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## COMMUNICATION

## 3D Hierarchical Ni(PO<sub>3</sub>)<sub>2</sub> Nanosheet Arrays with Superior Electrochemical Capacitance Behaviors

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A novel type of electrode material, three-dimensional (3D) hierarchical Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays, is expored via a rational topotactic strategy combining hydrothermal growth with a followed phosphorylation treatment. The as-synthesized Ni(PO<sub>3</sub>)<sub>2</sub> nanosheets arrays self-supported on activated carbon cloth (Ni(PO<sub>3</sub>)<sub>2</sub>@ACC) exhibit superior electrochemical capacitive behaviors than their analogue of Ni(OH)<sub>2</sub> with similar structual characteristics. Their areal and mass specific capacitances could be up to 4.43 F cm<sup>-2</sup> at a current density of 2 mA cm<sup>-2</sup> and 2237 F g<sup>-1</sup> at ~1 A g<sup>-1</sup>, respectively, which are comparable to the best ones among the Ni-based and Me-PO<sub>x</sub> battery-type electrodes ever reported. Furthermore, even at a high rate of 10 mA cm<sup>-2</sup>, they maintains ~90% charge retention after 2000 cycles, suggesting their robust stability and very promising applications for energy storage.

#### Introduction

The depletion of fossil fuels and aggravation of environmental crisis have triggered an urgent demanding for the sustainable and clean alternative energy technologies. Due to their intrinsic advantages such as high power-density, fast charging and long lifespan, the ultracapacitors represent a promising excellent candidate among various advanced energy storage devices. Especially, the hybrid ultracapacitors, often employ various battery-type or pseudocapacitive electrode materials with faradaic reactions including transition-metal oxides/hydroxides (Me-O/OH),<sup>1-3</sup> sulphides (Me-S), <sup>4</sup> nitrides (Me-N)<sup>5</sup> and phosphides (Me-P),<sup>6</sup> exhibiting higher energy densities than the electrical double-layer capacitors (EDLC) as well as larger power densities than the batteries. Nevertheless, the present hybrid devices are still suffered from poor reversibility and low rate capability which usually relate to the unfavorable reaction kinetics of their electrode materials. To achieve superior overall performances, the representative strategies have been developed, including 1) the fabrication of composites incorporated conductive carbon materials to improve electronic conductivity within the electrode, 2) the synthesis of electrode materials with rich nanostructural features, for instance, the ultrathin layered materials with most functionalities exposed to the electrolytes, could create abundant electroactive sites and thereby have an improved specific capacitance and energy density,<sup>7-9</sup> and 3) the exploration of novel electrode materials for energy storage. In brief, the development of novel synthetic routes and/or new class of transition metal-based electrode materials with excellent electrochemical performances has become a hot spot in the field of energy storage.

Transition metal phosphates (Me-PO<sub>x</sub>) have always drawn enormous attentions, because of their unique physical/chemical characteristics and potentially wide applications in energy conversion and storage.<sup>10, 11</sup> To date, a variety of nanostructured Me-PO<sub>x</sub> materials, such as phosphites of cobalt or nickel  $(M_{11}(HPO_3)_8(OH)_6, M=Co, Ni),^{12-14}$  phosphates of cobalt (CoHPO<sub>4</sub>·3H<sub>2</sub>O),<sup>15</sup> manganese  $(Mn_3(PO_4)_2)^{16}$  or vanadyl (VOPO<sub>4</sub>),<sup>17</sup> pyrophosphate of cobalt  $(Co_2P_2O_7),^{18}$  have emerged as the effective electrode materials for ultracapacitors. Notably, to the best of our knowledge, there still has no report on the metaphosphates of transition metal (Me-PO<sub>3</sub>) based electrode materials for electrochemical energy storage.

Several phases of Me-PO<sub>3</sub> including NiHPO<sub>3</sub>·H<sub>2</sub>O<sup>19</sup> and Co(PO<sub>3</sub>)<sub>2</sub>,<sup>20</sup> have been prepared via hydrothermal synthesis or thermolytic molecular precursor (TMP) methods. However, these works are limited by the necessity of long reaction time, the assistance of coordinating reagents/surfactants, and/or the prefabrication of complex precursors. Therefore, one of the big obstacles to explore Me-PO<sub>3</sub> based electrode materials is how to realize the facile growth of Me-PO<sub>3</sub> with well-arranged morphology and specified crystalline, which is still a grand challenge currently.

