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¹ Hierarchical Mn₃O₄/Graphene Microflowers Fabricated via a ² Selective Dissolution Strategy for Alkali-Metal-Ion Storage

³ Chen Tang,^{†,§} Fangyu Xiong,^{‡,§} Xuhui Yao,[‡] Shuangshuang Tan,[‡] Binxu Lan,[†] Qinyou An,^{*,‡} ⁴ Ping Luo,^{*,†} and Liqiang Mai^{*,‡}

s [†]Hubei Provincial Key Laboratory of Green Materials for Light Industry, Collaborative Innovation Center of Green Light-Weight

Materials and Processing, School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, P. R.
 China

⁸ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan
430070, P. R. China

10 Supporting Information

ABSTRACT: Mn_3O_4 is a potential anode for alkali-metal 11 (Li/Na/K)-ion batteries because of the high capacity, 12 abundant resources, and eco-friendliness. However, its ion 13 storage performance is limited by poor electronic conductivity 14 and large volume expansion during the charging/discharging 15 process. In this study, we presented a facile dissolution 16 17 strategy to fabricate ultrathin nanosheet-assembled hierarch-18 ical Mn₃O₄/graphene microflowers, realizing enhanced alkali-19 metal-ion storage performance. The synthetic mechanism was proven as the selective dissolution of vanadium via controlled 20 experiments with different reaction times. The as-synthesized 21 composites showed high lithium storage capacity (about 900 22 mA h g^{-1}) and superior cyclability (~400 mA h g^{-1} after 500 23



cycles). In addition, when evaluated as a Na-ion battery anode, the reversible capacity of about 200 mA h g^{-1} was attained, which remained at 167 mA h g^{-1} after 200 cycles. Moreover, to the best of our knowledge, the potassium storage properties of Mn_3O_4 were evaluated for the first time and a reversible capacity of about 230 mA h g^{-1} was achieved. We believe that our

27 findings will be instructive for future investigations of high-capacity anode materials for alkali-metal-ion batteries.

28 **KEYWORDS**: selective dissolution, Mn_3O_4 , hierarchical nanostructure, alkali-metal-ion battery, anode, graphene

29 INTRODUCTION

³⁰ Currently, the increasing demand for new green energy sources ³¹ is promoting the development of large-scale energy storage ³² systems (LSESSs). A lithium-ion battery (LIB) is a promising ³³ choice for LSESSs depending on its high-energy efficiency, ³⁴ energy density, and discharge voltage.¹⁻⁶ Recently, Na-ion ³⁵ battery (NIB) and K-ion battery (KIB) systems have attracted ³⁶ much attention and are expected to replace LIBs as they ³⁷ operate using similar mechanism, whereas Na and K are more ³⁸ abundant than Li.⁷⁻¹⁴ However, further development of all ³⁹ such battery systems requires the development of high-capacity ⁴⁰ anode materials.^{10,15,16}

⁴¹ Among a serious of anode materials, Mn_3O_4 has attracted ⁴² much attention according to its high capacity (936 mA h g⁻¹), ⁴³ high earth abundance, and eco-friendliness.^{17–21} Unfortu-⁴⁴ nately, its application is astricted by poor cycling stability and ⁴⁵ underutilized capacity caused by the large volume change ⁴⁶ during the cycling process, along with low electrical ⁴⁷ conductivity. Constructing hierarchical structures can effi-⁴⁸ ciently elevate the cycling stability by accommodating the ⁴⁹ volume change in the voids between substructures.^{22–24} On the other hand, introducing graphene to efficiently increase the 50 electrical conductivity has been demonstrated in many 51 instances.^{15,25–28} Therefore, Mn_3O_4 /graphene composites 52 with hierarchical structures hold high promise to realize 53 high-rate and long-life lithium storage, and exploiting a facile 54 and simple strategy to obtain such composite is significant.^{29,30} 55 Furthermore, Mn_3O_4 is hopeful to achieve high sodium/ 56 potassium storage capacity, but to our best knowledge, the 57 literatures about its sodium storage performance are rare and 58 its potassium storage performance has not been investigated 59 yet.

