

2. Experiment

2.2 Materials preparation

Anode material of CoSe₂ was prepared using one-step solvothermal method. In brief, glucose (0.6 g) and NaCl (0.6 g) were added into 30 ml distilled water with constant stirring. Then the solution was freeze-dried, and 0.6 g urea was added to the dried sample for grounding. Subsequently, the sample was sintered at 700 °C for 3 h in a tube furnace under a nitrogen atmosphere. The product after sintered was centrifuges and then washed several times with distilled water. Then the prepared nitrogen-doped carbon material was dissolved into Co(NO₃)₂·6H₂O (0.1 mol L⁻¹), stirred for 3h and dried it. After that, the mixture was ball-milled with a certain amount of Se powder and the product was sintered for 4h under an Ar/ H₂ atmosphere at 400 °C.

2.3 Characterization

The structural and phase of all samples were tested with X-ray diffraction (XRD, D/MAX 25000V, Rigaku, Japan) measurements and the specific structural parameters was refined by Rietveld analysis using the software of High score plus and GSAS. The morphologies of all particles were observed by scanning electron microscopy (SEM, Hitachi, SU8000). Lattice fringes and microtopography were screened by a transmission electron microscopy (TEM, JEOL, 2100F). The valance of elements is detected by X-ray Photoelectron Spectrometers (XPS, Thermo ESCALAB 250XI). The degree of graphitization is tested by Raman measurement (LabRam HR Evolution). Specific surface and pore size are surveyed through Brunner-Emmet-Teller (BET) measurements with the A JWGB, BK 122W instrument. The Mass fraction of carbon in Ca0.04-NVP@CNTs sample was tested by Thermogravimetric analysis (TGA, Mettler-Toledo). The actual molar of each sample was determined by inductively coupled plasma-mass spectrometer (ICP-MS, NexION™ 350D).

2.4 Electrochemical measurements

The CR2016-type half-cells were used to inspect the electrochemical performance with all cathode materials. Ball milling the active material prepared in

advance with carbon black and poly-vinylidene fluoride (PVDF) in a mass ratio of 7: 2: 1 to make a slurry with about 1.5 ml of N-methyl-2-pyrrolidone (NMP). Then the slurry was collected on aluminum foil current collectors in a coater, and the thickness of slurry was controlled at about 5~7 μm . The prepared positive electrodes were dried at 45 $^{\circ}\text{C}$ for 4 h and then dried at 120 $^{\circ}\text{C}$ for 12 h in vacuum at the heating rate of 10 $^{\circ}\text{C}/\text{min}$. The dried electrodes were punched into a 16 mm diameter disc and weighing the electrodes, the loading density of each disc was 1.5-1.8 mg cm^{-1} . And the Na metal foil as anode materials, a mixture of ethylene carbonate (E/C) and propylene carbonate (PC) in a volume ratio 1:1 as electrolyte, and the Clegard 2400 as separator. Above components were assembled sequentially in a nitrogen-filled glove box. All assembled cells were quiescence after rested overnight for the electrolyte is in full contact with the anode and cathode materials of the battery. The electrochemical measurements of galvanostatic charge/ discharge and galvanostatic intermittent titration technique (GITT) were operated in a LAND-2001A test system, and the range of voltage is 2.3-4.1 V vs. Na^+/Na . Na-ion diffusion coefficient was analyzed by Cyclic voltammetry (CV) testes in a workstation (IVIUMNSTAT) at the scan rate of 0.1, 0.2, 0.5, 1, 2 and 5 mV s^{-1} with the same voltage window of 2.3-4.1 V vs. Na^+/Na . And the electrochemical impedance spectroscopy (EIS) was tested in the workstation with the scan frequency range of 0.01Hz-10 kHz.