Given the intense interest in the exploration of the facile synthesis of  $Me-PO_3$  with controlled stoichiometry/desired morphology as well as their potential energy storage properties,

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Fig. 1 Schematic illumination for the growth of 3D hierarchical Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays on ACC.

we herein designed a rational two-step strategy by combining a hydrothermal fabrication of hierarchical morphologies and a followed phosphorylation (*i.e.*, topotactic fabrication). A Ni(PO<sub>3</sub>)<sub>2</sub> nanomaterial with homogeneous crystalline phase and 3D hierarchical structure was firstly prepared, and the resultant Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays self-supported on activated carbon cloth (ACC) (Ni(PO<sub>3</sub>)<sub>2</sub>@ACC) exhibit a superior capacitive activity as compared to the ACC-supported Ni(OH)<sub>2</sub> nanosheet arrays (Ni(OH)<sub>2</sub>@ACC) that possesses a similar morphology. The Ni(PO<sub>3</sub>)<sub>2</sub>@ACC hybrid has a high specific capacitance (4.43 F cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> and 2237 F g<sup>-1</sup> at ~1 A g<sup>-1</sup> in 3 M KOH), good rate capability, and excellent cycling stability (maintained 90% of the capacity at 10 mA cm<sup>-2</sup> after 2000 cycles), suggesting that the nanostructured metaphosphate of transition metal could be a novel but very promising electrode material for energy storage devices.

#### **Results and discussion**

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The fabrication of the self-supported electrode of Ni(PO<sub>3</sub>)<sub>2</sub> nanosheets arrays is designed by a topotactic strategy, schematically illuminated as Fig. 1. Firstly, a hydrothermal process was conducted aiming to achieve a uniform nanostructured morphology of Ni<sup>2+</sup> precursor, *i.e.*, nanosheets arrays. Then, a heattreated phosphorylation was applied to transform Ni<sup>2+</sup> precursor nanosheets arrays into  $Ni(PO_3)_2$  nanosheets arrays. Carbon cloth herein was chosen as the conductive support, which could provide a three-dimensional (3D) conducting network to enhance the charge/ion transfers within the hybrid electrode.<sup>21</sup> Prior to use, the commercial carbon cloth was pretreated via a reflux in concentrated nitric acid to create abundant defect/nucleation sites. This would result in an improved cohesion between the substrate and nickel precursor (i.e., a small contact resistance with a high structural stability), and also allow a uniform distribution even after sonication treatment. It is also confirmed from the fact that the Ni<sup>2+</sup> precursor just grown on pristine carbon cloth (Ni(OH)2@CC) could be easily detached from the CC substrate (see the digital photo of Fig. S1b, Supporting Information). Also, a serious surficial aggregation of the nanosheets with a low coverage around the carbon fibers can be observed in the Ni(OH)2@CC hybrid (see SEM images in Fig. S1c-f and the marked arrow heads in Fig. S1c, Supporting Information). In comparison, the growth of Ni(OH)<sub>2</sub> on ACC displays a more uniform dispersity of nanosheets with an



**Fig. 2** Typical XRD patterns of the Ni precursor (up) and its corresponding phosphorylated product (down).

obviously higher fibre coverage (see SEM images in Fig. S1g-j, Supporting Information), which implies that ACC plays a profound effect on the growth of the  $Ni(OH)_2@CC$  hybrids with desired 3D hierarchical nanostructures.

Fig. 2 shows the typical X-ray diffraction (XRD) patterns of the Ni<sup>2+</sup> precursor from the first-step hydrothermal process (the up pattern) and its phosphorylated product (the down one) grown on ACC thereby. Besides the detected signals at ~25.8° and ~43.0° ascribed to the substrate of carbon cloth, the others could be assigned to the Ni<sup>2+</sup> precursor of Ni(OH)<sub>2</sub> with an typical orthorhombic structure (JCPDS Card No. 14-0117). It verifies that, after phosphorylated treatment, the XRD pattern agrees (the down pattern) well to those of carbon cloth and monoclinic Ni(PO<sub>3</sub>)<sub>2</sub> (JCPDS Card No. 29-0497), suggesting that the Ni<sup>2+</sup> precursor has been successfully converted to the pure phase of Ni(PO<sub>3</sub>)<sub>2</sub>.

