High-Performance All-Solid-State Supercapacitor Based on the Assembly of Graphene and Manganese(II) Phosphate Nanosheets

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ABSTRACT: Manganese phosphate nanosheets (Mn₃(PO₄)₂·3H₂O NSs) with ~2 nm thickness were prepared by exfoliating the bulk material in dimethylformamide (DMF) under ultrasonication. They can spontaneously form face-to-face stacked assemblies with exfoliated graphene NSs in DMF. The assembled Mn₃(PO₄)₂·3H₂O and graphene NSs at the mass ratio of 1:10 (M₃G₀) revealed a specific capacitance of 2086 F g⁻¹ at 1 mV s⁻¹. These M₃G₀ assemblies were used to fabricate all-solid-state supercapacitor (M₃G₀-ASSS) on the basis of PVA/KOH solid polymer electrolytes, which exhibited a specific capacitance of 152 F g⁻¹ (or 40 mF cm⁻²) at 0.5 A g⁻¹, an energy density of 0.17 μW h cm⁻² at 0.5 A g⁻¹ (1.3 A m⁻²) and a power density of 46 μW cm⁻² at 2 A g⁻¹ (5.3 A m⁻²). M₃G₀-ASSS also showed excellent cycling stability and nearly 100% capacitance retention was achieved after 2000 galvanostatic charge–discharge cycles at 2 A g⁻¹. Such extraordinary properties were attributed to the synergistic effect of high pseudocapacitance of Mn₃(PO₄)₂·3H₂O NSs, high conductivity and surface areas of graphene NSs.

INTRODUCTION

Increasing demands of portable, flexible electronics and electrical vehicles promote rapid development of lightweight, highly efficient energy storage devices.¹² Electrochemical capacitors or supercapacitors (SCs), due to their fast charge–discharge rate and good cycle stability, have attracted considerable attention.⁵⁻⁶ Among a variety of electrode materials, two-dimensional nanostructured materials such as (1) graphene, which stores charge in electrochemical double layers by electro sorption of ions on porous carbon,⁷ and (2) pseudocapacitive nanosheets (NSs) such as transition-metal sulfides (TMSs), transition-metal oxides (TMOs), metal hydroxides, and layered double hydroxides (LDHs), have sparked strong interest due to their inherent structure feature and high specific capacitance.⁸⁻¹⁰ These NSs are easily obtained through exfoliating the bulk layered materials.¹¹ In view of the high activity, fascinating flexibility and extensibility, they have exhibited intriguing potential in constructing high performance all-solid-state supercapacitor (ASSS) devices.¹²⁻¹³ Nevertheless, both poor electronic conductivity and strong aggregation propensity have been critical challenges that restrict their practical applications.¹⁴ It is thus highly expected to establish effective approaches for making the best of advantages of these NSs in constructing high performance SCs.

Graphene provides a possible solution for the above issues. Hybridizing with graphene is not only able to provide conductive paths and avoid aggregation, also contributes to improve the cycling stability of composite electrodes.¹⁵ For instance, MnOₓ/graphene retained 92% of the initial capacitance after 7000 charge–discharge cycles;¹⁶ MoS₂/graphene revealed an energy density of 63 Wh kg⁻¹ and 92% retention of the initial capacitance after 1000 cycles;¹⁷ Ni(OH)₂/graphene achieved a specific capacitance of 660.8 F cm⁻³ and 98.2% capacitance retention after 2000 cycles.¹⁸ These results reflect the validity of using graphene to overcome the inherent shortcomings of two-dimensional layers and indicate a promising direction.

