Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Nb_2O_5/Graphene nanocomposites for Electrochemical Energy Storage

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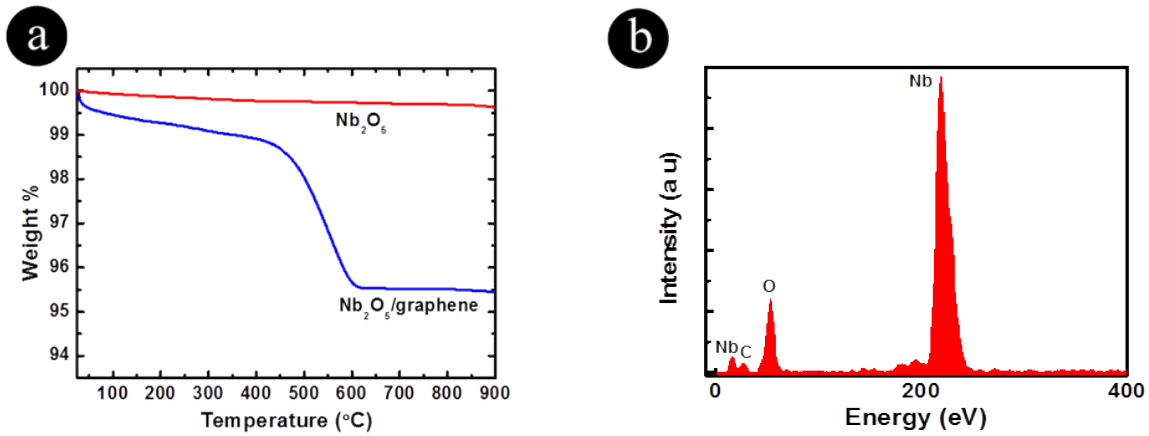

Fig. S1 (a) Thermogravimetric analysis of Nb_2O_5 nanocrystals and Nb_2O_5/Graphene nanocomposite (b) EDX spectra showing the presence of C, Nb band O.

Thermogravimetric analysis (Fig. S1a) was carried out on the Nb_2O_5/Graphene nanocomposite to determine the amount of graphene present in the composite. Thermogravimetric analysis was carried out in the presence of oxygen from room temperature to 900 °C at heating rate of 10 °C per min. The percentage of graphene in the nanocomposite was found to be 4.5% by weight. EDX measurement has been carried out to confirm the elements present in the sample (Fig. S1b).

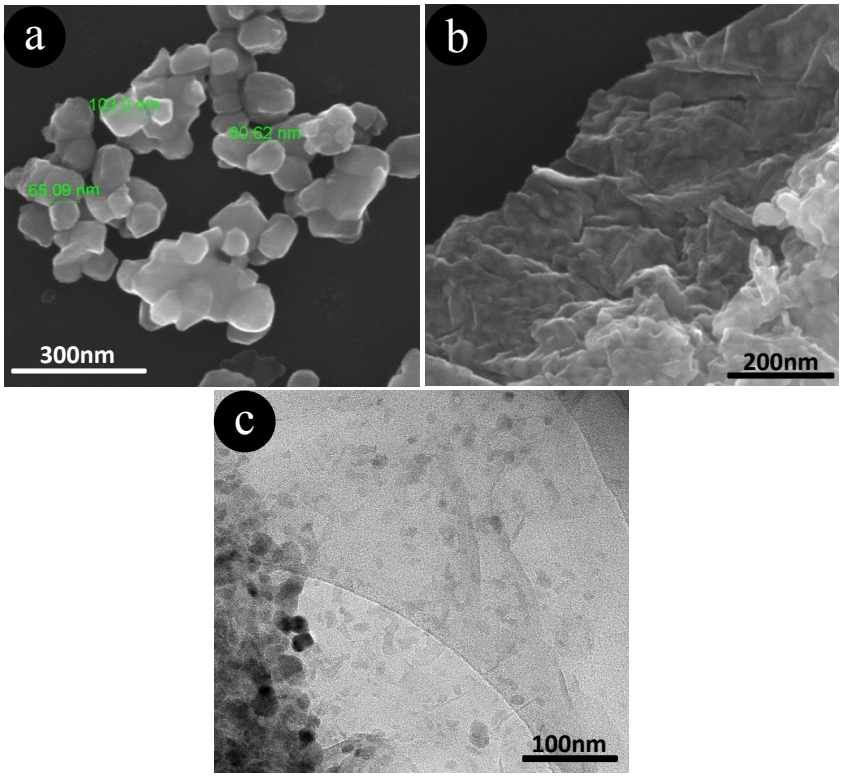

Fig. S2 SEM images showing (a) the clustered nature and sizes of pristine Nb_2O_5 nanoparticles (b) Nb_2O_5/graphene nanocomposite and (c) TEM image of Nb_2O_5/graphene nanocomposite.