The CR2025-type full-cells were assembled with cathode material (Ca0.04-NVP@CNTs) and anode material (CoSe_2). The mixture of anode material, Super p and sodium carboxymethylcellulose (CMC) with a weight of 8:1:1 was ground, then the obtained slurry was coated on Cu foil and dried at 100 $^{\circ}\text{C}$ for 12h under vacuum. The dried poles were cut into 13 mm diameter rounds. The cells were tested in two steps, firstly, CoSe_2 for the cathode electrode and Na for the counter electrode to assemble a CR2016 type half-cell, then the half-cell was measured at 0.1C for 2 cycles. After pre-sodiuimng, CoSe_2 was removed from half-cell and assembled as anode material for full-cell, Ca0.04-NVP@CNTs was as counter electrode, glass fiber paper was as separator. The rate and cycling performance were tested like half-cell.

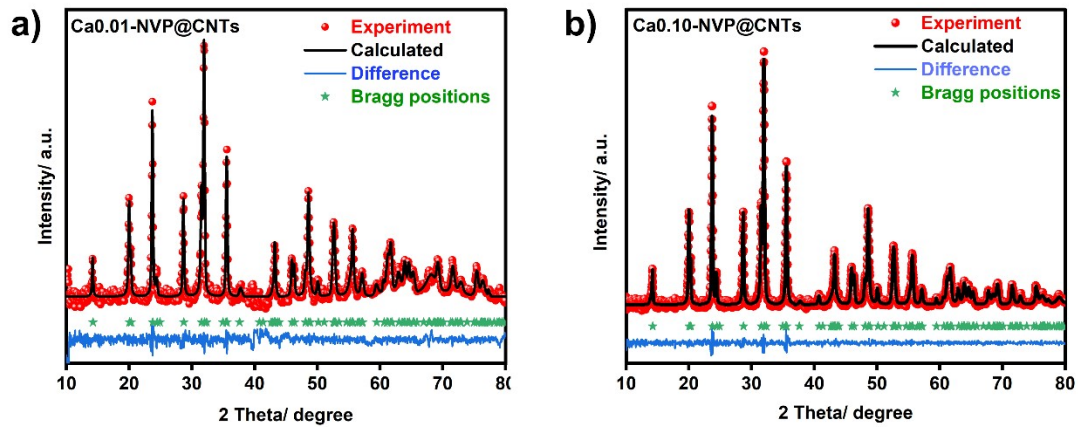


Fig.S1 (a) The refinement graph of XRD dates for Ca_{0.01}-NVP@CNTs. (b) The refinement graph of XRD dates for Ca_{0.10}-NVP@CNTs.

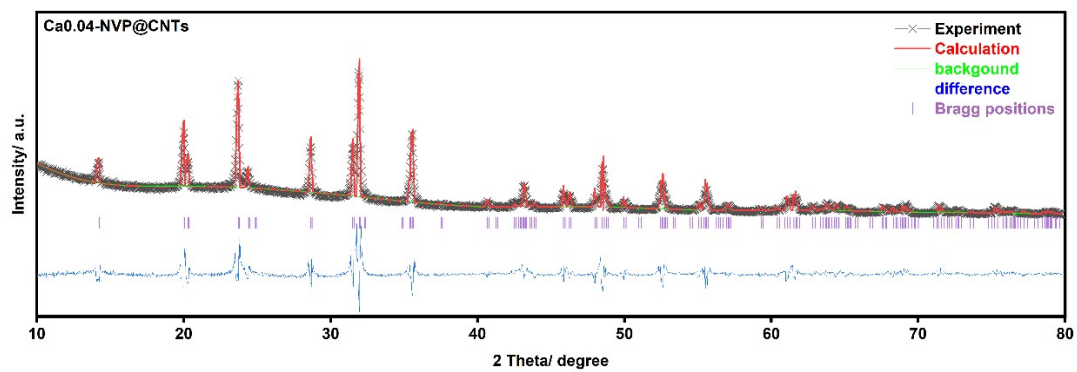


Fig.S2 Refinement graph of XRD dates for Ca_{0.04}-NVP@CNTs using GSAS software.

Table.S1 Chemical compositions of all samples.