As two-dimensional nanostructured materials, layered phosphates have been extensively explored in constructing high-performance solar cells, lithium battery and SCs.¹⁸⁻²¹ For instance, the electrode based on CoHPO₄·3H₂O NSs showed a specific capacitance of 413 F g⁻¹ and no obvious capacitance decay after 3000 charge–discharge cycles.²² LiMnPO₄ NSs revealed a flat potential at 4.1 V versus Li with a specific capacity of 168 mAh g⁻¹ and an excellent cycle stability.²³ In addition, LiMnPO₄ NSs, synthesized through one-pot solvothermal route, displayed a discharge capacity of 147 mA h g⁻¹ (@0.05 C).²⁴ Despite these advances, there are almost no report in the past studies involving the preparation of Mn₃(PO₄)₂·3H₂O NSs and hybridizing with graphene to improve the electrode properties of ASSS. In most studies, Mn₃(PO₄)₂·3H₂O was primarily used as an intermediate of transformations. In view of its excellent electronic features,²⁵⁻²⁶...
Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs are expected to exhibit promising prospects in electrode application of ASSS. In this study, we prepared ~2 nm thick Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs by exfoliating Mn$_3$(PO$_4$)$_2$·3H$_2$O bulk materials in dimethylformamide (DMF). The exfoliated NSs were assembled together with graphene in DMF by simply mixing Mn$_3$(PO$_4$)$_2$·3H$_2$O and graphene dispersions. The resulting composite electrode with a Mn$_3$(PO$_4$)$_2$·3H$_2$O/graphene mass ratio of 1:10 revealed an electrochemical capacitance of 2086 F g$^{-1}$ at the scan rate of 1 mV s$^{-1}$. When assembled into an ASSS device, the composite electrode revealed a mass capacitance of 152 F g$^{-1}$ (corresponding to an areal capacitance of 40 mF cm$^{-2}$), and excellent cycle stability. These results suggest a novel phosphate-based route for developing low-cost, high-performance, and excellent cycle stability. These results suggest a novel phosphate-based route for developing low-cost, high-performance flexible SCs.

# EXPERIMENTAL SECTION

## Synthesis of Graphene and Bulk Mn$_3$(PO$_4$)$_2$·3H$_2$O

Graphene was prepared by sonication-assisted exfoliation of graphite intercalation compounds (GICs).$^{27,28}$ Bulk Mn$_3$(PO$_4$)$_2$·3H$_2$O was synthesized following a reported method.$^{21}$ In a typical run, 6 g (NH$_4$)$_3$PO$_4$ was first dissolved in distilled water (25 mL) with the aid of ultrasonication, followed by adding 0.2 g 50 wt % Mn(NO$_3$)$_2$. The solution was stirred at room temperature for 0.5 h. The light pink precipitate was washed carefully with distilled water for several times and freeze-dried for 4–6 days before use.

**Exfoliation of Mn$_3$(PO$_4$)$_2$·3H$_2$O.** Mn$_3$(PO$_4$)$_2$·3H$_2$O (125 mg) was dispersed in a jacketed beaker with 250 mL DMF and subsequently, the dispersion was sonicated for 40 min (500 W at 20 kHz) to form Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs. For comparison, several different solvents including water, ethanol, and N-methylpyrrolidinone (NMP) were also utilized to prepare Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs.

**Synthesis of Graphene and Bulk Mn$_3$(PO$_4$)$_2$·3H$_2$O/Graphene Composite Film.** Mn$_3$(PO$_4$)$_2$·3H$_2$O and graphene NSs were dispersed in DMF with different mass ratios: 1:10, 1:5, 1:1, 5:1 and 10:1, which are denoted as M1G1, M5G1, M10G1, respectively. The exfoliated Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs were named as MG0. A cellulose membrane with 0.22 μm pores was used to filter the dispersion. The resulting composite films were washed with distilled water for several times and dried at room temperature for 10 h.

**Preparation of Gel Electrolyte.** Six grams of PVA powder ($M_w = 57000–66000$, Alfa Aesar) was dissolved in 40 mL distilled water at 90 °C.$^{29}$ After complete dissolution, 4.5 g KOH was added into the above solution with vigorous stirring until the mixture turned into a transparent, clear gel.

**Fabrication of ASSS.** ASSS consisted of the assembly films as electrodes, Cu foils as current collectors, PVA/KOH as electrolyte, and PPAT-CN1 composite membrane (Shanghai Shilong Hi-Tech Co. Ltd.) as separator.$^{30,31}$ The assembly films were pressed on Cu films at 10 MPa for 5 min, on which PVA/KOH was then coated. The PPAT-CN1 composite membrane was soaked in PVA/KOH for 5–10 min and then placed between two assembly/Cu electrodes to avoid short circuit. The whole device was solidified for ~1 h and then sealed carefully.