The SEM image of pristine Nb_2O_5 nanoparticles showed irregular and highly clustered particles varying in sizes in the range of 50-100 nm. Most of the particles were found to be large size (>100 nm) as shown in the Fig. S2a. When the nanocomposite was synthesized, graphene oxide nanosheets were introduced along with the precursors for Nb_2O_5 nanoparticles. Due to the synergic effect, the Nb_2O_5 nanoparticles formed were much smaller than that of the pristine. SEM image of the graphene composite are shown in the manuscript (Fig. 3b) and here as well (Fig. S2b). The variation in Nb_2O_5 nanoparticle sizes can be seen from the TEM images shown in the manuscript (Fig. 3d) and here (Fig. S2c). This also resulted in higher lithiation capacity in the Nb_2O_5/graphene nanocomposite in addition to the improvement seen in the material due to the presence of graphene sheets.

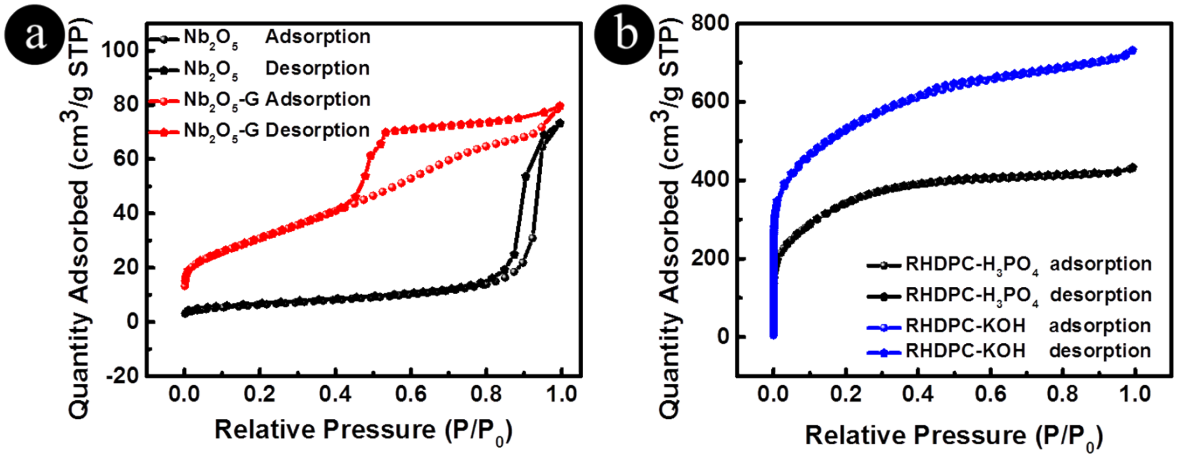

Fig. S3 N_2 adsorption / desorption isotherms of (a) Nb_2O_5 and Nb_2O_5/graphene, (b) RHDPC-KOH and RHDPC-H_3PO_4.

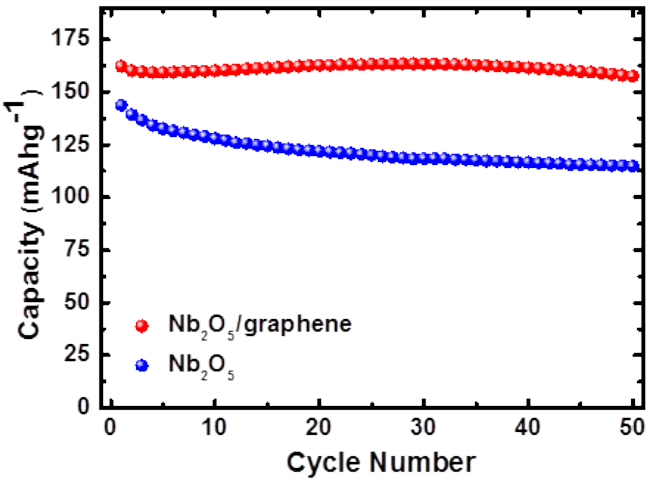

Fig. S4 Discharge capacity *vs.* cycle number for Nb_2O_5 and Nb_2O_5/graphene hybrid electrodes studied at 1 C rate.

