Lamellar structured $Ni_3P_2O_8$: First-ever use to design 1.8 V operated flexible all-solid-state symmetric supercapacitor

Akanksha Agarwal, Babasaheb R. Sankapal*

Department of Physics, Visvesvaraya National Institute of Technology, South Ambazari Road, Nagpur-440010, Maharashtra, India.

Supporting information S1

Tixo-tape peel off test

Using the tixo-tape peel-off method, the adherence of the $Ni_3P_2O_8$ thin film was evaluated [1]. For this, tixo-tape was put to the top surface of the film and then peeled off. Peel-off photos of the film on the stainless steel (SS) substrate reveal that just a few non-adhesive powdery particles were eliminated from the surface with no significant change. This indicates that the film adhered firmly to the SS substrate.
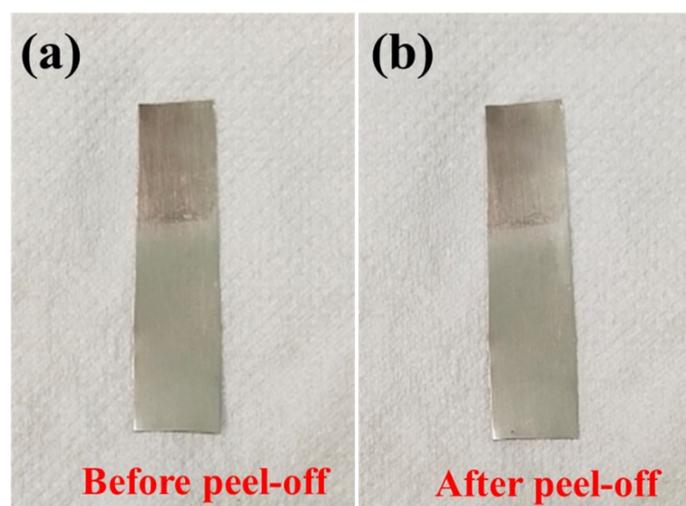
Figure: S1 Photographs of the $Ni_3P_2O_8$ thin film (a) before, and (b) after peel-off, respectively.

Supporting information S2

Materials characterization

X-ray diffractometer (XRD, Rigaku, SmartLab) with Cu k_α radiation (λ=1.54 A°) was employed to identify the phase and purity of the as-prepared composite $Ni_3P_2O_8$ thin film. With the aid of Thermo scientific Inc., UK, X-ray photoelectron spectroscopy (XPS) measurements were performed using Al as the source of excitation. Field emission scanning electron microscopy (FE-SEM, JSM-7800F, JEOL) with energy dispersive x-ray spectroscopy (EDS; Oxford, x-max) was used to study surface morphological properties. The JEOL JEM-2100F apparatus was adopted to acquire the high-resolution transmission electron micrographs (HRTEM). To estimate the Brunauer-Emmett-Teller (BET) surface area and pore-size distribution, the nitrogen adsorption-desorption isotherms were recorded on ASAP 2010, Micromeritics.

Electrochemical studies

Various electrochemical analysis techniques such as, cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS) were employed to examine the electrochemical properties of designed $Ni_3P_2O_8$ electrode. The electrode studies of as-designed binder-free electrode were performed via conventional tri-electrode configuration with Ag/AgCl and platinum wire as reference and counter electrodes, respectively.

Calculations performed

The specific capacitance (C_s) of the electrode was estimated using CV curves at various scan rates, as follows;

$$C_s\left(F\,g^{-1}\right)=\frac{\displaystyle\int i(V)dV}{m\,v\,V} \qquad\qquad (1)$$

While, the areal capacitance (C_a) of the electrode from CV curves at various scan rates was estimated using below;

$$C_a\left(F\,cm^{-2}\right)=\frac{\displaystyle\int i(V)dV}{A\,v\,V} \qquad\qquad (2)$$

where, $\displaystyle\int i(V)dV$ stands for CV integral area, m denotes mass loading, v signifies scan rate, and V represents active potential window of electrode.

Meanwhile, the C_s and C_a values at different current densities derived from GCD curves can be computed as follows;

$$C_s\left(F\,g^{-1}\right)=\frac{I\displaystyle\int Vdt}{m\,V^2} \qquad\qquad (3)$$

$$C_a\left(F\,cm^{-2}\right)=\frac{I\displaystyle\int Vdt}{A\,V^2} \qquad\qquad (4)$$

here, $\displaystyle\int Vdt$ accounts for the area under galvanostatic discharge curve and I is the discharge current density.

