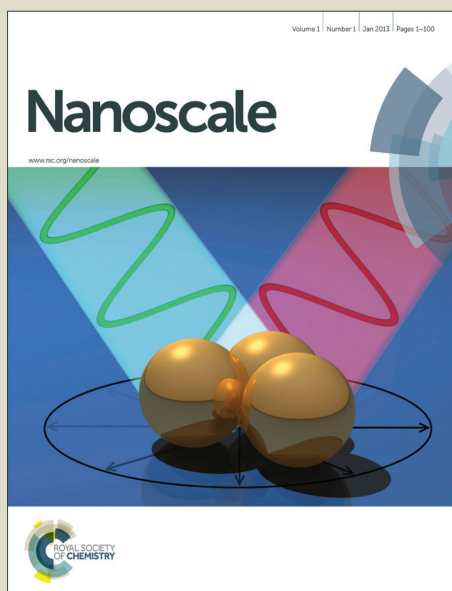


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Novel Peapoded Ni₂P Nanoparticles with Improved Electrochemical Properties for Hydrogen Evolution and Lithium Storage

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A novel peapod-like Ni₂P/C nanocomposite is designed and synthesized using NiNH₄PO₄H₂O nanorods as templates. With enriched nanoporosity and large active surface areas, the peapod-like composites offer superb dual functionality as both electrocatalysts for the hydrogen evolution reaction (HER) and anodes for lithium ion battery (LIB). Electrochemical tests demonstrate that Ni₂P/C nanocomposite exhibits an overpotential as low as 60 mV and a notably low Tafel slope of 54 mV/dec. When used as an anode material for lithium-ion batteries, the resulting peapod-like Ni₂P/C nanocomposite delivers high specific capacitances of 632 mAh/g at 0.1 A/g and 439 mAh/g at 3 A/g respectively, and also exhibits superior cycling performance with nearly 100% capacity retention even after 200 charge–discharge cycles at a charge–discharge rate of 0.1 A/g. The work demonstrates that the peapod-like materials reported herein are promising materials for electrochemical energy-related applications such as HER and LIBs.

Introduction

A worldwide effort has been undertaken to develop energy storage devices with sustainable, renewable and efficient technique that would reduce the global consumption of nonrenewable fossil fuels and alleviate the negative impact of greenhouse gas emission.¹⁻² Up to now, the fast development and demand in industry intensively focus on vast applications of nanosized and nanostructured materials because of the unusual properties endowed by confining their dimensions and the combination of bulk and surface properties to the overall behavior.³⁻⁹ Besides the conventional nanomaterials, such as 0-D (quantum dots),⁴ 1-D (nanowires, nanotubes, nanorods),⁵⁻⁷ 2-D (nanosheets)⁸ and 3-D nanocrystals,⁹ a plethora of new nanocomposite materials, that are sandwiched structures, yolk-shell architectures and peapod-like nanocomposites have attracted a great deal of interest because of their peculiar properties, and potential applications in catalysis, photonics, electronics, drug delivery, medical diagnostics, sensors, and magnetism.¹⁰⁻¹⁴ Among these morphologies, peapod-like nanostructures have aroused much interest due to the extraordinarily high active surface/interface and robust stability endowing them with technological significance in energy storage and conversion. As a good example of the peapod-like nanostructures for superior LIBs electrodes, the peapod-like structures with Co₃O₄ or Ni₁₂P₅ nanoparticles encapsulated in carbon fibers have been investigated to improve cycling stability and rate capabilities by minimizing the total volumetric expansion, incorporating pore or voids to accommodate expansion, or by reducing the electron transport length and ion diffusion distance

during the electrode process, which make them one of the most promising candidates for next generation energy storage and conversion devices.¹³⁻¹⁴

Hydrogen has been proposed as an ideal energy carrier of the future replacing fossil fuels because it is high gravimetric energy and environmentally friendly.¹⁵ The scalable and sustainable production of hydrogen fuel through water splitting demands electrocatalysts for the hydrogen evolution reaction (HER).¹⁶ Among many HER electrocatalysts, noble metals such as platinum are the best in acid media, but relatively scarcity in the Earth's crust and the high cost hinders their large-scale commercial applications.¹⁷ Therefore, the discovery of robust and efficient alternative catalysts that are inexpensive and earth abundant is highly needed. Among such catalysts, Transition metal phosphides (M_xP_y , where $M=Ni, Co, Fe, Mn$ or Cu , etc) have recently attracted attention due to their high performance catalytic, electronic, and magnetic application.¹⁸⁻²³ Recently, nanostructured Ni_2P have shown a tremendous potential as highly active HER catalysts, exhibiting an overpotential of -130 mV at a current density of -20 $mAcm^{-2}$ in 0.5 M H_2SO_4 .¹⁸

Lithium ion secondary batteries are the most promising power sources for portable electronic devices and electrical/hybrid vehicles owing to their high power density, long lifespan and environmental benignity.²⁴ The Nickel phosphide (Ni_xP_y) has been considered as one of the most promising anode material for high-performance Li-ion batteries due to its high gravimetric and volumetric capacities associated with low electrode volume expansions.^{14,25} Moreover, nanostructured materials can enhance the electrochemical performances that could not be achieved in bulk materials, benefiting from the larger surface area and shorter diffusion path. Much research has been conducted on synthesizing various materials with different desired nanostructure and morphology. Among all the different special structure electrode materials for LIBs, peapod-like nanostructures with nanoscale active materials encapsulated in carbon fibers, as an advanced functional materials have been found to be excellent electrodes because of their ideal synergic effect in electrochemical energy storage derived from the unique conformation. For example, Li's group designed the $MnO/Carbon$ nanopeapods exhibit a very high reversible capacity (as high as 1119 mAh/g at even 0.5 A/g) and fast charge/discharge capability (463 mAh/g at 5 A/g).²⁶ In our previous study, a peapod-like composite consisting of $Ni_{12}P_5$ nanoparticles encapsulated in carbon fibers was prepared, which demonstrates enhanced rate capability, cyclability, and prolonged lifespan.¹⁴