The cycling stability of Nb_2O_5 nanoparticles and Nb_2O_5/graphene composites were studied at 1C rate as well and is shown in the Fig. S4. In this experiment, the graphene nanocomposite showed higher capacity compared to pristine Nb_2O_5 nanoparticles and gave a capacity of 160 $mAhg^{-1}$ as compared to 115 $mAhg^{-1}$ for pristine Nb_2O_5 nanoparticles after 50 cycles under 1C rate.

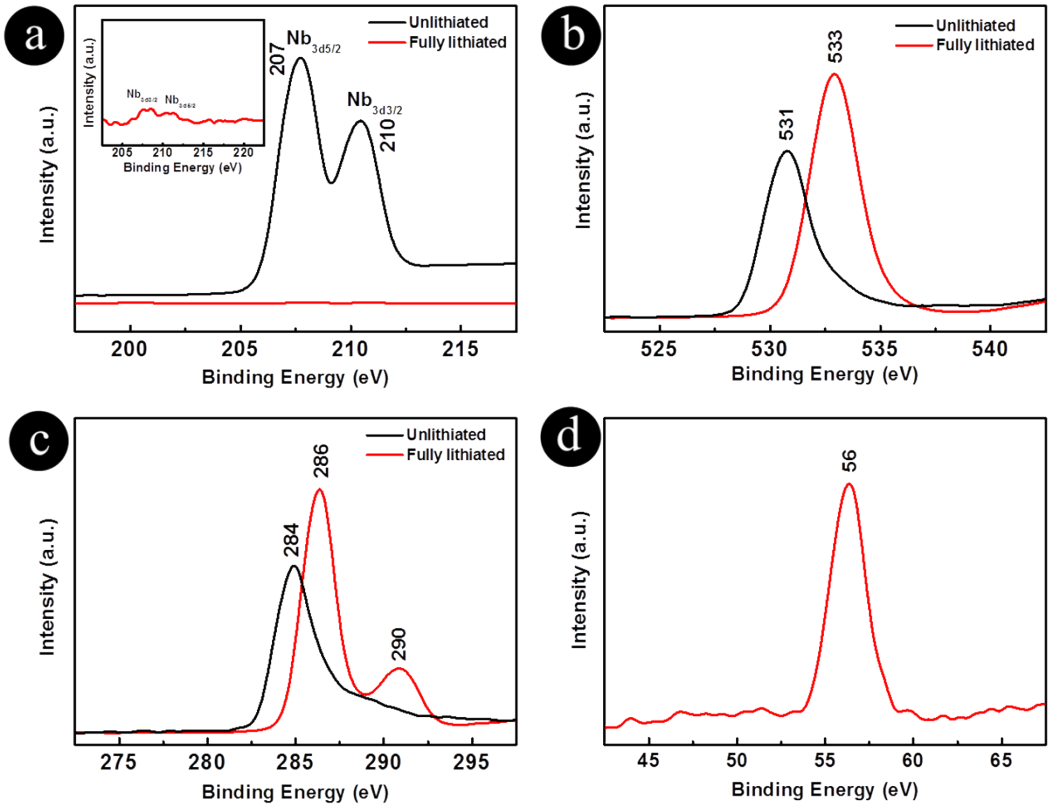

Fig. S5 XPS spectra of lithiated and unlithiated Nb_2O_5/graphene composite (a) Nb_{3d} (b) O_{1s} (c) C_{1s} and (d) Li_{1s}

X-ray photoelectron spectroscopy was used to determine the oxidation states of the elements in the Nb_2O_5/graphene nanocomposite material. Core level XPS spectra of lithiated and unlithiated Nb_2O_5/graphene are shown in Fig. S5. Fig. S4a shows $3d_{3/2}$ and $3d_{5/2}$ peaks of Nb were seen at 210 eV and 207 eV respectively in the unlithiated sample whereas in the lithiated sample these peaks were absent. This is due to the fact that under lithiation Nb^{5+} reduces to Nb^{4+} state.[1] Fig. S5b showing the XPS spectra comparison of O_{1s} indicates that the peak gets shifted from 531 eV to 533 eV as reported elsewhere.[1] The 1s peak of carbon in the pristine sample is seen near 284 eV in Fig. S5c whereas the XPS spectra in the lithiated samples resembles that of carbon containing functional groups. The presence of these peaks might be due to the slight oxidation of carbon in the graphene nanosheets and the presence of other functional groups in them. As XPS spectra only give an idea about the area that is investigated on, this anomaly could be a localized one. Finally Fig. S5d shows the XPS spectra of lithium in the lithiated sample which is at 56 eV.