The C_s and C_a values of the $Ni_3P_2O_8$ symmetric device can be evaluated from above eqns. with mass loading as 2m. Subsequently, energy density (E) and power density (P) calculations were based on following eqns.;

$$E\left(Wh\,kg^{-1}\right) = \frac{0.5\,C_s V^2}{3.6} \tag{5}$$

$$P\left(W\,kg^{-1}\right) = \frac{3600\,E}{\Delta t} \tag{6}$$

where, Δt stands for discharge time.

Supporting information S3

Concentration optimization of Na$_2$SO$_4$ electrolyte

The effects of increasing the Na$_2$SO$_4$ concentration from 0.5 to 2 M are explored via CV measurement at a constant scan rate of 100 mV s^{-1}, as shown in Fig. S2(a). Fig. S2(b) depicts the corresponding specific capacitance values obtained at various Na$_2$SO$_4$ concentrations with 1 M Na$_2$SO$_4$ exhibiting the largest value of specific capacitance (221 F g^{-1}). At this concentration, ion species are not only abundant but also in a stable state (in terms of activity), resulting in efficient double layer formation [2]. As a result, 1 M Na$_2$SO$_4$ is determined to be the best electrolyte formulation for electrochemical characterization of the as-prepared Ni$_3$P$_2$O$_8$ thin film electrode.
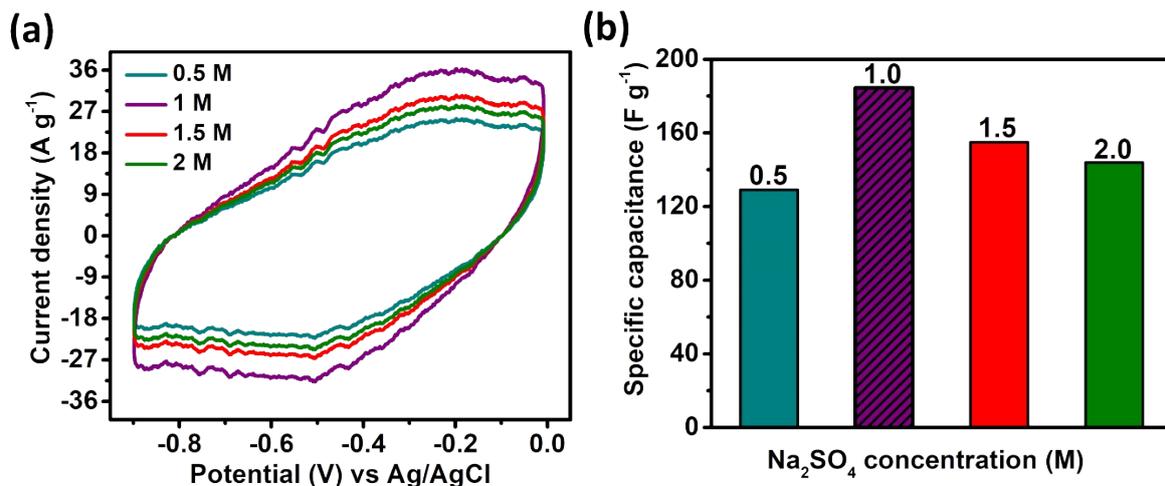
Figure: S2 (a) CV curves of Ni$_3$P$_2$O$_8$ electrode for different Na$_2$SO$_4$ concentrations, and (b) variation of specific capacitance with different Na$_2$SO$_4$ concentrations.