Fig. 3 shows the typical SEM and TEM images of the resultant  $Ni(OH)_2@ACC$  and  $Ni(PO_3)_2@ACC$  hybrids. It further confirms that the  $Ni(OH)_2$  nanosheet arrays grow uniformly on the ACC fibers, making the formation of 3D hierarchical nanostructures. The nanosheets are of typically a few micrometers in width and ~20 nm in thickness (Fig. 3a and b). After phosphorylation, the obtained  $Ni(PO_3)_2$  nanosheets become thinner with rougher surfaces, as shown in Fig. 3c and d. More SEM images of  $Ni(PO_3)_2@ACC$  are provided in Fig. S2, Supporting Information. The representative TEM observation (Fig. 3e) further verifies that the  $Ni(OH)_2$  nanosheets possess a smooth surface with curled tips. However,  $Ni(PO_3)_2$ 

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**Fig. 3** Typical SEM images of Ni(OH)<sub>2</sub>@ACC (a-b) and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC (c-d). Typical TEM image of Ni(OH)<sub>2</sub> (e) and Ni(PO<sub>3</sub>)<sub>2</sub> (f) scratched from ACC. Typical HRTEM images of Ni(PO<sub>3</sub>)<sub>2</sub> (g-i). The inset in Fig. 3g is the corresponding SAED pattern.



Fig. 4 (a) Representative XPS survey spectrum of  $Ni(PO_3)_2@ACC$ . (b-d) The core-level photoelectron spectra of Ni 2p, O 1s and P 2p, respectively.

nanosheets exhibit a rough and porous surface (Fig. 3f), disclosing that they are assembled by the interconnected nanoparticles. This structural change might arise from the gas release and the dehydration of Ni(OH)<sub>2</sub> during the annealing process. The corresponding HRTEM image (Fig. 3g) discloses that the nanoparticles are uniformly sized in ~5 nm. Their typical SAED pattern (the inset in Fig. 3g) shows the nanoparticles are monoclinic Ni(PO<sub>3</sub>)<sub>2</sub> (JCPDS Card No. 29-0497) with a highly crystalline nature. The measured interplane spaces between two neighbored lattice fringes of 2.35, 2.83, 3.15 and 2.98 Å in Fig. 3h and i respond to the crystal plane spaces of (-323), (013), (310) and (-222) of monoclinic Ni(PO<sub>3</sub>)<sub>2</sub>, respectively.

X-ray photoelectron spectroscopy (XPS) was further conducted to investigate the electronic state of the present elements in near

surface region. The survey spectrum (Fig. 4a) reveals the presence of Ni, P, O and C in Ni(PO<sub>3</sub>)<sub>2</sub>@ACC hybrid. The uniform distribution of Ni, P and O atoms can also be demonstrated by their elementalmapping images (Fig. S3, Supporting Information). The multiplet splittings were carried out for assigning Ni 2p, P 2p and O 1s spectral profiles and their chemical states. The Ni 2p spectrum can be deconvoluted into two spin-orbit doublets and two shakeup satellites (Fig. 4b), indicating the coexist of Ni<sup>2+</sup> and Ni<sup>3+</sup> species <sup>22-24</sup> on the surface of  $Ni(PO_3)_2@ACC$  hybrid. The presence of  $Ni^{3+}$  ions suggests a non-reductive process involved in the transformation of Ni(PO<sub>3</sub>)<sub>2</sub> nanocrystals from Ni(OH)<sub>2</sub> precursor. According to the probed O 1s XPS spectrum (Fig. 4c), it seem like that the oxygen species exhibit two distinct forms such as P-O-Ni non-bridging oxygen atoms (533.1 eV) and P-O-P bridging oxygen ones (531.8 eV),<sup>25</sup> further confirming the formation of nickel phosphate. The asymmetric peak envelope from overlapping components in Fig. 4d can be split into two signals at 133.5 and 134.8 eV, which could be assigned to  $PO_4^{3-26}$  and  $PO_3^{2-27}$  species respectively. The presence of large amounts of surficial  $PO_4^{3-}$  ions evidences that the formation of Ni(PO<sub>3</sub>)<sub>2</sub> nanocrystals involves the transformation from  $PO_4^{3-}$  to  $PO_3^{2-}$  species.