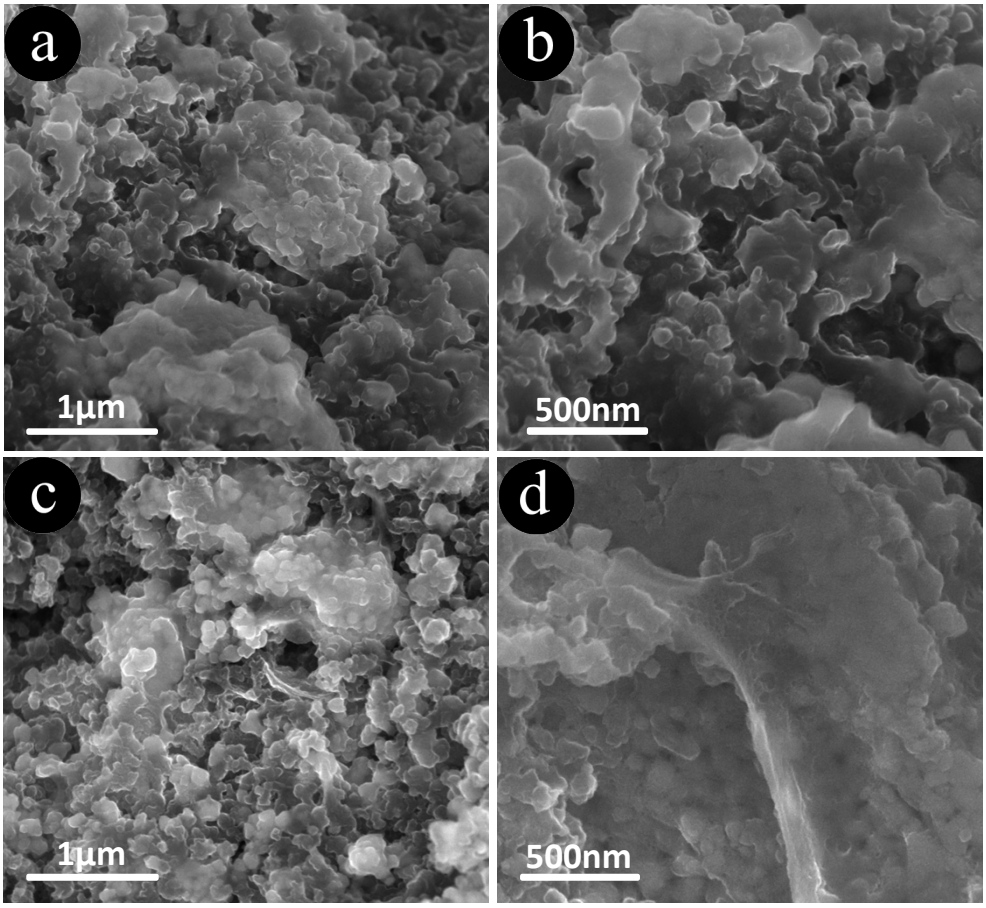

Fig. S6 SEM images showing the nature of (a, b) pristine Nb_2O_5 nanoparticles and (c, d) Nb_2O_5/graphene nanocomposite after battery cycling

Postmortem SEM imaging of pristine Nb_2O_5 and Nb_2O_5/graphene nanocomposites were carried out to check the change in the morphologies of the electrode material and are shown in the Fig. S6. The cycled cells were cut open inside argon filled glove box and the electrodes were washed with diethyl carbonate to remove the electrolyte and the lithium salts. These were then dried in air at a temperature of 65ºC. These were then loaded into the SEM sample holders for imaging. The images show a clustered form with the presence of graphene sheets in the nanocomposite. The highly agglomerated nature in both the samples is due to the presence of acetylene black and poly(vinylidenefluoride) that were used as conducting and non-conducting binders respectively during the electrode preparation. These images also show that Nb_2O_5 nanoparticles had no morphological change after lithiation/deliathation cycles. These are due to the superior structural stability and near zero volume expansion of Nb_2O_5 nanoparticles.