It is not an easy job to design and synthesize nanostructures with enriched active sites and large specific surface areas, because the fabrication of the nanostructure, which realizes all the potential advantages, is very complex and usually has less controllability on the crystalline phase and morphology of active materials which are critical for the material performance. Herein, utilizing glucose as a low-cost and environmentally friendly carbon source, we have designed and developed a peapod-like composite with nickel phosphide (Ni_2P) nanoparticles encapsulated in carbon fibers for the first time. As a novel non-noble-metal HER catalyst operating in acidic electrolytes, peapod-like composite exhibits high electrocatalytic activity toward HER with a low overpotential (~ 60 mV) and small Tafel slope (~ 54 mV per decade), long-term durability and a good temperature efficiency. As electrode materials for LIBs, the peapods display high reversible capacity of about 632 mAh/g , superior rate capability (e.g., 439 mAh/g at 3 A/g), and long cycle-life (e.g., ≥ 200 cycles).

Results and discussion

In this study, the peapod-like Ni_2P/C nanocomposite is introduced for the first time based on the

formation $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorod as the precursor and its subsequent reaction with H_2 at 700°C , as illustrated schematically in Fig. 1. Firstly, nanorod precursor is synthesized by a hydrothermal method, which includes a great deal of hydrated or hydroxyl groups on the surface. Then, the green carbon source (glucose molecule) is introduced and absorbed on the surface of the $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ with the aid of hydrogen-bonding actions under solvothermal conditions. In the process, the adsorbed glucose molecules were gradually polymerized into polymeric layers. Subsequently, the polymeric layers can be carbonized to carbon fiber upon calcination in a H_2 atmosphere; meanwhile, hydrated precursors decomposed with the release of the gaseous species and are converted into peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite. Finally, the Ni_2P nanoparticles encapsulated in carbon fibers is obtained. In this process, the $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorods with uniform size are synthesized on a large scale. Fig. 2a and Fig. S1a (supporting information) show the scanning electron microscopy (SEM) image of the $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorods. The X-ray diffraction (XRD) analysis (Fig. 2b) of the bulk sample confirms the overall phase purity of the nanorod, with all peaks corresponding to $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ (JCPDS Card No. 50-0425). Transmission electron microscopy (TEM) images exhibit that the diameter of these rod falls into a narrow range of 40-50 nm (Fig. 2c and Fig. S2b (supporting information)). High-resolution TEM (HRTEM) images reveal that the $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorod is single crystalline (Fig. 2d). Well-resolved lattice fringes are observed from these rod-like structure, which correspond to d-spacing values of 0.88 nm with the (010) crystal planes.

Peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite is easily achieved through a thermal annealing process, as illustrated in Figure. 1. In Fig. 3a, a typical SEM image shows the uniform peapod-like structure. Moreover, a clear low-magnification SEM image (Fig. S2a, supporting information) demonstrates that, under the typical condition, scalability of the peapod is feasibly accessible. Impurity phases often form together with Ni_2P . In order to identify the only existence of purity phases in the obtained product, the X-ray diffraction pattern is collected for the samples and the resultant XRD pattern is shown in Fig. 3b. All the diffraction peaks can be indexed as the Ni_2P phase (JCPDS No.74-1385) and their sharpness has indicated the good crystallinity. No impurity peaks are detected. Energy-dispersive spectrum (EDS) analysis suggests the existence of Ni, P, C and O elements whereas Si peaks emanating from the silicon substrate used for SEM sample' support also exist (Fig. 3e). These observations imply the high stability of $\text{Ni}_2\text{P}/\text{C}$ nanocomposite. In additional, the carbon content in the composite is about 10.3wt % (see the Experimental Section). From a low magnification TEM image (Fig. 3c), it is clear that the Ni_2P nanoparticles with around 20-50 nm in diameter are uniformly encapsulated in the carbon fiber along the nanorod' axial direction with periodic intervals. The Barrett –Joyner – Halenda (BJH) pore-size distribution curve (Fig. 3f, inset) shows a broad peak ranging from 2 to 15 nm and two narrow peaks at 2.0 and 3 nm, confirming the nanoporous nature of the $\text{Ni}_2\text{P}/\text{C}$ nanocomposite. The surface area (S_{BET}) is calculated as $113.7 \text{ m}^2/\text{g}$. The large surface area and nanoporous structure are beneficial for providing sufficient interface between the electroactive materials and the electrolyte.²⁷ The encapsulated Ni_2P nanoparticles are precisely investigated by HRTEM techniques, as shown in Figure. 3d, disclosed the crystal structure. The lattice fringes with d-spacing values of 0.501 and 0.221 nm correspond to the (010) and (111) plane of the Ni_2P nanocrystal, respectively.