In this work, a facile selective dissolution strategy was $_{61}$ utilized to produce ultrathin nanosheet-assembled hierarchical $_{62}$ Mn_3O_4 /graphene microflowers (Mn_3O_4 -G). The structure $_{63}$ evolution during the dissolution process was investigated, and $_{64}$ the synthetic mechanism was demonstrated as the selective $_{65}$ dissolution of vanadium. Benefiting from the ultrathin $_{66}$

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Figure 1. TEM images of (a) MVO–G precursor, (b) sample obtained from MVO–G precursor by selective dissolution treatment for 30 and (c) 180 min. The Raman spectrum of (d) MVO–G precursor, (e) sample obtained from MVO–G precursor by selective dissolution treatment for 30 and (f) 180 min. (g) Schematic illustration of the process of structural evolution from a MnV_2O_6 nanorod bundle to Mn_3O_4 microflower during the selective dissolution treatment.

67 nanosheet-assembled hierarchical structure and graphene 68 decoration, the Mn_3O_4 -G displayed high lithium storage 69 capacity and outstanding cycling performance. Moreover, the 70 Mn_3O_4 -G also displayed attractive sodium/potassium storage 71 performance.

72 RESULTS AND DISCUSSION

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73 The Mn_3O_4-G was obtained from the MnV_2O_6 /graphene 74 composite (MVO-G) by a NaOH solution treatment process. 75 The structural evolution and reaction mechanism for the 76 transformation from MVO-G to Mn_3O_4-G were also studied. 77 The X-ray diffraction (XRD) pattern (Figure S1a) of MVO-G 78 was indexed to MnV_2O_6 . As shown in Figures 1a and S1b, the 79 MnV_2O_6 had nanorod-bundle morphology and was wrapped 80 by graphene. In the high-resolution transmission electron 81 microscopy (HRTEM) image (Figure S1c,d), the lattice fringe 82 spacing of 0.322 nm accords with the *d*-spacing of (110) facets 83 in MnV_2O_6 . In addition, all of the bands in the Raman 84 spectrum (Figure 1d) originate from the vibration of VO_3^- 85 units.³¹ After dissolution treatment in a NaOH solution for 30 86 min, some nanosheets were formed on the nanorod bundle 87 (Figure 1b). In the corresponding Raman spectrum (Figure

1e), a new band appeared at $\sim 650 \text{ cm}^{-1}$, which was the 88 characteristic band of Mn₃O₄, indicating that the composition 89 of the nanosheets on the nanorod bundle was Mn₃O₄.³² After 90 dissolution treatment for 180 min, the nanorod bundle was 91 completely transformed to nanosheet-assembled microflowers 92 (Figure 1c). Meanwhile, the bands of VO_3^- disappeared in the 93 Raman spectrum, testifying the complete dissolution of 94 metavanadate (Figure 1f). A schematic illustration of structural 95 evolution mechanism during the selective dissolution treat- 96 ment is shown in Figure 1g. The dissolution of MnV_2O_6 97 nanorod bundles was accompanied by the growing of Mn₃O₄ 98 nanosheets on the nanorod bundles, which can be considered 99 as a process of selective dissolution of vanadium. After 100 complete dissolution of MnV2O6 nanorod bundles, the 101 Mn₃O₄ nanosheets formed microflowers. The possible reaction 102 mechanism of selective dissolution is described as follows: 103

(Dissolution)
$$MnV_2O_6(s) \to 2VO_3^- + Mn^{2+}$$
 (1) 104

(Precipitation) $6Mn^{2+} + O_2 + 12OH^-$

$$\rightarrow 2Mn_{3}O_{4}(s) + 6H_{2}O$$
 (2) 105



Figure 2. (a) XRD pattern, (b) XPS spectrum, (c) FESEM image, (d,e) TEM images, (f) HRTEM image, and (g) EDXS elemental mappings of Mn_3O_4-G .



Figure 3. (a) CV curves of Mn_3O_4-G at 0.1 mV s⁻¹. (b) Cycling performance of Mn_3O_4 microflowers, MVO-G, and Mn_3O_4-G at 0.2 A g⁻¹ and (c) corresponding discharge/charge profiles of Mn_3O_4-G . (d) Rate performance of Mn_3O_4 microflowers, MVO-G, and Mn_3O_4-G . (e) Long-term cycling stability of Mn_3O_4-G at 0.5 A g⁻¹.

(Overall)
$$6MnV_2O_6(s) + O_2 + 12OH^-$$

 $\rightarrow 12VO_3^- + 2Mn_3O_4(s) + 6H_2O$ (3)

¹⁰⁷ Oxygen dissolved in solution participates in the reaction and ¹⁰⁸ facilitated the oxidation of Mn^{2+} to Mn^{3+} . Meanwhile, the ¹⁰⁹ reaction shown by eq 2 will enhance the dissolution of ¹¹⁰ MnV_2O_6 (eq 1).