To further disclose the growth mechanism of the 3D hierarchical Ni(PO<sub>3</sub>)<sub>2</sub>@ACC nanosheet arrays, the phosphorylation temperatures were tailored at 250~350 °C with an interval of 50 °C. Their XRD patterns of the corresponding samples are presented in Fig. 5. Similar to Fig. 2, the diffractions at ~25.8° and ~43.0° relate to the substrates of ACC. It suggests that the resultant product treated at a lower temperature of 250 °C retains the original crystalline form of Ni(OH)<sub>2</sub>, while the Ni(PO<sub>3</sub>)<sub>2</sub> can be obtained at 300 and 350 °C, indicating that the phosphorylation reaction is triggered once the temperature is up to 300 °C. It is quite different from the cases of previous reports, <sup>28, 29</sup> in which PH<sub>3</sub> can be generated upon heating of NiH<sub>2</sub>PO<sub>2</sub> below 250 °C (see Equation 1) and subsequently cause the phosphorization reaction to form Ni-P with various crystal phases.

$$5NaH_2PO_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2$$
(1)

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To clarify this point, the hydrothermally-obtained Ni(OH)<sub>2</sub> powder and NaH<sub>2</sub>PO<sub>2</sub> without the use of the ACC substrate are heated at 300 °C with the same experimental conditions. The XRD characterization discloses that the obtained product is single phase of nickel phosphide (Ni<sub>2</sub>P) with a high crystallinity (Fig. S4, Supporting Information), in which PH<sub>3</sub> might act as the launcher to drive the formation of Ni<sub>2</sub>P via Equation 2 as bellow:

$$2PH_3 + 2Ni(OH)_2 = Ni_2P + P + 4H_2O + H_2 (\geq 300 °C)$$
 (2)

To confirm this point, a lower temperature of 250 °C was fixed for the pyrolysis of the mixture of Ni(OH)<sub>2</sub> and NaH<sub>2</sub>PO<sub>2</sub> under the same other conditions as mentioned above. The XRD pattern of asobtained sample (Fig. S5, Supporting Information) suggests the coexistence of Ni, Ni<sub>2</sub>P and P, in which the metallic Ni is dominant. It suggests that the formation of Ni<sub>2</sub>P might start from the generation of metallic Ni (shown as Equation 3). This further confirms that the reaction of the Ni(OH)<sub>2</sub> precursor without ACC is through a PH<sub>3</sub>-involved reduction-dominant mode.

$$2PH_3+3Ni(OH)_2=3Ni+2P+6H_2O (\leq 250 °C)$$
 (3)

The comparison experiments as mentioned above (see the summary in Table S1, Supporting information) strongly imply that, besides the high phosphorylation temperature, the ACC substrates also plays a determined role on the formation of  $Ni(PO_3)_2$ nanocrystals, which is similar to the reported work that the SiO<sub>2</sub> substrate is critical to the compositions of final products.<sup>30</sup> The formation of Ni(PO<sub>3</sub>)<sub>2</sub> rather than Ni<sub>2</sub>P is thus speculated to be ascribable to the strong interaction between the  $\mathrm{Ni}^{2^{+}}$  precursor and ACC, which could reduce the potential of Ni<sup>2+</sup>/Ni pair and thus hinder the reduction of  $Ni^{2+} \rightarrow Ni_2P/Ni$ . In this case, the anchored Ni(OH)<sub>2</sub> precursor becomes prior to react with the high-valence phosphate products (H<sub>3</sub>PO<sub>3</sub> or H<sub>3</sub>PO<sub>4</sub>) obtained from the dismutation reaction of  $H_2PO_2^-$ , making the formation of  $Ni(PO_3)_2$ through the substitution of  $PO_3^-$  for  $OH^-$  in the Ni-OH lattice. Accordingly, the decomposition of  $NaH_2PO_2$  is deduced to release not only gaseous  $PH_3$  (see Equation 2), but also  $H_3PO_3$  or  $H_3PO_4$  via Equation 4 and 5:

