g	90 mAh/g @ 100 mA/g ~0 mAh/g at higher current densities	[16] 2018
17.	$SnP_{0.94}$@GO	0.01-2 V	190 mAh/g @ 50 mA/g (42%)	146 mAh/g @ 100 mA/g 118 mAh/g @ 500 mA/g 84 mAh/g @ 1 A/g	[17] 2019

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