Sample name	Target composition	Measured composition
NVP	Na ₃ V ₂ (PO ₄) ₃	Na _{2.98} V _{1.99} (P _{0.99} O _{4-x}) _{2.99}
Ca _{0.01} -NVP@CNTs	Na ₃ V _{1.99} Ca _{0.01} (PO ₄) ₃ @CNTs	Na _{2.98} V _{1.98} Ca _{0.01} (P _{0.99} O _{4-x}) _{2.99} @CNTs
Ca _{0.04} -NVP@CNTs	Na ₃ V _{1.96} Ca _{0.04} (PO ₄) ₃ @CNTs	Na _{2.99} V _{1.95} Ca _{0.03} (P _{0.99} O _{4-x}) _{2.99} @CNTs
Ca _{0.10} -NVP@CNTs	Na ₃ V _{1.90} Ca _{0.10} (PO ₄) ₃ @CNTs	Na _{2.99} V _{1.89} Ca _{0.08} (P _{0.98} O _{4-x}) _{2.98} @CNTs

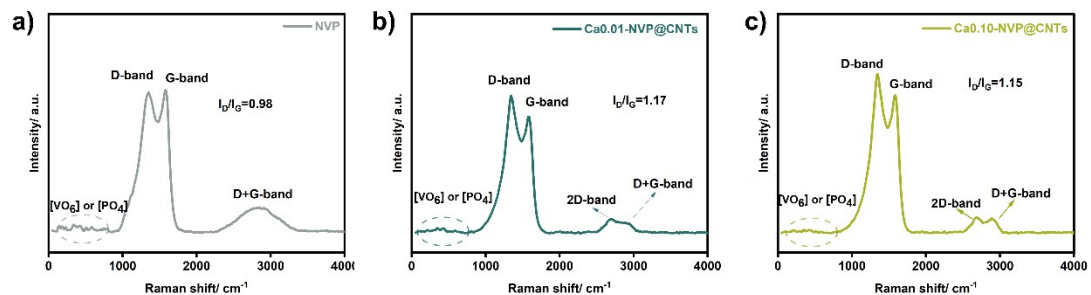


Fig.S3 The Raman spectrum of NVP (a), Ca_{0.01}-NVP@CNTs (b), and Ca_{0.10}-NVP@CNTs (c).

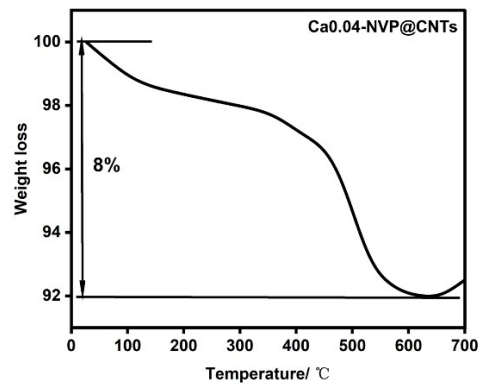


Fig.S4 TG curve of Ca_{0.04}-NVP@CNTs.