To examine their electrocatalytic HER activities, the $\text{Ni}_2\text{P}/\text{C}$ nanocomposites and the Ni_2P particles are deposited with the same loading of approximately $0.285 \text{ mg}/\text{cm}^2$ on glassy carbon

electrodes (GCEs), and the HER activities are measured in H_2SO_4 solution (0.5 M) using a typical three-electrode setup. For comparison, pure Ni_2P particle, $\text{Ni}_2\text{P}/\text{C}$ nanocomposite and commercial Pt/C (20 wt %) are also performed with the same measurement. Fig. 4a shows the polarization curves without IR compensation. As expected, Pt/C shows superior HER activity. The peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite has been demonstrated to be more active than Ni_2P particles due to the much smaller size and additional catalytically active sites on the surface. The Ni_2P nanoparticles encapsulated carbon layer exhibit an overpotential as low as 60 mV and a lower Tafel slope of 54 mV/dec. Even to achieve current densities of 5, 10 and 20 mA cm^{-2} , the $\text{Ni}_2\text{P}/\text{C}$ nanocomposite only needs overpotentials (η) of 64, 87 and 115 mV, respectively. These values for $\text{Ni}_2\text{P}/\text{C}$ nanocomposites compare favorably to the behavior of other non-noble-metal HER catalysts in acidic media, such as WS_2 nanosheets and some Molybdenum compounds.^{28,29} Fig. 4b shows the corresponding Tafel plots of $\text{Ni}_2\text{P}/\text{C}$ and Ni_2P , which are fit with the Tafel equation ($\eta = b \log(j) + a$, where b is the Tafel slope). Typically, the Tafel slope of Pt/C is 30 mV/dec in accordance with the Tafel mechanism. The Tafel slopes of $\text{Ni}_2\text{P}/\text{C}$ and Ni_2P are calculated as 54, and 86 mV/dec, respectively. Stability is a critical aspect in the development of electrocatalysts. For this reason, we further probe the durability of the $\text{Ni}_2\text{P}/\text{C}$ catalysts in acidic media by long-term cycling tests. As shown in Fig. 4c, the LSV curves are measured for $\text{Ni}_2\text{P}/\text{C}$ before and after 2000 cyclic voltammetry (CV) cycles ranging from +0.2 to -0.5 V vs. RHE at a scan rate of 50 mV s^{-1} . At the end of the cycling experiment, the LSV curve exhibits no measurable loss in current density compared to the initial curve. Moreover, the $\text{Ni}_2\text{P}/\text{C}$ nanocomposite exhibits good stability with negligible current loss after 1000 circles in the durability test (Fig. 4d) at a scan rate of 5 mV s^{-1} . Fig. 4e shows the time dependence of the current density for $\text{Ni}_2\text{P}/\text{C}$ at overpotential of -122 mV, suggesting that the peapod-like $\text{Ni}_2\text{P}/\text{C}$ maintains its catalytic activity for at least 50 hours. The exceptional durability indicates that $\text{Ni}_2\text{P}/\text{C}$ is of superior stability in a long-term electrochemical process. We attribute these efficient electrochemical performance to their enriched nanoporosity and large active surface areas that more efficient use of active sites in $\text{Ni}_2\text{P}/\text{C}$.

We have also carried out measurements for the polarization of the $\text{Ni}_2\text{P}/\text{C}$ catalysts with a scan rate of 5 mV/s collected in 0.5 M H_2SO_4 at different temperature. As shown in Fig. 4f, along with the elevation in temperature from 273 K to 323 K, the overpotential (η) of $\text{Ni}_2\text{P}/\text{C}$ nanocomposite decreased, which is consistent with the previous work.³⁰ Remarkably, the peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite exhibits the overpotential (η) of 60 mV at 273 K, and as low as 40 mV at 323 K, which indicating that the peapod-like $\text{Ni}_2\text{P}/\text{C}$ is a high efficient catalysts in acid solution at a relatively low or high temperature.

Motivated by the unique inherent structural features of the peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposites, we also evaluate the electrochemical properties as anode materials for LIBs. The representative galvanostatic discharge-charge voltage profile of the peapods at a current density of 100 mA/g in the voltage range of 0.01-3.0 V is shown in Fig. 5a. It is interesting to observed that the as-synthesized peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite exhibits a very high initial discharge capacities of 1027 mAh/g , which is even higher than that of theoretical capacity for Ni_2P (542 mAh/g). According to the previously reported results, the excess discharge capacity could be associated with the initial formation of the solid-electrolyte-interface (SEI) layer generated from electrolyte degradation, which is very common in many anode materials especially during the low potential range.^{13,14,26,31} In addition, the irreversible transformation from crystalline Ni_2P nanoparticles to pulverized tiny ones is another reason for the changes in current densities.

Afterward, the following charge-discharge curves tend to be stable, implying that the electrochemical reaction is proceeding into cycle stages. This situation echoes in the cyclic voltammetry (CV) curve, as shown in Fig. 5b. Cyclic voltammograms (CVs) are taken of the samples within a potential window between 0.01-3.0 V at a scan rate of 0.1 mV/s to investigate the electrochemical reactions that occur during the initial charge/discharge cycles. By assigning the cathodic and anodic peaks to the redox reactions, P-based alloying/dealloying reaction are identified as: $\text{Ni}_2\text{P} + 3\text{Li}^+ + 3\text{e}^- \leftrightarrow \text{Li}_3\text{P} + 2\text{Ni}$.^{14,32}