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¹¹¹ The crystalline composition of Mn_3O_4-G was identified ¹¹² using XRD (Figure 2a). All XRD peaks were indexed to ¹¹³ Mn_3O_4 . In addition, the Raman spectrum of Mn_3O_4-G (Figure S2), the bands situated at 1350 and 1610 cm⁻¹ were ¹¹⁴ belonging to the D and G bands of graphene, respectively.²⁵ It ¹¹⁵ was clearly indicated the presence of graphene in Mn_3O_4 . ¹¹⁶ Besides, in the X-ray photoelectron spectroscopy (XPS) ¹¹⁷ spectrum of Mn_3O_4 –G (Figure 2b), the energy gap between ¹¹⁸ Mn $2p_{3/2}$ and $2p_{1/2}$ levels was 11.7 eV, conforming to that of ¹¹⁹ Mn_3O_4 .³³ In addition, a similar spectrum was obtained for Mn ¹²⁰ 2p for the Mn_3O_4 microflowers without graphene (Figure S3). ¹²¹

FESEM (field-emission scanning electron microscope) and 122 TEM were employed to analyze the microstructure of Mn_3O_4 - 123 G. The FESEM images (Figure 2c) showed that the Mn_3O_4 -G 124



Figure 4. (a–c) Sodium storage performance of Mn_3O_4 –G: (a) cycling performance at 0.2 A g⁻¹, (b) corresponded charge/discharge curves, and (c) rate performance. (d–f) Potassium storage performance of Mn_3O_4 –G: (d) cycling performance at 0.1 A g⁻¹, (e) corresponded charge/discharge curves, and (f) rate performance.

125 sample was composed of nanosheet-assembled microflowers 126 with a diameter of 1–2 μ m. The TEM images of Mn₃O₄–G (Figure 2d) revealed that the microflower was composed of 127 ltrathin nanosheets with thickness of below 10 nm. Some 128 nterstices were observed between nanosheets, corresponding 129 well with the FESEM images. In Figure 2e, mesopores in the 130 nanosheets were observed. In addition, distances of lattice 131 fringes in the HRTEM image of Mn₃O₄-G (Figure 2f) are 132 0.276 and 0.249 nm, corresponding to the *d*-spacings of (103) 133 and (211) planes in Mn_3O_4 , respectively. In addition, energy-134 dispersive X-ray spectroscopy (EDXS) elemental mappings 135 showed that Mn, O, and C were distributed uniformly in 136 Mn_3O_4-G (Figure 2g), indicating a homogeneous composite 137 of Mn₃O₄ and graphene nanosheets. Furthermore, thermogra-138 vimetric (TG) analysis of Mn₃O₄-G was performed. In the 139 140 TG curve of Mn_3O_4 -G (Figure S4), a mass loss of 18.5% was observed at around 350 °C, indicating a graphene content of 141 142 18.5 wt % in Mn_3O_4-G .

The specific surface area and pore structure of as-prepared t44 samples were investigated by nitrogen isothermal absorption/ t45 desorption tests. The isotherm of Mn_3O_4-G is shown in t46 Figure S5a, which was identified as a type-II curve with H4 t47 hysteresis loop, implying the existence of narrow slit-like pores. t48 The Mn_3O_4-G sample had a specific surface area of 113.3 m² g⁻¹, which was greater than that of MVO-G (21.5 m² g⁻¹). t50 The large increase in specific surface area implied a drastic t51 structural evolution during the selective dissolution treatment. t52 The pore size distribution plot (Figure S5b) showed that the t53 pores in Mn_3O_4-G were mainly in the 2–4 and 10–100 nm t54 size ranges, corresponding to the mesopores in the nanosheets t55 and interstices between nanosheets, respectively.