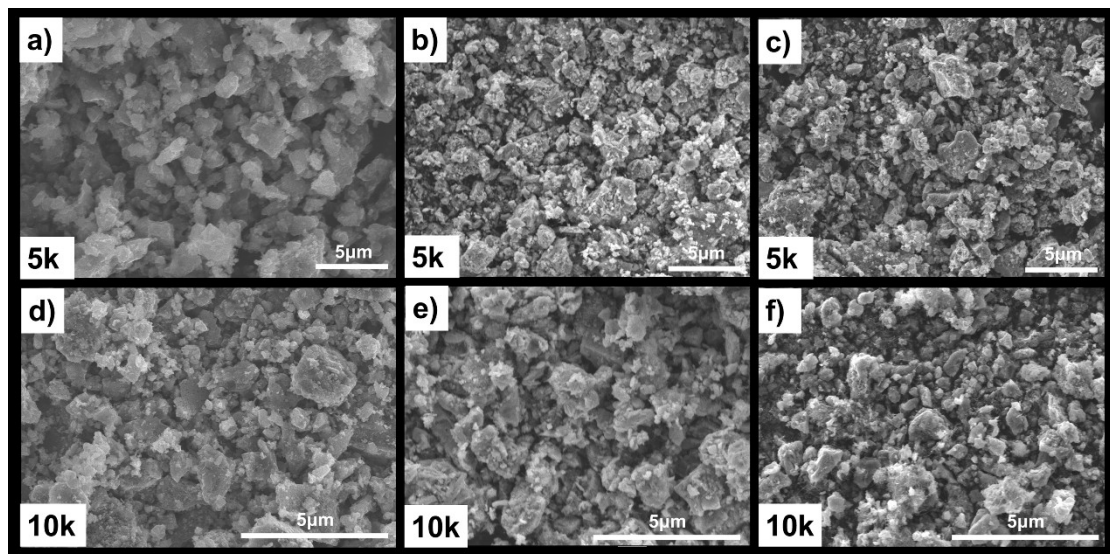


Fig.S5 The microscopic morphological features of NVP (a, d), Ca_{0.01}-NVP@CNTs (b, e) and Ca_{0.10}-NVP@CNTs (c, f) at the magnification of 5 k and 10 k.

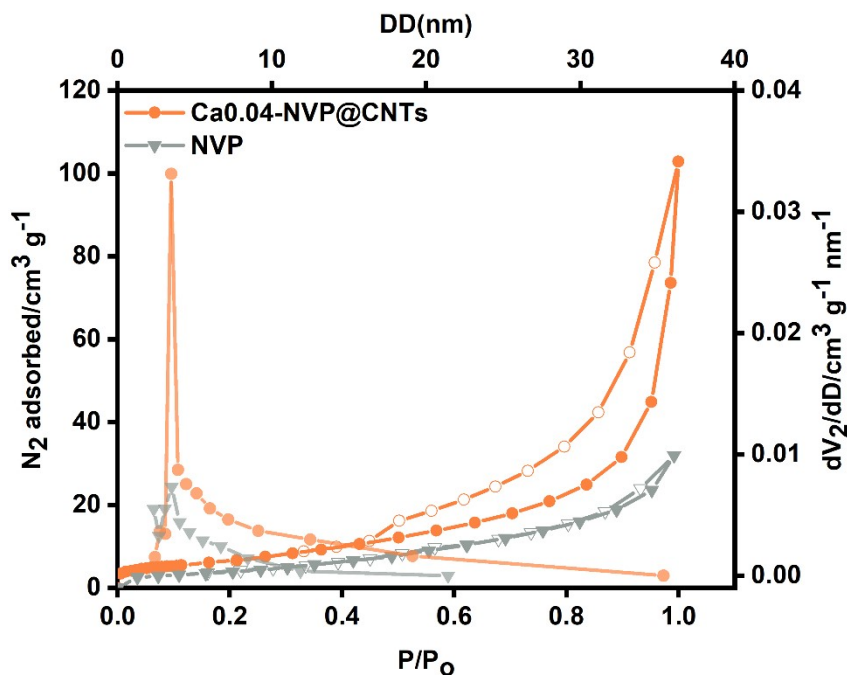


Fig.S6 The particle size and specific surface of Ca0.04-NVP@CNTs and NVP.

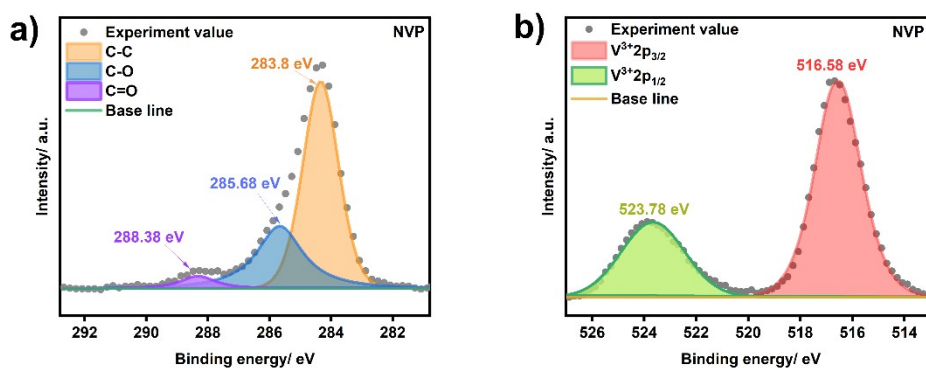


Fig.S7 (a) The forms of C presence in NVP. (b) The valence of V in NVP.