 $6NaH_2PO_2=3Na_2HPO_3+H_3PO_3+2PH_3$  (4)  $4H_3PO_3=PH_3+3H_3PO_4$  (5)

That is to say, the as-prepared Ni(OH)<sub>2</sub> nanostructures participate in two competitive reactions, which favor the formations of the Ni<sub>2</sub>P and Ni(PO<sub>3</sub>)<sub>2</sub> respectively. Assisted by the ACC substrate, the PH<sub>3</sub>-involved reduction reaction would be suppressed; this thus allows the H<sub>3</sub>PO<sub>3</sub>/H<sub>3</sub>PO<sub>4</sub>-involved phosphorylation reaction become dominant, leading to the formation of the single phase of Ni(PO<sub>3</sub>)<sub>2</sub>. On the above basis, the synthesis mechanism of Ni(PO<sub>3</sub>)<sub>2</sub> nanocrystals follows two possible routes: i) the reaction between H<sub>3</sub>PO<sub>3</sub> and Ni(OH)<sub>2</sub> (Equation 6); ii) the reaction between Ni(OH)<sub>2</sub> and (HPO<sub>3</sub>)<sub>4</sub> (Equation 7) converted from H<sub>3</sub>PO<sub>4</sub> via Equation 8.

$$10H_3PO_3+3Ni(OH)_2=3Ni(PO_3)_2+4P+18H_2O (\geq 300)$$
 (6)

$$2Ni(OH)_2 + (HPO_3)_4 = 4H_2O + 2Ni(PO_3)_2 (\ge 300 °C)$$
 (7)

$$4H_{3}PO_{4} = (HPO_{3})_{4} + 4H_{2}O$$
(8)

Then the electrochemical performance of  $Ni(PO_3)_2@ACC$  was



**Fig. 5** Typical XRD patterns of the resultant samples with the phosphorylation temperatures fixed at 250, 300 and 350 °C.

firstly investigated for the exploration of their potential application in electrochemical energy storage, via the cyclic voltammogram (CV) and galvanostatic charge-discharge (GCD) methods in threeelectrode configuration. The annealed product of the hydrothermally obtained Ni<sup>2+</sup> precursor on ACC, identified as Ni(OH)<sub>2</sub>@ACC (see XRD pattern in Fig. S6, Supporting information), was used as a comparison. The representative CV curves for  $Ni(PO_3)_2@ACC$  and  $Ni(OH)_2@ACC$  at different scan rates are shown in Fig. 6a and b. The strong redox peaks for both electrodes indicate their battery-type electrode characteristics, which are mainly due to Faradaic redox reactions, and the symmetry of anodic/cathodic peaks suggests their good reversibility. The shift of the anodic and cathodic peaks with the increase of the scan rates is attributed to the internal resistance of the electrode.<sup>31</sup> The subtle change in the CV shape of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC with the increase of the scan rates from 5 to 50 mV  $s^{-1}$  thereby implies a smaller equivalent series resistance, as compared to that of Ni(OH)2@ACC electrode. Interestingly, the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode responses an obviously much larger redox current density than Ni(OH)<sub>2</sub>@ACC counterpart at all scan rates, verifying that Ni(PO<sub>3</sub>)<sub>2</sub>@ACC is capable of storing much more electrical energy than Ni(OH)2@ACC. Notably, the CV profile of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode in Fig. 6b shows two sets of redox activities as indicated by two pairs of anodic/cathodic current peaks. The first and dominant set of a redox couple, which appears in the potential range of 0.15~0.45 V vs. Hg/HgO, is associated with the conversion of  $Ni^{2+} \leftrightarrow Ni^{3+}$ . The second set at the right neighbour pertains is assigned to the  $Ni^{3+} \leftrightarrow Ni^{4+}$  redox couple, which is usually observed in many nickel-based electrode materials and would contribute to the overall energy-storage performance,  $^{\rm 23,\,32}$  while it is absent in CV curves of Ni(OH)<sub>2</sub>@ACC electrode (Fig. 6a). The Ni<sup>3+</sup> species is known to possess high conductivity, which could facilitate an increased mobility rate of surface charge and electrolyte-transfer and thus render an enhanced pseudocapacitive activity to the electrodes.<sup>24, 33</sup> Moreover, A much smaller peak potential difference  $(\Delta E_p = E_{pa} - E_{pc})$  between Ni<sup>2+</sup> $\leftrightarrow$ Ni<sup>3+</sup> pairs observed on CV curves of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC in Fig. 6b, indicates a better Ni<sup>2+</sup> $\leftrightarrow$ Ni<sup>3+</sup> reversibility in Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes.<sup>34</sup>