**Structure Characterization.** Atomic force microscopy (AFM) images were acquired using a Multimode Nano 4 in the tapping mode. The samples for AFM observation were prepared by depositing the DFM dispersion containing Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs on freshly cleaved mica surfaces. Transmission electron microscopy (TEM, Tecnai G2 F20 Twin, operating at 200 kV) was used to observe morphology of the bulk Mn$_3$(PO$_4$)$_2$·3H$_2$O, exfoliated Mn$_3$(PO$_4$)$_2$·3H$_2$O NSs, graphene NSs, and assemblies. All samples for imaging were prepared by depositing the corresponding DMF dispersions on holey copper grids. X-ray diffraction (XRD) tests were carried out using PANalytical X’Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å) in 2θ range from 40° to 90°, operating at 40 kV and 40 mA. Scanning electron microscopy (SEM, VEGA TS 5136MM) and field-emission scanning electron microscopy (FESEM, Ultra 55) were used to observe morphology of the bulk materials and the assemblies, both operating at 20 kV. Energy Dispersive Analysis of X-ray (EDX) was performed on CM200FEG HR-TEM. Fourier infrared spectroscopy (FTIR) was recorded on a NEXUS 6700 spectrometer with a resolution of 2 cm$^{-1}$ in a range from 400 to 4000 cm$^{-1}$. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. The conductivity was measured on a SX1944 four-point probe instrument (Suzhou Baishen Tech Co. Ltd.).

**Electrochemical Tests of the Single Electrode and Symmetric Supercapacitor.** All electrochemical measurements were conducted by CHI 660E electrochemical workstation (CHI Instruments) at room temperature. A three-electrode configuration was used to measure the cyclic voltammetry where a nickel foam including the active material assembly was used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the pseudo-reference electrode.
The working electrode was prepared by mechanically mixing assembly powders, acetylene black, and polytetrafluoroethylene (PTFE) binder with a weight ratio of 80:10:10. The mixture was then ground, and a small amount of isopropyl alcohol was added for improving homogeneity. Finally, the mixture was pressed on a nickel foam current collector with a 10 MPa pressure and then dried for 8 h at room temperature. The electrolyte used in all measurements was 6 M KOH aqueous solution.

The cyclic voltammetry test was conducted at scan rates of 1, 2, 5, 10, 20, 50, and 100 mV s⁻¹ with a potential window of 0–0.35 V, respectively. Galvanostatic charge–discharge tests of the as-fabricated ASSS were performed at different current densities.

### RESULTS AND DISCUSSION

The assembly process and ASSS fabrication procedure is schematically illustrated in Scheme 1. We exfoliated the bulk Mn₃(PO₄)₂·3H₂O in DMF into 2D NSs (Figure S1, Supporting Information) under sonication. The obtained dispersion is homogeneous and reveals the typical Tyndall effect (Figure S2), suggesting that DMF is a suitable solvent for exfoliation of Mn₃(PO₄)₂·3H₂O. The exfoliated Mn₃(PO₄)₂·3H₂O NSs exhibit a homogeneous morphology, with lateral sizes from 100 to 400 nm, as shown in Figure 1a. The nearly transparent characteristic (Figure 1d) indicates that the resulting NSs are well exfoliated. The AFM image (Figure 1e) shows that the exfoliated Mn₃(PO₄)₂·3H₂O NSs is ∼2 nm thick, a single-layer morphology that is similar to those of other exfoliated 2D NSs, for example, VS₂ (2.5 nm), Ti₅Si₆O₇S₇ (4 nm), and VOPO₄ (4.07 nm). For the exfoliation of Mn₃(PO₄)₂·3H₂O NSs, we present a possible mechanism as follows. The layered structure of bulk Mn₃(PO₄)₂·3H₂O is stabilized by the H-bond interaction between H₂O molecules and surface oxygen atoms on Mn₃(PO₄)₂ layers. When bulk Mn₃(PO₄)₂·3H₂O is dispersed in DMF, H-bonds can be formed likewise between H₂O and DMF molecules. This enables DMF molecules to diffuse into the interlayer spacing of bulk particles and weakens the interlayer interaction of Mn₃(PO₄)₂·3H₂O layers. It is especially possible when sonication is used to intensify the diffusion of solvent molecules into the interlayer spacing with H₂O molecules (DMF is well compatible with H₂O). In addition, due to the formation of H-bonds, DMF has a good affinity for the Mn₃(PO₄)₂ surface, enabling the resulting NS dispersion to be stabilized.

However, the stability of the above dispersion was changed after adding graphene. We observed apparent aggregates while mixing it with graphene–DMF dispersion (0.1 mg mL⁻¹) and standing for 30 min (Figure 1f). TEM and SEM images (Figure 2) showed the morphology of the aggregates. It is observed that Mn₃(PO₄)₂·3H₂O NSs and graphene NSs form face-to-face stacking structures (Figure 1c). The less C atoms in Mn₃(PO₄)₂·3H₂O NSs revealed in EDX patterns (Figure 1d) primarily originate from the use of sample carbon grids, while the more C atoms in M₅G₁₀ suggest the existence of graphene. In addition, the atomic ratios of P, Mn, and O are consistent with the theoretical value of Mn₃(PO₄)₂·3H₂O (1:1:5:7 vs 1:1.5:5.5). Likewise, the excessive O atoms result from the use of carbon grids.