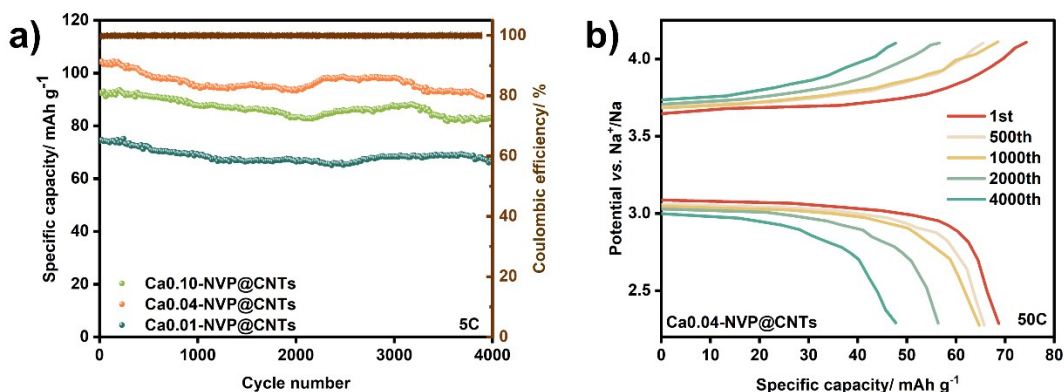


Fig.S8 (a) The cycling performance of Ca-doped samples at 5 C. (b) The charge/ discharge curves of different cycles for Ca0.04-NVP@CNTs at 50 C.

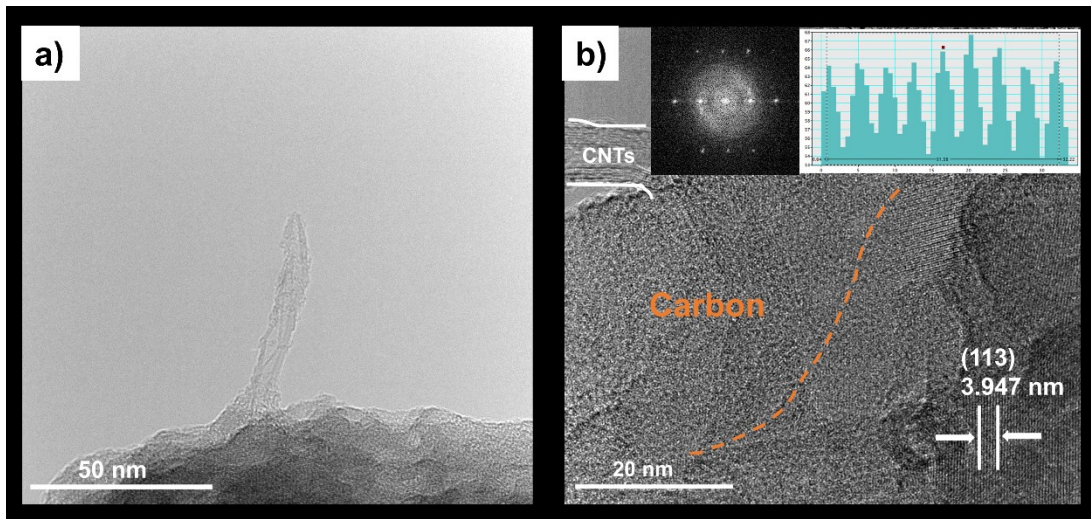


Fig.S9 (a) TEM and (b) HRTEM images of Ca_{0.04}-NVP@CNTs after 4000-cycles at 50 C .