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**Fig. 6** Typical CV curves of Ni(OH)<sub>2</sub>@ACC (a) and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes (b) with different scan rates. Typical discharge curves of Ni(OH)<sub>2</sub>@ACC (c) and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes (d) at various discharge current densities. (e) The ca. areal specific capacitance of Ni(OH)<sub>2</sub>@ACC and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes as a function of discharge currents. (f) Typical Nyquist plots of Ni(OH)<sub>2</sub>@ACC and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes.



**Fig. 7** (a) Typical cycling performance of the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode at a current density of 10 mA cm<sup>-2</sup>. The inset shows the GCD comparison of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes at 1th, 800th and 2000th cycles. (b) Typical Nyquist plots of the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode before and after 2000 cycles.

The as-fabricated Ni(PO<sub>3</sub>)<sub>2</sub>@ACC and Ni(OH)<sub>2</sub>@ACC electrodes were further evaluated by the GCD method, which was carried out at various current densities ranged from 2 to 30 mA cm<sup>-2</sup> under a potential window of 0–0.48 V and 0–0.40 V (vs. Hg/HgO), respectively. The nonlinear behavior of the discharge curves in Fig. View Article Online DOI: 10.1039/C6TA09528C COMMUNICATION

6c and d further verifies the results from the CV measurements, i.e., the battery-type charge storage property. The specific capacitances of both electrodes at various discharge current densities, calculated from their GCD curves, are shown in Fig. 6e. It is evident that the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode exhibits very high specific capacitances, which is two folds higher than the Ni(OH)<sub>2</sub>@ACC counterpart under the identical test conditions. In detail, the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode possesses excellent areal capacitances of 4.43, 3.39, 2.95, 2.87 and  $2.75 \text{ F cm}^{-2}$  at the current densities fixed at 2, 5, 10, 20 and 30 mA cm<sup>-2</sup>, respectively. Meanwhile, its mass specific capacitance can reach up to 2237 F  $g^{-1}$  at ~1 A  $g^{-1}$  (mass loading: 1.98 mg cm<sup>-2</sup>). In comparison, ACC shows a much smaller areal capacitance of 0.28 F  $\text{cm}^{-2}$  at the discharge current of 2 mA  $\text{cm}^{-2}$  (see CV and GCD curves of ACC electrode in Fig. S7, Supporting Information). It implies that ACC mainly acts as the electronic conductive support for fully performing the electrochemical activity of Ni(PO<sub>3</sub>)<sub>2</sub> nanostructures and with a negligible capacitance contribution to the integral performance of the hybrid material. Furthermore, the capacitance of the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode at 30 mA cm<sup>-2</sup> is *ca*. 62% of that at 2 mA  $cm^{-2}$ , revealing its good high-rate capability. This mainly benefits from the high dispersity nature of Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays and the constructed 3D hierarchical nanostructure of the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC hybrids, which could profoundly facilitate the electrolyte transportation. Moreover, it should be pointed out that the mass specific capacitance (*i.e.*, 2237 F  $g^{-1}$ ) of our Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode is comparable to the best one of Ni-based ultracapacitor electrodes ever reported (see Table S2 in Supporting Information), which are often ranged in 500~2600 F  $g^{-1}$ . It also could be the highest one among those of the previously reported Me-PO<sub>x</sub> pseudocapacitor materials (see Table S3 in Supporting Information). Meanwhile, its areal capacitance (*i.e.*, 4.43 F cm<sup>-2</sup>) stands in a high level in comparison with other self-supported electrode materials (typically of  $2^{5}$  F cm<sup>-2</sup>) (see Table S4 in Supporting Information). These further verify that the current 3D hierarchical  $Ni(PO_3)_2$ nanosheet arrays could be a novel and very promising candidate to be utilized as the electrode material for the next generation ultracapacitors.