The lithium storage behaviors of Mn_3O_4 microflowers, 157 MVO–G, and Mn_3O_4 –G were evaluated using CR2016-type 158 half cells. The cyclic voltammetry (CV) curves of Mn_3O_4 –G in 159 0.01–3 V (vs Li⁺/Li) are displayed in Figure 3a. The peak at 160 ~0.8 V in the first cycle was attributed to electrolyte

decomposition and the reduction of Mn₃O₄ to MnO, that is, 161 $Mn_3O_4 + 2Li^+ + 2e^- \rightarrow 3MnO + Li_2O_{,27,34}^{,27,34}$ In addition, the 162 sharp peak at ~0.15 V was due to the further reduction 163 progress of manganese oxide, that is, MnO + $2Li^+$ + $2e^- \rightarrow Mn_{164}$ + Li_2O .^{27,34} In the second and third cathodic scans, this sharp 165 reduction peak shifted to higher potential (~0.25 V) because 166 of the enhanced reaction kinetics, which corresponded well 167 with results of previous studies.³⁵ In the anodic scans, the 168 peaks at ~ 1.2 and ~ 2.1 V were assigned to the oxidation from 169 metallic Mn to MnO and MnO to higher oxidation states, 170 respectively.^{34,35} The CV curve at the third cycle almost 171 overlapped with that of the second cycle, indicating the high 172 reversibility of the Mn₃O₄-G anode. A fully reversible 173 transformation reaction can be expressed as: Mn₃O₄ + 8Li⁺ 174 + $8e^- \leftrightarrow 3Mn^0$ + $8Li_2O$. The CV curves of Mn_3O_4 (Figure S6) 175 display similar with larger overpotential, indicating that the 176 introduction of graphene improves conductivity and reduces 177 polarization. In addition, the lithium storage performances of 178 Mn₃O₄-G, MVO-G, and Mn₃O₄ microflowers were further 179 evaluated by galvanostatic charge/discharge tests (Figure 3b). 180 At 0.2 A g^{-1} , the Mn₃O₄-G delivers a high reversible capacity 181 of 893 mA h g^{-1} , outperforming that of Mn_3O_4 microflowers 182 (502 mA h g^{-1}) and MVO-G (472 mA h g^{-1}). Discharge 183 plateaus at ~0.7 and ~0.3 V were observed in first cycles 184 (Figure 3c), whereas only one discharge plateau at ~0.4 V 185 appeared in the subsequent cycles, which agreed well with the 186 CV curves. In addition, Mn₃O₄-G also displayed enhanced 187 rate performance (Figure 3d). At 1 A g^{-1} , Mn_3O_4-G still 188 showed a capacity of about 615 mA h g^{-1} , whereas those of 189 Mn₃O₄ microflowers and MVO-G were only 272 and 427 mA 190 h g⁻¹, respectively. The superior rate performance of Mn_3O_4 - 191 G was attributed to the ultrathin porous nanosheet-assembled 192 microstructure and graphene decoration. The charge/discharge 193 curves of Mn₃O₄-G at 0.1-1 A g⁻¹ (Figure S7) showed that 194 the overpotentials were similar. In addition, the long-term 195 cycling stability of Mn₃O₄-G was evaluated at 0.5 A g⁻¹ 196

197 (Figure 3e). After 500 cycles, a capacity of ~400 mA h g⁻¹ was 198 maintained, which surpasses the theoretical capacity of 199 graphite. This excellent cycling stability was ascribed to the 200 hierarchical structure containing voids between the nanosheets 201 that could accommodate volume changes during the charge/ 202 discharge process.

203 Furthermore, the electrochemical performances of the 204 Mn₃O₄-G anode in NIB and KIB were evaluated. At 0.2 A 205 g^{-1} , the Mn₃O₄-G showed a reversible sodium-ion storage 206 capacity of ~200 mA h g⁻¹ (Figure 4a). No obvious plateau 207 was observed at low potential in the discharge curves of 207 Was observed at low potential in the discharge cartes of 208 Mn_3O_4-G (Figure 4b). At 1 A g⁻¹, a sodium storage capacity 209 of about 160 mA h g⁻¹ was still attained (Figure 4c). As an 210 anode KIB material, the Mn_3O_4-G displays a reversible 211 capacity of about 230 mA h g⁻¹ at 0.1 A g⁻¹. Similar to that in 212 sodium storage, no obvious plateau displays in the 213 corresponded charge/discharge curves (Figure 4e). The rate 214 performance of Mn₃O₄-G as an anode material for KIB has 215 also been evaluated. After current density increasing to 1 A g^{-1} , 216 the potassium storage capacity of Mn₃O₄-G reduces to 83 mA 217 h g⁻¹. Because of the higher redox potentials of Na⁺/Na and 218 K⁺/K couple [-2.71 and -2.94 V vs standard hydrogen 219 electrode (SHE), respectively] compared to that of Li⁺/Li 220 couple (-3.04 V vs SHE),³⁶ the discharge cutoff potential of 221 Mn₃O₄ is higher in NIBs and KIBs (Figure S8). Meanwhile, 222 the sluggish diffusion kinetics of sodium-ion and potassium-ion 223 results in greater polarization. Thus, the reaction of Mn₃O₄ in 224 NIBs and KIBs are incomplete, leading to the limited capacity. The electrochemical kinetics of Mn₃O₄-G and Mn₃O₄ 225 226 microflowers was investigated by electrochemical impedance 227 spectroscopy tests. In the Nyquist plots, the charge-transfer 228 resistance of Mn₃O₄-G (25.77 Ω) was clearly smaller than 229 that of Mn_3O_4 (73.77 Ω) (Figure S9, Table S1). This confirms 230 that graphene decoration effectively enhanced the electrical 231 conductivity, which was responsible for the improved rate 232 performance. After 100 cycles, the integrity of the Mn_3O_4 -G 233 microparticle was maintained with the SEI film on the surface 234 (Figure S10), implying the good electrode robustness.