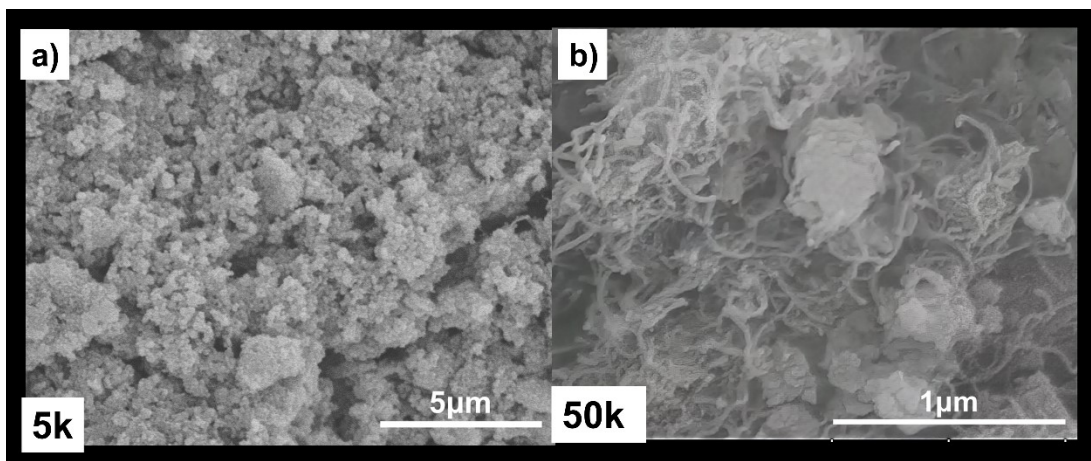


Fig.S10 (a, b) SEM images of Ca_{0.04}-NVP@CNTs after 2000s cycling at 100 C with magnification of 5 k and 50 k.

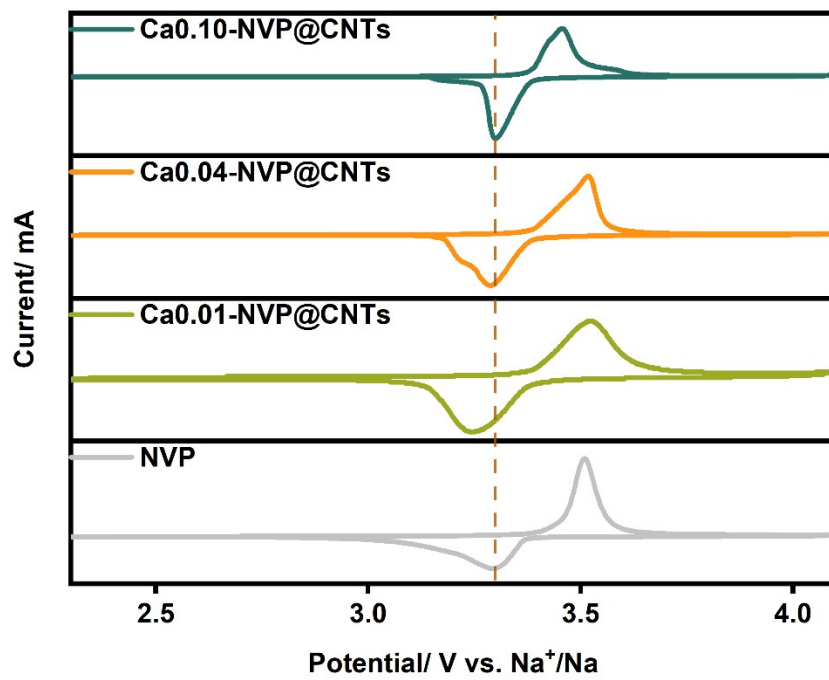


Fig.S11 CV curves of all samples at the scan rate of 2 mV s⁻¹.