To elucidate the dynamic behaviors of Ni(OH)<sub>2</sub>@ACC and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrodes, the electrochemical impedance spectrum (EIS) was collected, and their corresponding Nyquist plots are shown in Fig. 6f. It suggests that the obtained EIS spectra of both electrodes consist of an arc in the high frequency with a sloped line in the low frequency. The near-semicircle arises because of the parallel combination of charge transfer resistance (R<sub>ct</sub>) and double layer capacitance  $(C_{rll})$ .<sup>35</sup> In general, if the electrochemical kinetics is governed by a diffusion-controlled process, the linear plot should be 45° to the real axis. Otherwise, it should be 90° if it is a capacitive behavior in nature. The linear plot of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode exhibits much steeper than that of Ni(OH)2@ACC counterpart, suggesting its much more rapid ion diffusion and better capacitor behavior. The observed smaller semicircle diameter of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode clarifies that it has a much smaller  $R_{ct}$  and a larger C<sub>dl</sub> than Ni(OH)<sub>2</sub>@ACC.

The cycling stability of  $Ni(PO_3)_2@ACC$  electrode was also

evaluated at a current density of 10 mA  $cm^{-2}$  in the potential range of 0 to 0.48 V for 2000 cycles, as shown in Fig. 7a. The capacitance increases at the beginning, which suggests the electrode selfactivation process to make better electrode/electrolyte contact and more active sites participated in the electrochemical reaction. Afterwards, the capacitance exhibits a slight decrease at the start of ~850<sup>th</sup> cycling. It still remains ~90.7% after 2,000 cycles as compared to the peak value, and nearly no loss with respect to the first cycle. This is accordance with the charge-discharge curves of the electrodes at 1<sup>th</sup>, 800<sup>th</sup> and 2000<sup>th</sup> cycling (the inset in Fig. 7a). Furthermore, the nanostructures almost remain after cycling test (see SEM images in Fig. S8, Supporting Information), implying the satisfied stability of the as-synthesized nanosheet arrays. Moreover, a slight detachment can be observed after the prolonged cycling of 2000 times. Meanwhile, it will contribute to the capacitance decrease of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode with extending cycle time. Overall, the experiments above confirm that the as-synthesized 3D hierarchical Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays exhibit an excellent cycling stability at a high current density. The impedance spectra of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC before and after 2000 cycles were conducted, which are shown in Fig. 7b. It seems that the diffusive resistance of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC becomes larger (from 1.10 to 5.29  $\Omega$ ) with a higher R<sub>ct</sub> after 2000 cycles, which could be possibly ascribed to the microstructural adjustment of  $Ni(PO_3)_2$  nanosheets caused by the repetitive charge/discharge. In addition, the linear part of the Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode becomes even closer to 90° after the 2000 cycles, further representing its excellent capacitive behavior and stability.

#### Conclusions

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In summary, we have demonstrated the exploration of novel electrode material of 3D hierarchical Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays, which is firstly synthesized via a rationally topotactic strategy combined a hydrothermal growth of nickel precursors with a followed phosphorylation treatment. The as-synthesized 3D hierarchical Ni(PO<sub>3</sub>)<sub>2</sub>@ACC exhibits a superior capacitive activity as compared to Ni(OH)2@ACC counterpart. The areal and mass specific capacitance of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC electrode could be up to 4.43 F cm  $^{-2}$  at a current density of 2 mA cm  $^{-2}$  and 2237 F g  $^{-1}$  at ~1 A g  $^{-1},$ respectively, which is twice higher than that of Ni(OH)2@ACC electrode, and comparable to the best one among the Ni-based and Me-PO<sub>x</sub> ultracapacitor electrodes ever reported. It can maintain ~90% charge retention after 2000 cycles at a high rate of 10 mA cm<sup>-2</sup>, suggesting its robust stability. This work makes an innovation to the synthesis of Ni(PO<sub>3</sub>)<sub>2</sub> nanostructures with desired structures as well as their potential applications in advanced electrodes for ultracapacitors, which would open an exciting new avenue for the rational design of Me-PO<sub>3</sub> materials for energy storage devices with superior performances.