In contrast, Ni_2P particles without any carbon coating layers show inferior discharge-charge performances, as shown in Fig. S3 (supporting information). The galvanostatic measurement at same 0.1 A/g current density shows an initial discharge capacity of 904 mAh/g, which rapidly drops to 456 mAh/g at the second cycle and is retained at ~186 mAh/g after 50 cycles, corresponding to a capacity retention of 40.7% compared to that of the second cycle. This comparison clearly indicates that the Ni_2P nanoparticle encapsulated in carbon fibers has significantly improved electrochemical properties. Such excellent electrochemical performance should be attributed to the peapod-like structure of $\text{Ni}_2\text{P}/\text{C}$ nanocomposite, in which the nanoporous structure provides sufficient electrochemical interface and accessible electronic and ionic channels, thereby leading to an effective release of its potential high capacity and a fast rate capability, and the structure of $\text{Ni}_2\text{P}/\text{C}$ could keep stable by buffering the large volume expansion and aggregation of active nanoparticles.

In addition, the $\text{Ni}_2\text{P}/\text{C}$ nanocomposite anode presents an excellent cycling performance (Fig.5c). The Coulombic efficiency (the ratio between charge capacity and discharge capacity) is only 65% in the initial cycle. However, the discharge capacity becomes stable from the second cycle, with the Coulombic efficiency of each cycle over 95% with an excellent cycling performance achieved. After 200 cycles, the discharge capacity is well retained at ~ 630 mAh/g, corresponding to ~100% that of the second cycle. The specific capacity is still considerably higher (at the current densities of 0.1 A/g) when compared to previous reports on Ni_2P nanomaterials in the literature.^{25,32} Capacity retention relates to the ability of the peapod-like structure to physically accommodate the dramatic volumetric changes associated with de/lithiation. To verify structural integrity of the peapod-like anodes after lithium cycling, batteries are disassembled and examined by TEM. Fig. S4 (supporting information) shows that the peapod-like structure is well maintained after the 200th cycle. Moreover, the cycling performance of the $\text{Ni}_2\text{P}/\text{C}$ nanocomposite anode is further interrogated, where each step consists of 20 discharge/charge cycles at different current densities in the range of 0.1-3.0 A/g (Fig. 5d). The discharge capacities are retained at 632, 603, 555, 512, 439 mAh/g at the current densities of 0.1, 0.2, 0.5, 1 and 3 A/g, respectively, with a Coulombic efficiency of almost 100% for each cycle. When the current density is reseted to 0.1 A/g, the capacity is recovered to 628 mAh/g, suggesting excellent capacity retention at higher rates of the peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite. To the best of our knowledge, a Ni_2P anode, with such a high capacity, long cycle life and superior rate capability, has never been reported before. Such excellent electrochemical performance should be attributed to the novel peapod-like structure.

To confirm the enhanced charge transport by the carbon coating and the reduction of the size, the electrochemical impedance spectroscopy (EIS) is carried out for the $\text{Ni}_2\text{P}/\text{C}$ nanocomposite and Ni_2P particle (Fig. S5, supporting information). The Nyquist plots are recorded at a frequency range of 0.01 Hz–100 kHz at an amplitude of 5 mV. The $\text{Ni}_2\text{P}/\text{C}$ nanocomposite shows a smaller

high–medium frequency semicircle than Ni_2P particles, which indicates the lithium ions and electrons can transfer more easily on $\text{Ni}_2\text{P}/\text{C}$ /electrolyte interfaces rather than on that of Ni_2P particles. The decreasing charge–discharge impedance would result in the enhanced electrode process kinetics and improved electrochemical performance, especially at a high charge–discharge current density. The result reveals that the charge-transfer resistance of $\text{Ni}_2\text{P}/\text{C}$ is much lower than that of Ni_2P particles. It is believed that the peapod-like structure possesses a large specific area, thus the electrical current can spread in various directions and the lithium ions can transfer at more sites on solid–liquid interfaces.

Conclusion

In summary, we have successfully designed and prepared a novel peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite architecture with high surface areas ($113.7 \text{ m}^2/\text{g}$). Remarkably, when used as a non-noble-metal HER catalyst, this peapods exhibit an onset overpotential of 60 mV, a Tafel slope of 54 mV/dec and maintain its activity for at least 50 hours under acidic conditions. When used as anode material for LIB, the unique peapods features lead to a high-capacity up to 632 mAh/g at 0.1 A/g and impressive rate capabilities with a capacity of 439 mAh/g even at a current density of as high as 3 A/g. Remarkably, a pretty high capacity of 628 mAh/g with a long cycle life (200 cycles with almost 100% capacity retention) at 0.1 A/g is achieved. These results confirm that this novel peapod-like structure is generally applicable for enhancing the catalytic activity and electrochemical performance of $\text{Ni}_2\text{P}/\text{C}$ materials. We anticipate this novel insight into the design and synthesis of peapod-like materials should inspire the development of a wide range of other fields, such as photonics, electronics, sensors, magnetism and so on.

Experimental Section

Materials: All chemicals or materials were used directly without any further purification before use. Ethylene Glycol (Fisher Chemical, 99.99%), Ammonia Hydroxide ($\text{NH}_3\text{H}_2\text{O}$, 28–30 wt%, J. T. Baker), Nickel Nitrate ($\text{Ni}(\text{NO}_3)_2$, 99.9%, Aldrich), Sodium dihydrogen phosphate (NaH_2PO_4 , 99.9%), Sodium Carbonate (Na_2CO_3 , 99.9%, Aldrich), D(+)-Glucose (Cica-Reagent, Kanto Chemical), concentrated hydrochloric acid (37.5%), sulfuric acid [99.999%], metallic Li foil (99.9 %, Aldrich) and Nafion solution [5% in a mixture of EtOH] (Sigma-Aldrich), were used as received.