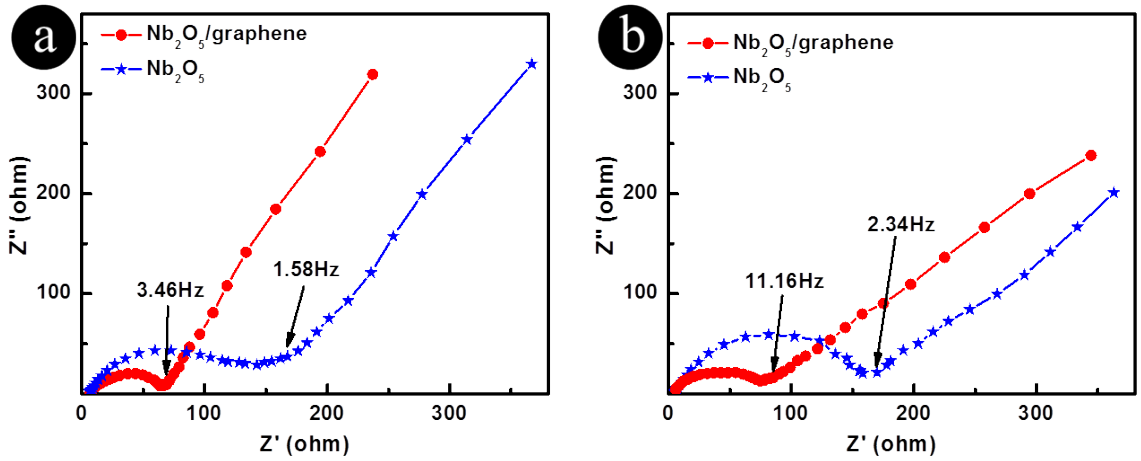

Fig. S7 Frequency analysis of the pristine Nb_2O_5 and Nb_2O_5/graphene hybrid electrode (a) before cycling and (b) after cycling.

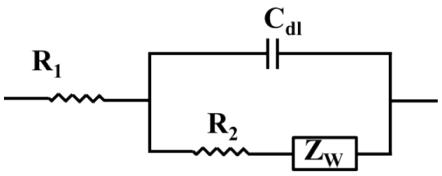

Table S1: Equivalent circuit components of pristine Nb_2O_5 nanoparticles and Nb_2O_5/graphene nanocomposite before and after electrochemical cycling process.

Sample	R_1 (Ω)	R_2 (Ω)	C_{dl} (μF)	a_1
Pristine Nb_2O_5 (Before cycling)	5.52	135.3	48.18	0.733
Nb_2O_5/graphene (Before cycling)	6.31	61.2	90.08	0.699
Pristine Nb_2O_5 (After 50 cycles)	4.836	150.9	27.09	0.794
Nb_2O_5/graphene (After 50 cycles)	3.039	67.49	30.19	0.701

EIS analysis is done by applying the sinusoidal potential of 10 mV amplitude by varying the frequency from 40 kHz to 10 mHz and are shown in the Fig. S7. The kinetics of the sample can be determined from the frequency response of the sample in the EIS spectrum.[2] Higher the frequency at the onset between the slope and the semi-circle in the EIS spectrum, higher is the kinetics of the sample. From the analysis given below, it is clear Nb_2O_5/graphene nanocomposite has better kinetics as compared to pristine Nb_2O_5 nanoparticles.

The equivalent circuit based on Randel's model was fitted from the Nyquist plots obtained in the EIS analysis of the samples using EC-Lab software V10.32.[3] R_1 represents the solution resistance, R_2 the charge transfer resistance, C_{dl} the double layer capacitance, Z_W the Warburg impedance and a_2 an empirical electrode roughness parameter.