As mentioned above, bulk phosphate materials are attractive candidates for high-performance SCs devices. Given the morphology and structure of exfoliated Mn₃(PO₄)₂·3H₂O NSs and the assembly (face-to-face stacking aggregates), we expect that the assembly could exhibit desired electrochemical properties owing to the ultrathin geometry and possible pseudocapacitive characteristics of Mn₃(PO₄)₂·3H₂O NSs. As previous studies revealed, two-dimensional NSs tended to achieve better performance than the corresponding bulk or other nanostructured materials owing to the quantum confinement effect, which can improve their electronic properties tremendously. For instance, the photoelectrode based on ZnSe single layers displayed photocurrent density 195 times higher than the bulk 2 mm thick SnSe NSs exhibited a specific...
capacitance \(\sim 1.4\) times higher than that of the 9 nm thick NSs, and SnO\(_2\) NSs grown on graphene also achieved a much higher reversible capacity and better cycle performance relative to SnO\(_2\) particles.

The electrochemical properties of the assembly were measured with a three-electrode system in 6 M KOH. Figure 4a shows the CV loops of M\(_1\)G\(_{10}\) at scan rates of 1, 2, 5, 10, 20, 50, and 100 mV s\(^{-1}\), respectively. Their shape obviously deviates from that of electric double-layer capacitance, suggesting a pseudocapacitive attribute (Figure 3e). The pseudocapacitance of Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O NSs primarily originates from the surface redox reaction. The large areas of the CV loops and the redox peaks is scan-rate dependent, indicating that the redox reaction occurred rapidly during the scans, and possible mechanisms can be described as follows:

\[
\begin{align*}
\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O} + 3\text{OH}^- & \rightarrow \text{Mn}_3(\text{OH})_6(\text{PO}_4)_2 + 3\text{H}_2\text{O} \\
\text{Mn}_3(\text{PO}_4)_2\cdot3\text{H}_2\text{O} + 3\text{K}^+ + 3\text{e}^- & \rightarrow \text{K}_3\text{Mn}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O}
\end{align*}
\]

In common, specific capacitance \(C_s\), power density \(P\), and energy density \(E\) are important parameters used to evaluate the electrochemical properties. They are calculated by the following equations:

\[
C_s = Q/\left(\Delta V \times m\right) = \int I \, dV/\left(\Delta V \times \nu \times m\right)
\]

\[
E = \left[C_s(\Delta V)^2\right]/2
\]

\[
P = \left[C_s(\Delta V)^2\right]/2
\]

where \(Q\), \(\Delta V\), \(m\), \(I\), and \(\nu\) were the quantity of electricity (C), voltage (V), mass of the active materials on work electrode (g), current function to potential, and scan rate (V s\(^{-1}\)), respectively.

As expected, compared with the \(C_s\) of the pure bulk Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O (139 F g\(^{-1}\) at 1 mV s\(^{-1}\), Figure S9b), exfoliated Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O NSs achieve a higher value (302 F g\(^{-1}\), Figure 3e) due to the quantum confinement effect originated from their ultrathin property. Interestingly, compared to the limited \(C_s\) of Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O NSs and pure graphene (Figure S9), M\(_1\)G\(_{10}\) shows quite a high specific capacitance. The highest mass specific capacitance \((C_s)\) of M\(_1\)G\(_{10}\) was 2086 F g\(^{-1}\) at 1 mV s\(^{-1}\), along with a high power density \((P)\) of 35.5 Wh kg\(^{-1}\) and energy density \((E)\) of 365 W kg\(^{-1}\). These results are far higher than the results reported in the literature (see Figure S5) \((C_s)\) calculated by CV loops in the three-electrode system. This suggests a synergistic effect.