Preparation of NiNH_4PO_4 nanorods

In a typical synthesis, ethylene glycol (10 mL), concentrated $\text{NH}_3\text{H}_2\text{O}$ (10 mL, 28–30 wt %), an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ (5 mL, 1 M), an aqueous solution of NaH_2PO_4 (7.5 mL, 1 M), and an aqueous solution of Na_2CO_3 (5 mL, 1 M) were mixed step by step under vigorous stirring at intervals of 2 min. The reaction solution was then rapidly stirred in ambient air for 5 min. Then, was transferred into a Teflon-lined stainless-steel autoclave (45 mL), a thermal treatment was performed for the Teflon-liner in an electric oven at 170°C for 24 h. After the autoclave was cooled naturally to room temperature in a fumehood, samples deposited at the bottom were collected and washed by centrifugation for at least three cycles using deionized water and for one cycle using pure ethanol. The as-synthesized samples were then dried in a vacuum oven at 60°C overnight to remove absorbed water and ethanol for subsequent characterizations.

Preparation of peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposites and Ni_2P particles

NiNH_4PO_4 nanorods (100 mg) were ultrasonically mixed with an aqueous solution of glucose (2 mL, 1 M) together with additional deionized water (28 mL) to form a homogeneous solution after

5 min. The above solution was introduced into a Teflon-lined autoclave (40 mL) and sealed tightly. Then, the liner was heated in an electric oven at 180 °C for 8 h. After that, the samples were washed by centrifugation three times with deionized water and one time with ethanol and were dried in air at 60 °C overnight to remove residual water and ethanol. Afterwards, the dried samples were loaded into the tube furnace and calcined in an H₂ atmosphere at 700 °C for 200 min. The process yields the formation of the peapod-like Ni₂P/C nanocomposite. For comparison, the Ni₂P particles were synthesized with the same process except the addition of glucose.

Characterization

A field-emission scanning electron microscope (JEOL, JSM-7800F, 15 kV), a transmission electron microscope (Philips, Tecnai, F30, 300 kV) coupled with an energy dispersive spectrometer (EDS) analyzer, a X-ray diffractometer with Cu K_α radiation (XRD, Bruker D8 Advance), a BET surface-area and pore-size analyzer (Quantachrome Autosorb-6B), and a X-ray photoelectron spectrometer with an ES-CALAB250 analyzer were employed to characterize the obtained samples.

Carbon content tests

Firstly, 200.00 mg of the samples (Ni₂P/C) were added in concentrated hydrochloric acid. After 24 h stirring and standing, the Ni₂P nanoparticles were completely dissolved in acid. The carbon remain was collected, washed with deionized water and absolute ethanol to remove impurities, and dried in an oven at 60 °C overnight to remove absorbed water and ethanol. The carbon weight measurements were made using a Mettler-Toledo analytical balance. The carbon content of Ni₂P/C was then calculated using the formula:

$$C\% = W(C)/W(\text{Ni}_2\text{P/C}) \times 100\%$$

Where W(C) and W (Ni₂P/C) were the weight of carbon and Ni₂P/C, respectively. Results show that the carbon content in the composite is about 10.3 wt%. For comparison, the Ni₂P particles (200.00mg) were dissolved in concentrated hydrochloric acid with the same process.

Electrochemical measurements

Hydrogen evolution reaction: Electrochemical measurements are performed with a CHI660D electrochemical workstation (CH Instruments, Inc., Shanghai). A three-electrode cell is used, including a glassy carbon electrode (GCE, geometric area = 0.07 cm²) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. To prepare the working electrode, 3 mg of the catalyst and 100 μL of 5 wt% Nafion solution were dispersed in 300 μL of ethanol solvent, followed by ultrasounded at least 5 min. Then 4 μL of the ink was dropped onto a GCE (~loading: 0.36 mg cm⁻²). Linear sweep voltammetry (LSV) was performed solution of 0.5 M H₂SO₄ with a scan rate of 5 mV s⁻¹ in a range from -0.2 V to -0.5 V. Durability test was then carried out by cyclic voltammetry (CV) scanning from -0.5 to 0 vs. SCE for 20000 at a scan rate of 50 mV s⁻¹. In all measurements, (SCE) was used as the reference, and all the potentials reported in our work were vs. the reversible hydrogen electrode (RHE). In 0.5 M H₂SO₄, E (RHE) = E (SCE) + 0.281 V.³³

Lithium-ion batteries: A homogeneous mixture composed of Ni₂P/C nanocomposite active material, carbon black, and polyvinyl difluoride (PVDF) using 1-methyl-2-pyrrolidinone (NMP) as solvent in weight ratio of 80:10:10 was prepared under strong magnetic stirring for at least 3 days and then extracted, and some samples were spread to Al foils. Before and after the samples were spread, the Al foils had to be weighed in a high-precision analytical balance (Sartorius, max weight 41 g, d = 0.01 mg). The reading difference was the exact mass for the coated samples on Al

foils. Normally, the mass loading is around 2–3 mg/cm². The obtained pieces of Al covered with samples were then used as working electrodes with 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (EC-DEC, v/v = 1:1) as electrolyte. Celgard 2400 was used as the separator film to isolate the two electrodes. Pure Li foil was accepted to serve as counter electrode and reference electrode. The cell was assembled in an argon-filled glovebox where moisture and oxygen concentrations were strictly limited to below 0.1ppm. Galvanostatic charge–discharge tests were conducted on LAND battery program-control test system (CT-2001A, Jinnuo electronic Co.). Cyclic voltammogram (CV) tests were performed on a CHI660D electrochemistry workstation (Chenhua Instrument Co.) at a scan rate of 0.1 mV/s between 0.01 and 3.0 V vs. Li/Li⁺. Electrochemical impedance spectroscopy (EIS) measurements were performed on this apparatus over a frequency range from 0.01 Hz to 100 kHz.