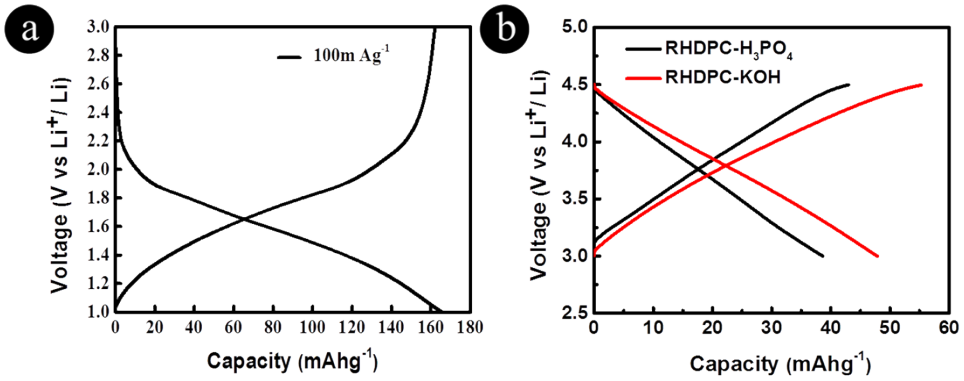

Fig. S8 Galvanostatic charge-discharge curves of (a) Li/Nb_2O_5-graphene half-cells tested between 1-3 V, (b) Li/ RHDPC-KOH and Li/ RHDPC-H_3PO_4 half-cells cycled between 3 - 4.5 V at constant current density of 100 mA g^{-1}.