Supporting information S4

Distributions of diffusion-controlled and capacitive type current response at different scanning speeds
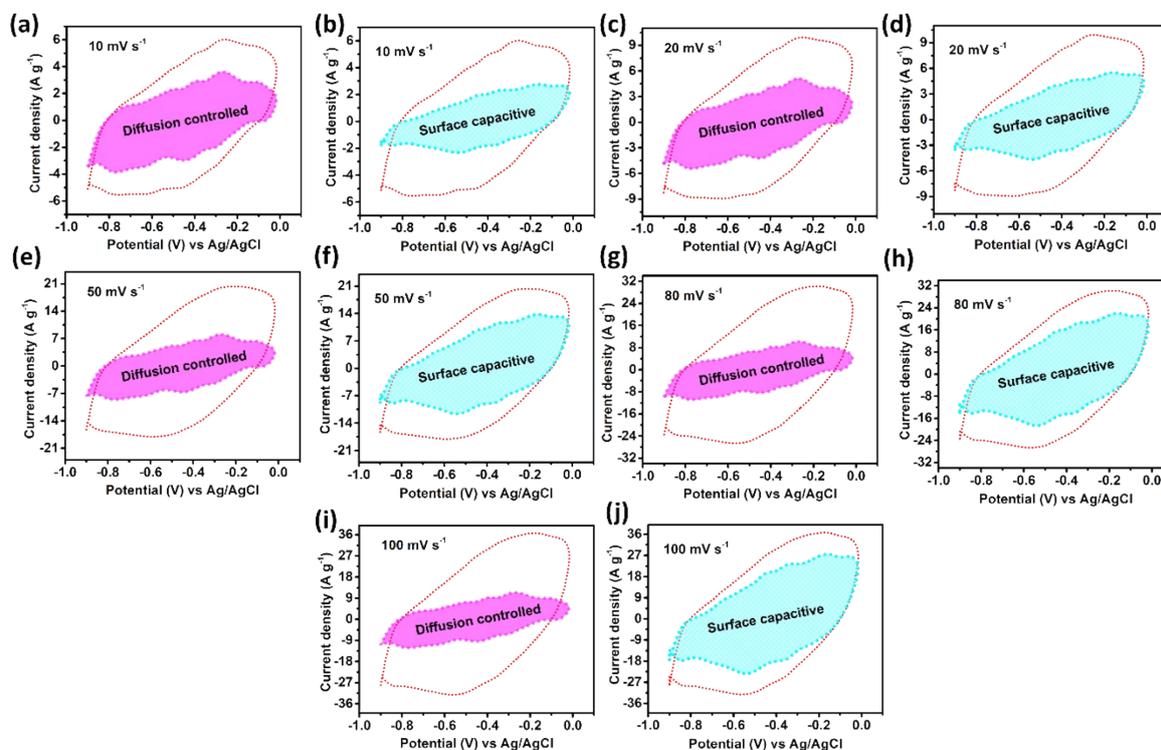
Figure: S3 Distributions of diffusion-controlled and surface-capacitive type current responses at different scanning speeds.

Supporting information S5

Device assembly

Solid-state carboxy methyl cellulose-Na_2SO_4 (CMC-Na_2SO_4) electrolyte membrane was used to stack two identical $Ni_3P_2O_8$ electrodes within a device assembly. At the first, a homogeneous mixture of 1 g Na_2SO_4, 2 g CMC, and 30 mL DDW was prepared at the temperature of 90 °C. Then evenly poured into a petri dish to obtain a solid-state free-standing CMC-Na_2SO_4 flexible membrane after overnight drying. Further, two $Ni_3P_2O_8$ thin film electrodes were placed on top of one another with as-prepared CMC-Na_2SO_4 electrolyte

membrane in between. The entire assembly was then normally pressed to realize all-solid-state $Ni_3P_2O_8$//CMC-Na_2SO_4// $Ni_3P_2O_8$ supercapacitor.

Supporting information S6

Table S1: EIS equivalent circuit parameters of flexible all-solid-state symmetric $Ni_3P_2O_8$ device.

Parameters	R_s (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	C_{dl} (μF cm^{-2})	W
Value	0.65	2.23	1.36	52.83

References

[1]   Bidhan Pandit, Akanksha Agarwal, Priyanka Patel, "Electrochemical kinetics of cerium selenide nano-pebbles: Design of device grade symmetric configured wide-potential flexible solid-state supercapacitor," *Nanoscale Adv.*, pp. 814–823, 2021, doi: 10.1039/D0NA00893A.

[2]   K. C. Tsay, L. Zhang, and J. Zhang, "Effects of electrode layer composition/thickness and electrolyte concentration on both specific capacitance and energy density of supercapacitor," *Electrochim. Acta*, vol. 60, pp. 428–436, 2012, doi: 10.1016/j.electacta.2011.11.087.