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Supporting Information Available: More SEM, TEM and electrochemical test dates are available in the supporting information for this paper.

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Figures and Captions:

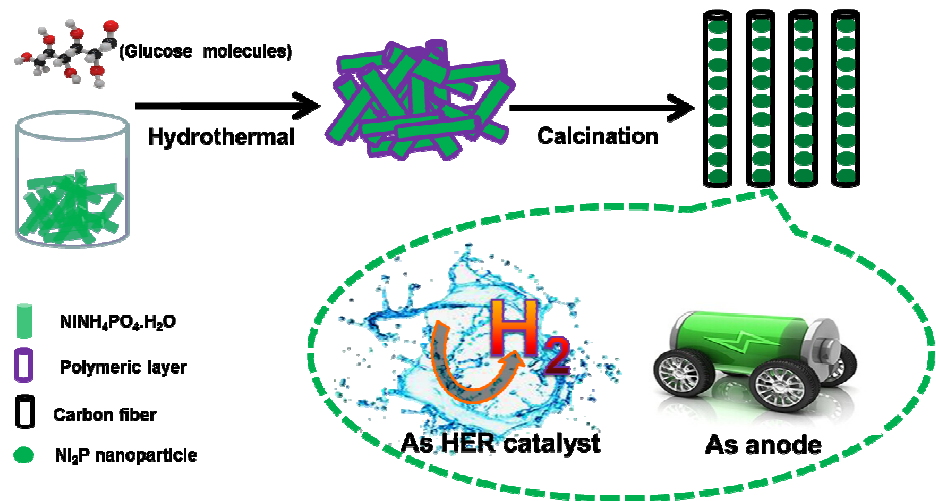


Fig. 1 Schematics illustrate the synthetic procedure of the peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite. Originally, the prepared $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ nanorods serve as the precursors and sacrificial templates. The green and sustainable glucose molecules act as the carbon source. Undergoing a hydrothermal polymerization and H_2 calcinations at elevated temperatures in sequence, the final peapod-like composite is harvested. The lower right panel is the optical picture to vividly describe the typical application of the peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite.

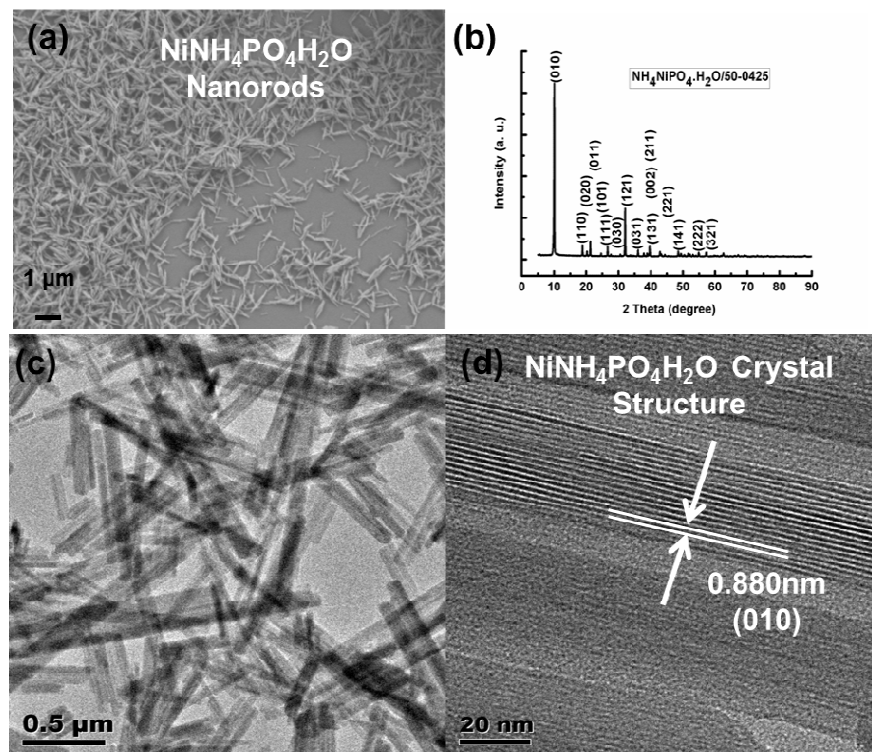


Fig. 2 (a) Typical scanning electron microscopy (SEM) images. From panel, a large scale production of the $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorods samples can be clearly detected; (b) XRD data to verify the obtained pure-phase $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorods; (c) Low-magnification transmission electron microscopy (TEM) image to confirm the uniformity and regularity of our precursors; The corresponding high-resolution TEM (HRTEM) image (d) indicates that the nanorods exhibit well-crystallized features.