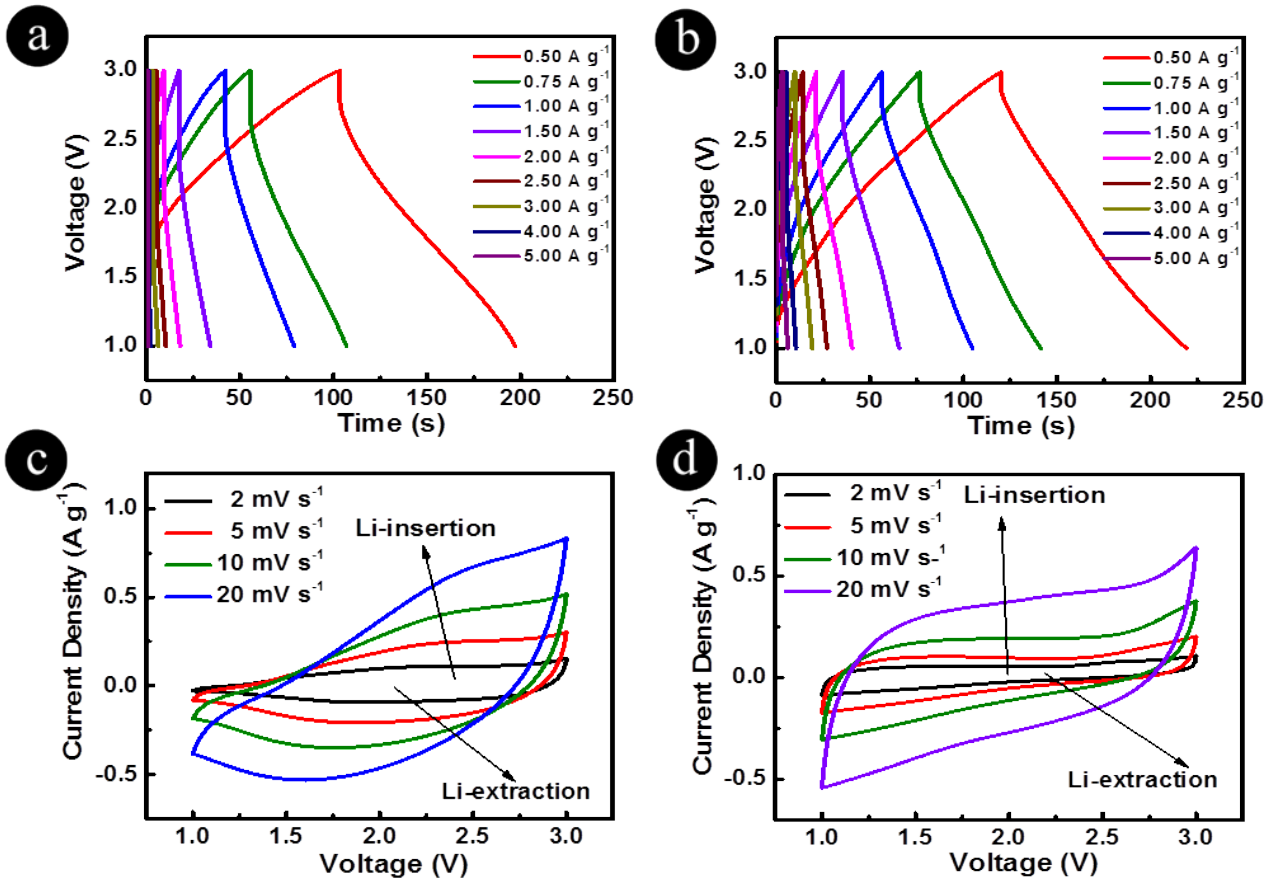

Fig. S9 Galvanostatic charge-discharge curves of Li-HEC (a) Nb_2O_5 / RHDPC- H_3PO_4 (b) Nb_2O_5 / RHDPC - KOH at different applied current densities. Cyclic Voltammetry of (c) Nb_2O_5 / RHDPC- H_3PO_4 and (d) Nb_2O_5 / RHDPC-KOH cells.

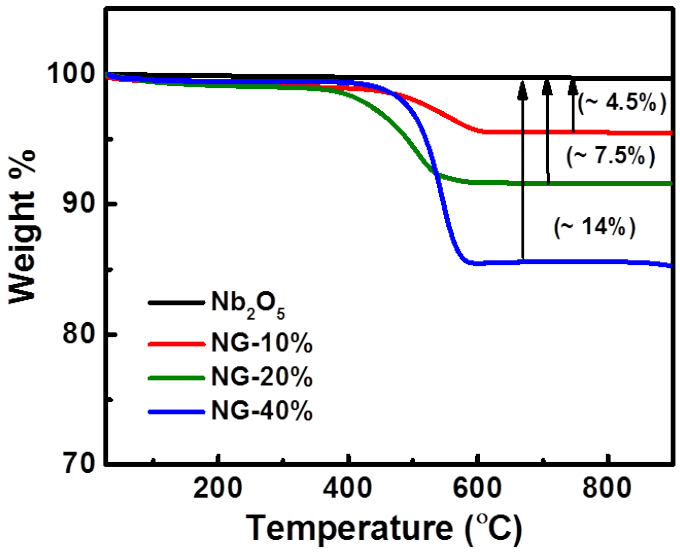

Fig. S10 Thermogravimetric analysis of Nb_2O_5 nanocrystals and Nb_2O_5/Graphene nanocomposite with varying graphene content.

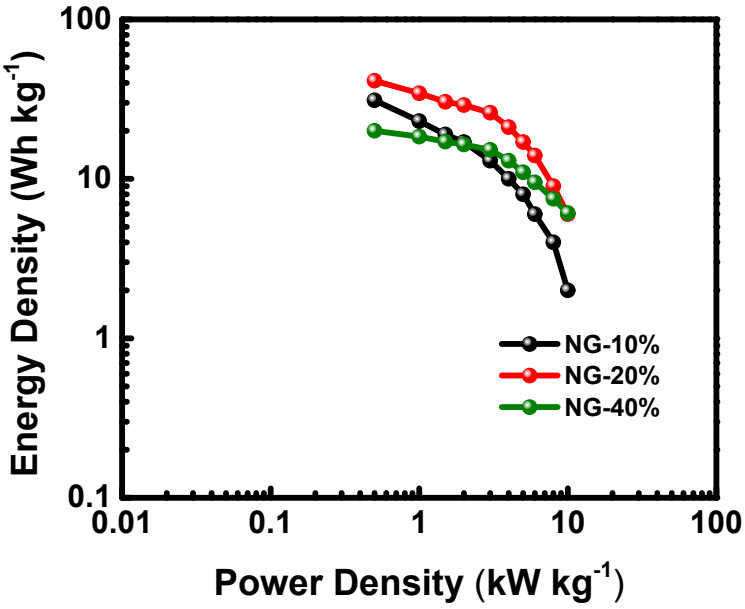

Fig. S11 Ragone plot of Li-HEC device fabricated with Nb_2O_5-graphene / RHDPC-KOH electrodes (with varying graphene content).

References

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2. P. Meduri, H. Chen, J. Xiao, J. J. Martinez, T. Carlson, J.-G. Zhang and Z. D. Deng, *J. Mater. Chem. A*, 2013, 1, 7866-7869.
3. C. Ho, I. D. Raistrick and R. A. Huggins, *J. Electrochem. Soc.*, 1980, 127, 343-350.