**Figure 3.** Electrochemical properties of the assembly (a–e) CV loops of M\(_1\)G\(_0\), M\(_1\)G\(_5\), M\(_5\)G\(_1\), M\(_{10}\)G\(_1\), and MG\(_0\) at various scan rates, respectively. (f) Influence of the Mn\(_3\)(PO\(_4\))\(_2\)·3H\(_2\)O contents on the specific capacitance of the assembly.
between Mn3(PO4)2·3H2O and graphene NSs, which might involve three aspects. First, the two-dimensional ultrathin Mn3(PO4)2·3H2O NSs and graphene NSs provide a possibility to maximize surface areas of the electrochemical active material (Mn3(PO4)2·3H2O), which contributes to shorten ion diffusion lengths.\textsuperscript{17,49} Second, graphene NSs with high electric conductivity can act as electron bridges for fast electron transfer.\textsuperscript{50} Third, less Mn3(PO4)2·3H2O NSs deposited on graphene sheets fail to form densely packed structures, which is beneficial for fast charge transfer, especially for the diffusion of electrolyte ions. In addition, Mn3(PO4)2·3H2O NSs deposited on graphene sheets can inhibit dense stacking of graphene NSs, and thus enhance accessible surface areas and long-term cycling stability.\textsuperscript{51}

Figure 3a–d shows the CV loops of M1G10, M1G1, M5G1, and M1G10 at different scan rates and yield \(C_\text{Sc}\) of 1741, 1400, 365, and 300 F g\(^{-1}\), respectively, which are also summarized in Figure 3f. It reveals the significant dependence of specific capacitance on the content of Mn3(PO4)2·3H2O in the assemblies. The optimum content of Mn3(PO4)2·3H2O in the assemblies was evaluated as \(~10\%\), revealing a maximum specific capacitance of 2086 F g\(^{-1}\). By comparison, M1G1 shows a lower specific capacitance. As shown in Figure S8, M10G1 gives a lower BET specific surface areas of about 4 m\(^2\) g\(^{-1}\) compared with that of M2G1 (69.35 m\(^2\) g\(^{-1}\)), but exhibits a much higher conductivity of about 2.1 \times 10^6 \Omega^{-1}\ (Table S1). It explains that the high conductivity could play a more significant role in the much improved supercapacitor performance of the M1G10.

ASSS was constructed using the assembly films to further study the electrochemical property of the assembly. As illustrated in Scheme 1, the as-fabricated ASSS has a planar dimension of 1−2 cm\(^2\) (Figure 4f). The slight drop of the internal resistance (0.026 V; see Figure 4e) implies a small intrinsic series resistance for the M1G10 film, and thus less energy loss during the charge−discharge process. Figure 4c shows the galvanostatic charge−discharge curves of the ASSS fabricated using M1G10 film (M1G10-ASSS) at a current density of 2 A g\(^{-1}\), a capacitive behavior of almost symmetric charge−discharge curves suggesting a desired performance. The deviation to linearity is typical of a pseudocapacitive contribution, which primarily originates from Mn3(PO4)2·3H2O NSs. Figure 4b shows the discharge curves of M1G10-ASSS at a current density of 0.5, 1, 2, 4 A g\(^{-1}\). The discharge

![Figure 4. Electrochemical properties of M1G10 (a) CV loops in three-electrode system. (b) Discharge curve of M1G10-ASSS at various discharge current densities. (c) Galvanostatic charge−discharge curve of M1G10-ASSS at a current density of 2 A g\(^{-1}\). (d) Performance comparison with various materials, where solid shapes stand for energy density and open shapes stand for power density. (e) Galvanostatic charge−discharge curve of M1G10-ASSS at 1st cycle and 2000th cycle. (f) Cycling test of M1G10-ASSS over 2000 cycles and digital photographs inserted of M1G10-ASSS under normal (left), bending (right) conditions. Scale bar, 1 cm.](https://dx.doi.org/10.1021/jp504741u)
Curves of M1G1-ASSS and M5G1-ASSS are presented in Figure S6b,c. These results allow us to further evaluate the performance of ASSS containing assemblies.

The specific capacitance, power density and energy density of electrodes in ASSS were calculated as follows, respectively.\(^\text{(6)}\)

\[
C_s = \frac{2 \times I \times \Delta t}{(\Delta V \times m)}
\]

\[
E = \frac{1}{8} \times C_s(\Delta V)^2
\]

\[
P = \frac{E}{\Delta t}
\]

Where \(\Delta V\), \(I\), \(m\), and \(\Delta t\) are the voltage (V), mass of the single electrode (g), constant current (A), and discharge time (s), respectively.