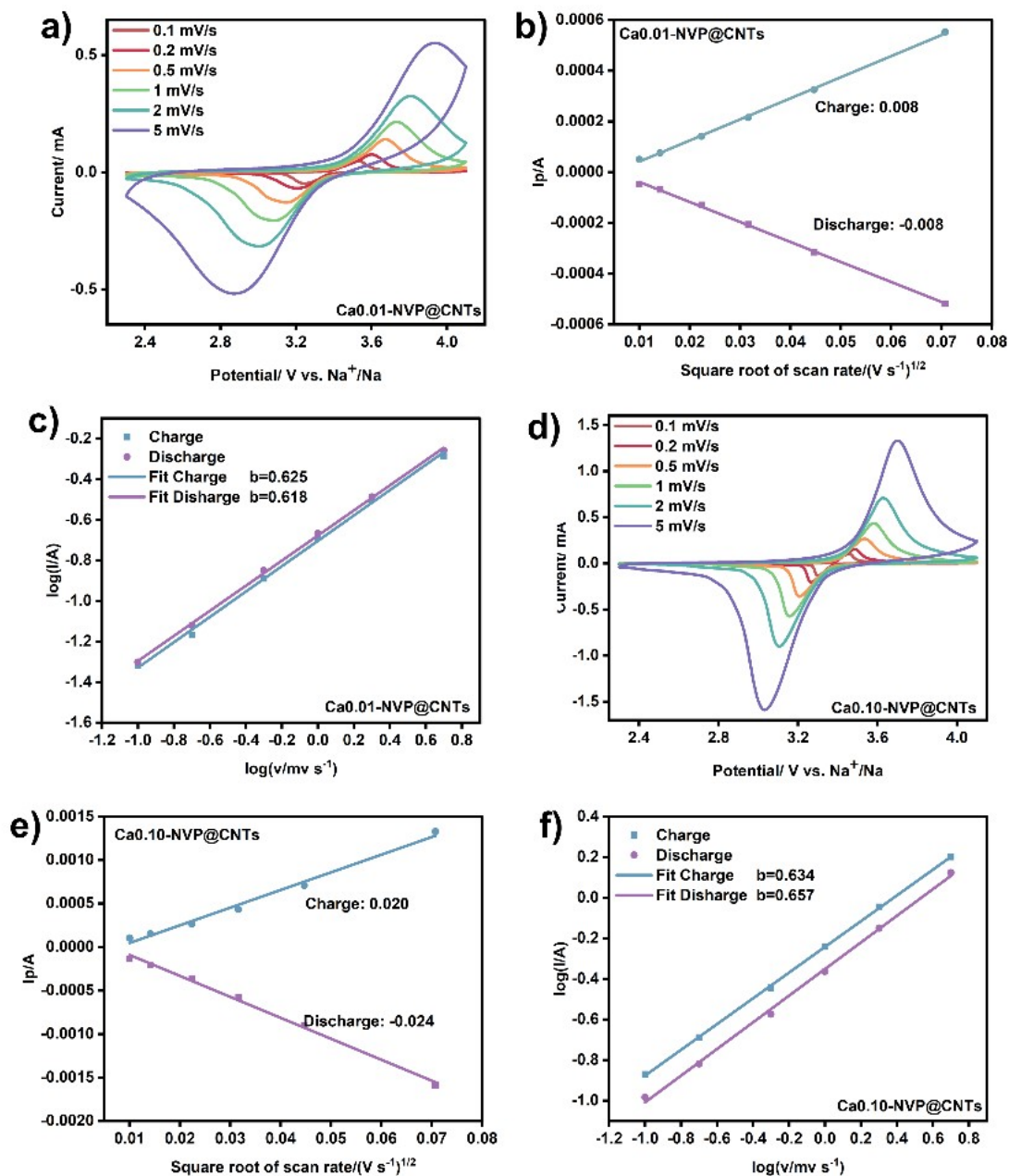


Fig.S12 (a, d) CV plots of Ca_{0.04}-NVP@CNTs and Ca_{0.10}-NVP@CNTs with increased scan rate of 0.1, 0.2, 0.5, 1, 2 and 5 mV s⁻¹. (b, e) The visual description of *I*_p and $(V s^{-1})^{1/2}$. (c, e) The visual description of *I*_p and *v*.