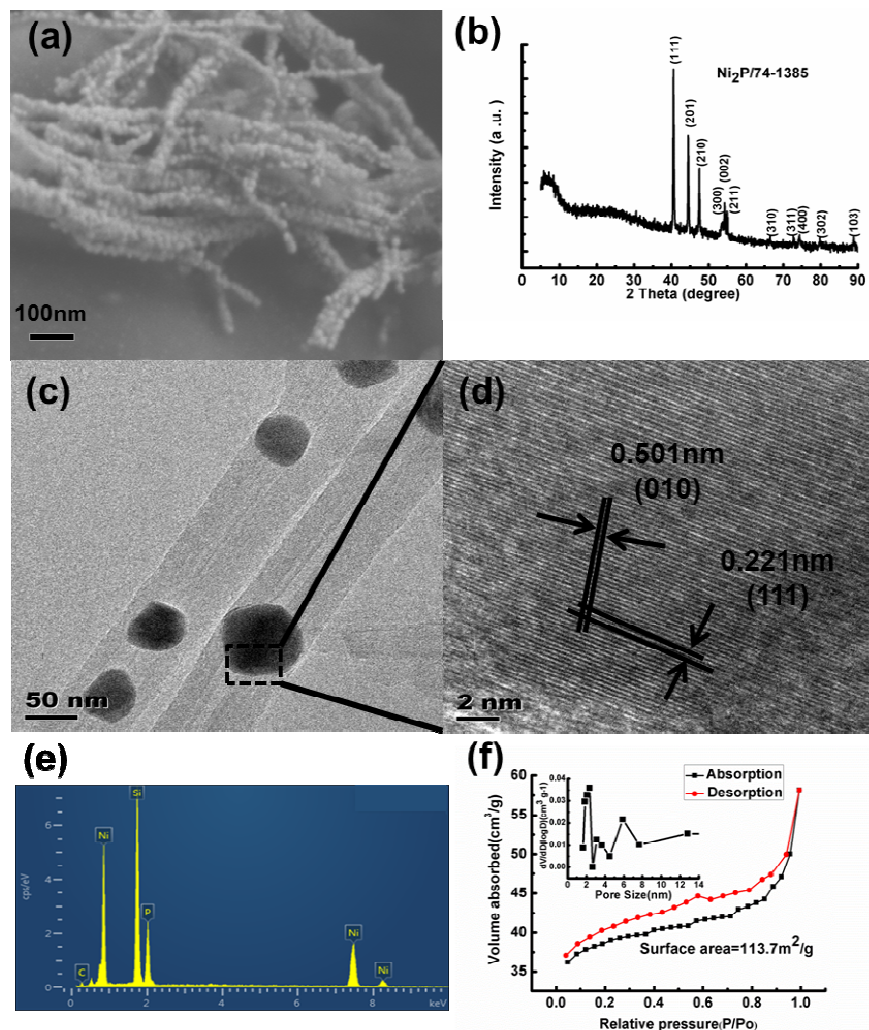


Fig. 3 (a) Low-magnification SEM image is introduced to show the specific peapod-like structure; (b) XRD data to verify the obtained pure-phase Ni_2P ; (c) Magnified TEM image to show the peapod-like morphology for $\text{Ni}_2\text{P}/\text{C}$ nanocomposite; (d) HRTEM image to clearly demonstrate the well-crystallized structure for $\text{Ni}_2\text{P}/\text{C}$ nanocomposite; (e) The energy dispersive spectroscopy (EDS) analysis to determine the co-existence of nickel and phosphorous in the peapods; (f) Nitrogen sorption isotherm of the peapod-like $\text{Ni}_2\text{P}/\text{C}$ nanocomposite. The inset is the corresponding pore size distribution calculated using the BJH formula from the adsorption branch.