Consistent with the results of CV measurement, M1G1-ASSS and M5G1-ASSS have lower specific capacitances than that of M5G5-ASSS; the latter exhibited 152 and 118 F g\(^{-1}\) at current densities of 0.5 and 2 A g\(^{-1}\), indicating a good rate performance (Figure S6a). They are apparently superior to the results reported previously (Figure S6d). On the other hand, area-normalized capacitance, power and energy densities are likewise important for many applications. In this regard, M4G10-ASSS also revealed an area capacitance of about 40 mF cm\(^{-2}\), an energy density of 0.17 μWh cm\(^{-2}\) (0.5 A g\(^{-1}\)) and a power density of 46 μW cm\(^{-2}\) (2 A g\(^{-1}\)) (0.5 A g\(^{-1}\) corresponds to ~1.3 A m\(^{-2}\)). These results are likewise very attractive compared to other reported ASSSs (Figure 4d),\(^{22,12,32,53}\) which makes it highly competitive for many energy devices. As shown in Figure 4g, the as-fabricated M1G10-ASSS exhibits an excellent cycle life, nearly 100% capacitance retention after over 2000 charge–discharge cycles, which is much superior to other samples (Figure S7). Such excellent long-term cycling stability clearly indicates a good potential for SC electrode application. In addition, we note that the specific capacitance M1G10-ASSS practically decreased ~28% at 1000 cycles but increased after that. Such a cyclability fluctuation reflects the dependence of specific capacitance on the intrinsic nature, activation degree of electrode, electrolyte ion diffusion and destruction of electrode films during cycling tests.\(^{56-58}\) Figure 4e shows the charge–discharge curve of M1G10-ASSS at first and 2000th cycle, where better symmetry at 2000th cycle relative to first cycle suggests a faster charge–discharge process and smaller intrinsic series resistance,\(^{39}\) despite its slight large internal resistance drop (0.062 Ω). In view of the fascinating capacitance and cycle performance of M1G10-ASSS, we expect that this study will be helpful for development of high-performance ASSSs.

**CONCLUSION**

We prepared Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O NSs (~2 nm in thickness) by exfoliating bulk materials in DMF solution under sonication. The obtained Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O NSs were assembled with graphene and the latter revealed a high specific capacitance (2086 F g\(^{-1}\)) at the mass ratio of 1:10. We attributed it to the synergistic effect between Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O NSs and graphene, which fully exploited the double-layer and pseudocapacitive potential of the assembly due to the shortened ion diffusion lengths, fast electron transfer, and high surface areas. After assembling into ASSS, the M1G10-ASSS exhibited excellent electrochemical properties, with a specific capacitance of 152 F g\(^{-1}\) (0.5 A g\(^{-1}\)) and 40 mF cm\(^{-2}\), an energy density of 0.17 μWh cm\(^{-2}\) (0.5 A g\(^{-1}\)), and a power density of 46 μW cm\(^{-2}\) (2 A g\(^{-1}\)). These results are apparently superior to the majority of reported similar ASSSs. Although the specific capacitance of M1G10-ASSS partially reduced before 1000 cycles, but it recovered to nearly 100% of the initial specific capacitance after 2000 cycles. We suppose that it primarily originates from the activation process of the electrode and the diffusion limitation of ions into the inner region of the assembly. The present study indicates promising potential of manganese phosphate–graphene assemblies as electrode materials and is helpful for development of high-performance SCs.

**ASSOCIATED CONTENT**

Supporting Information

SEM images, XRD patterns, and TEM images of bulk Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O; TGA and DTG curves of Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O bulk materials and NSs; TEM images and optical images of the Tyndall Effect observed in the as-prepared Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O NSs by horn sonication treatment for 40 min in water, ethanol, NMP, and DMF; XRD patterns of M1G10, M5G5, M1G1, and M5G1; FT-IR spectra of Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O; M1G10, M5G1, M1G1, and M5G1; performance comparison with different materials in a three-electrode system; the specific capacitance changes with the discharge rate; discharge curve of M1G5-ASSS and M5G5-ASSS at different discharge current densities; performance comparison with the reported electrode materials; cycling tests of M1G10, M5G1, M1G1, and M5G1; ASSS; N\(_2\) adsorption–desorption isotherms of the pure graphene, Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O, M1G10, and M5G5; CV loops of pure graphene and Mn\(_3\)(PO\(_4\))\(_2\)-3H\(_2\)O at different scan rates; conductivities of films. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**

C.Y. designed the experiments and performed the microscopy observation and chemical characterizations, H.L. supervised the research work. L.D. performed the AFM observation. C.Y. wrote the manuscript draft, and Z.C. and H.L. revised it. All the authors discussed the results and commented on the manuscript.

**Notes**

The authors declare no competing financial interest.

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