#### **Experimental Methods**

All the reagents were of analytical grade, and commercially

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available from Shanghai Chemical Reagent Co. Ltd, which were used directly without any further purification. Carbon cloth (CC) was purchased from CeTech, Taiwan. Prior to the synthesis, carbon cloth was cleaned by acetone, ethanol and deionized water in sequence by sonication, and then activated in 65% HNO<sub>3</sub> at 90 °C for 6 h. Afterwards, the activated carbon cloth (ACC) was rinsed by deionized water until pH~7.0, and dried at 60 °C in vacuum overnight.

The fabrication of the self-supported electrode of  $Ni(PO_3)_2$ nanosheet arrays were achieved via a two-step process. Firstly, a hydrothermal process was conducted to achieve a uniform nanostructured Ni<sup>2+</sup> precursor, *i.e.*, nanosheet arrays. Secondly, a heat-treated phosphorylation was applied to convert the Ni2+ precursors to Ni(PO<sub>3</sub>)<sub>2</sub> nanosheet arrays. In details, 2 mmol of NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 40 mL of deionized water, followed by introducing 6 mmol of NH<sub>4</sub>F and 10 mmol of urea with continuous stirring. Then, the ACC (area: 2×3 cm<sup>2</sup>) was immersed in the above solution at 50 °C for 2 h. Subsequently, the solution with the ACC was transferred into a Teflon-lined stainless autoclave (50 mL). The autoclave was sealed and maintained at 110 °C for 4 h. After cooling to room temperature (RT), the obtained hybrid was collected, and washed by the deionized water for more than three times, and then dried at 60 °C in vacuum for 8 h. Afterwards, the resultant product was cut in half. One piece was treated with 5 mmol of  $NaH_2PO_2$  at 300 °C for 2 h under Ar (heating rate: 4 °C min<sup>-1</sup>) for phosphorylation treatment, leading to the growth of Ni(PO<sub>3</sub>)<sub>2</sub>@ACC. The other piece was treated under the similar conditions for the preparation of annealed Ni(OH)2@ACC, which was used as the comparison sample for the performance characterizations. Notably, the NaH<sub>2</sub>PO<sub>2</sub> powders were placed at the upstream side of the crucible and the as-grown hybrids were located at the opposite end, as shown in Fig. S1a (Supporting information). To investigate the effect of the reaction parameters on the formation of nickel salts, the annealing temperatures were varied during the heat treatment process.

The resultant products were characterized by the X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) and field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). The nickel metaphosphates scratched from the ACC were supported on microgrid for the observation on high-resolution transmission electron microscopy (HRTEM, JEM-2010F, JEOL, Japan) and selected area electron diffraction (SAED) pattern. X-ray photoelectron spectra (XPS) were determined on an X-ray photoelectron spectrometer (XPS, AXIS ULTRA DLD, Shimadzu, Japan) with an excitation source of Mg K $\alpha$  radiation (1253.6 eV), in which all the binding energies were referenced by the C1s peak at 284.8 eV.

The electrochemical performances of the ultracapacitor electrodes based on as-fabricated Ni(OH)<sub>2</sub>@ACC and Ni(PO<sub>3</sub>)<sub>2</sub>@ACC were evaluated by the cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) on a CHI 660D electrochemical workstation. EIS was conducted at the open circuit voltage with a alternate current amplitude of 5.0 mV in the frequency range of 10 mHz to 10 kHz.

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The as-fabricated Ni(PO<sub>3</sub>)<sub>2</sub>@ACC and annealed Ni(OH)<sub>2</sub>@ACC (1.0×1.0 cm<sup>2</sup>) were directly used as the working electrodes, in which the platinum foil (1.5×1.5 cm<sup>2</sup>), the Hg/HgO electrode and 3 M KOH were used as the counter electrode, the reference and the electrolyte, respectively.

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3D hierarchical  $Ni(PO_3)_2$  nanosheet arrays are developed as a novel electrode material with superior energy storage behaviors.