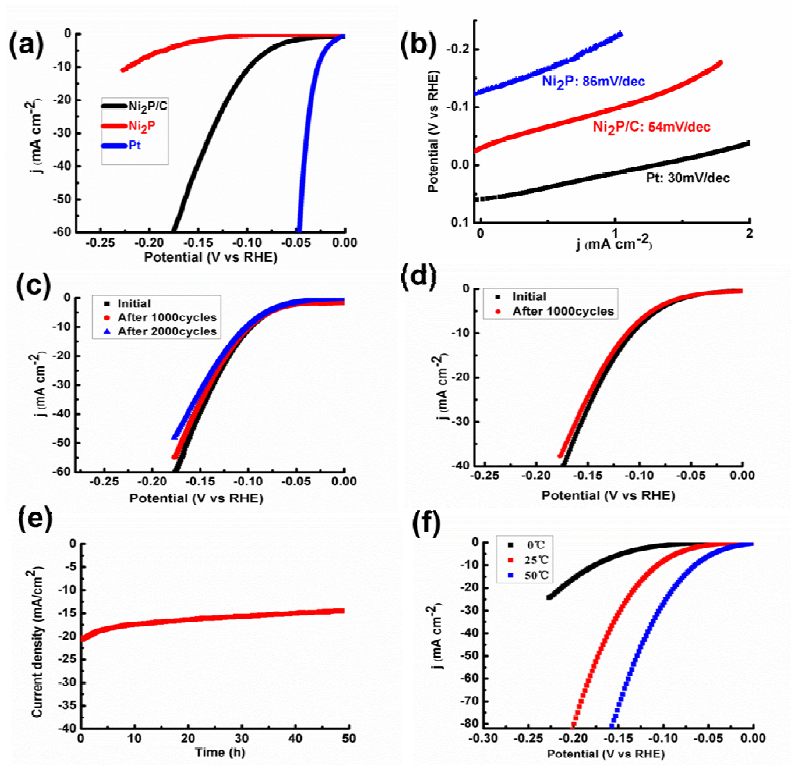


Fig. 4 (a) Polarization curves of the Ni_2P , $\text{Ni}_2\text{P/C}$ and Pt catalysts with a scan rate of 5 mV/s in 0.5 M H_2SO_4 ; (b) Tafel plots of Ni_2P , $\text{Ni}_2\text{P/C}$ and Pt/C; (c) Polarization curves for $\text{Ni}_2\text{P/C}$ in H_2SO_4 solution (0.5 M) with a scan rate of 50 mV/s before and after 1000 and 2000 cycles between +0.2 and -0.5 V; (d) Polarization curves for $\text{Ni}_2\text{P/C}$ in H_2SO_4 solution (0.5 M) with a scan rate of 5 mV/s before and after 1000 cycles between +0.2 and -0.5 V; (e) Time-dependent current density curve for $\text{Ni}_2\text{P/C}$ under static overpotential of -122 mV for 50 h; (f) Polarization curves of the $\text{Ni}_2\text{P/C}$ catalysts with a scan rate of 5 mV/s in 0.5 M H_2SO_4 collected at different temperature, maintained using a thermostatic water bath.

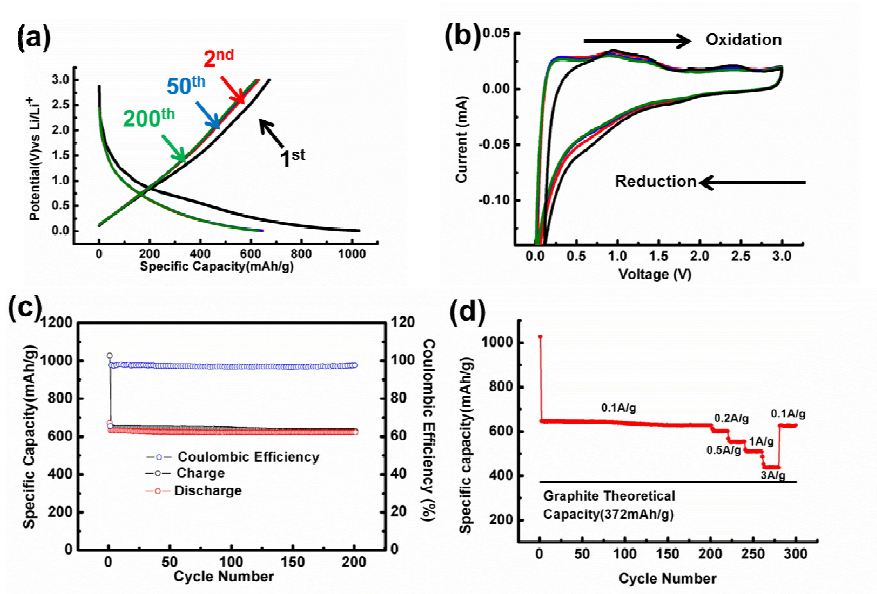
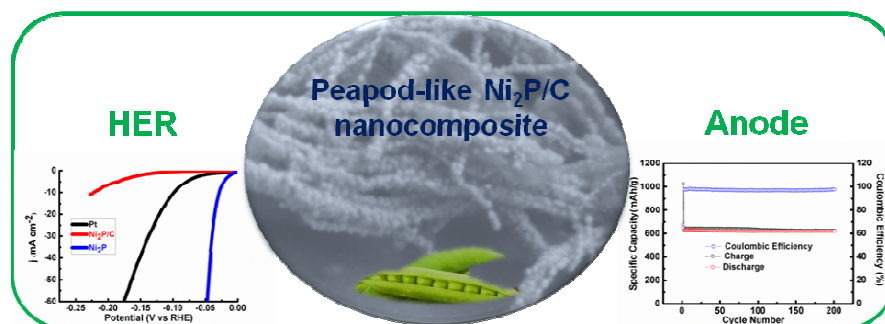


Fig. 5 Electrochemical measurements are performed to characterize the peapod-like composites : (a) Galvanostatic charge/discharge profile at a current density of 0.1 A/g; (b) CV curves to reveal the samples' reduction/oxidation features; (c) Cycling performance and Coulombic efficiency within a voltage range of 0.01-3.0 V vs Li/Li^+ at 0.1 A/g; (d) Wonderful cyclability and good capacity retention of the samples when the charge/discharge rates increase gradually from 0.1 A/g to 3 A/g and decrease back to 0.1 A/g are demonstrated.

Table of Contents Entry



The electron transfer of Ni_2P structures, along with the fast development of versatile structures controlled during the growth, has offered excellent properties and technological application in diverse fields. As a promising candidate for active catalyst and electrode material, Ni_2P nanoparticles have attracted much interest owing to their lower toxicity, lower cost and abundance. However, it remains challenging to achieve pure phase of transition-metal phosphides because various phosphides exist with different, but fixed molar ratios between the transition metal and phosphorous. In addition, to design and synthesize nanostructures with enriched active sites and large specific surface areas is of key importance. In this work, a novel peapod-like $\text{Ni}_2\text{P/C}$ nanocomposite is designed and synthesized using $\text{NiNH}_4\text{PO}_4\text{H}_2\text{O}$ nanorods sacrificial templates. As a result, the peapod-like $\text{Ni}_2\text{P/C}$ nanocomposite exhibits high activity and stability for HER and excellent electrochemical performance for anode materials in lithium ion batteries (LIBs).