The superior electrochemical performance of Mn_3O_4-G is attributed to the porous nanosheet-assembled hierarchical $Mn_3O_4/graphene$ composite structure. The porous ultrathin anosheets provide large electrode—electrolyte interface and short-ion diffusion pathway, and graphene nanosheets facilitate electronic conductivity, which are benefit for realizing higher anosheets and interstices between nanosheets can accomanosheets and acomanosheets and accomanosheets and

245 CONCLUSIONS

246 Ultrathin nanosheet-assembled hierarchical $Mn_3O_4/graphene$ 247 microflowers were obtained successfully from MnV_2O_6 nano-248 rod bundle/graphene composite precursors via the selective 249 dissolution strategy. The selective dissolution mechanism was 250 confirmed by investigating the structural evolution during the 251 dissolution process. The Mn_3O_4-G displayed high lithium 252 storage capacity (about 900 mA h g⁻¹) and outstanding cycling 253 stability at 0.5 A g⁻¹ (about 400 mA h g⁻¹ after 500 cycles). 254 The enhanced lithium storage performance originates from the 255 structural advantages. The ultrathin nanosheets and graphene 256 provided short diffusion pathways and fast electrical con-257 duction pathway, respectively, which improved the capacity 258 and rate capability. Moreover, the voids between nanosheets 270

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could hold volume changes during cycling and enhance the 259 cycling performance. Furthermore, the sodium/potassium 260 storage properties of Mn_3O_4 were also evaluated. The 261 differences in the Li/Na/K storage performances are attributed 262 to the different discharge cutoff potentials and ion diffusion 263 kinetics in LIB, NIB, and KIB. We believe that the selective 264 dissolution strategy can be employed to synthesize other 265 hierarchical nanomaterials, and this work will contribute to 266 further development of high-capacity anode materials for 267 alkali-metal-ion batteries.

S Supporting Information

The Supporting Information is available free of charge on the 271 ACS Publications website at DOI: 10.1021/acsami.9b00771. 272

Experimental section; electrode resistance obtained from 273 the equivalent circuit fitting of EIS results; XRD pattern, 274 SEM, TEM, and HRTEM images of MVO-G; Raman 275 spectrum of Mn_3O_4 -G, D, and G bands; Mn 2p XPS 276 spectrum of Mn_3O_4 -G, D, and G bands; Mn 2p XPS 277 of Mn_3O_4 -G; nitrogen adsorption–desorption iso- 278 therms; charge/discharge curves of Mn_3O_4 -G at different 279 current densities; first discharge curves of Mn_3O_4 -G in 280 LIB, NIB, and KIB; Nyquist plots of Mn_3O_4 -G and 281 Mn_3O_4 ; and SEM images of the Mn_3O_4 -G after 100 282 cycles (PDF) 283

AUTHOR INFORMATION	284
Corresponding Authors	285
*E-mail: anqinyou86@whut.edu.cn (Q.A.).	286
*E-mail: blueknight_0930@163.com (P.L.).	287
*E-mail: mlq518@whut.edu.cn (L.M.).	288
ORCID [©]	289
Liqiang Mai: 0000-0003-4259-7725	290
Author Contributions	291
[§] C.T. and F.X. contributed equally to this work.	292
Notes	293
The authors declare no competing financial interest.	294

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