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1 **Fungal biomineralization of manganese as a novel source of**
2 **electrochemical materials**

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21 **SUMMARY**

22 Electrical energy storage systems such as rechargeable lithium-ion batteries (LiB) and supercapacitors
23 have shown great promise as sustainable energy storage systems [1-4]. However, LiB have high specific
24 energy density (energy stored per unit mass) and act as slow, steady suppliers for large energy demands.
25 In contrast, supercapacitors possess high specific power (energy transferred per unit mass per unit time)
26 and can charge and discharge quickly for low energy demands. In LiB, graphite is the most common
27 anode material, although high electrolyte sensitivity and low charge capacity can limit performance.
28 Efforts have been made to improve LiB or supercapacitor performance using alternative electrode
29 materials such as carbon nanotubes and manganese oxides (Mn_xO_y) [3,5-14]. Microorganisms play
30 significant roles in metal and mineral biotransformations [15-22]. Fungi possess various
31 biomineralization properties as well as a filamentous mycelium which may provide mechanical support
32 for mineral deposition. Although some research has been done on application of biomass as a carbon
33 precursor [8,9,23], biomineralizing fungal systems have not been investigated. In this research, novel
34 electrochemical materials have been synthesized using a fungal Mn biomineralization process based on
35 urease-mediated carbonate bioprecipitation [24]. The carbonized fungal biomass-mineral composite
36 ($MycMnO_x/C$) showed a high specific capacitance ($>350 \text{ F g}^{-1}$) in a supercapacitor and excellent cycling
37 stability ($>90\%$ capacity was retained after 200 cycles) in LiB. This is the first demonstration of the
38 synthesis of electrode materials using a fungal biomineralization process therefore providing a novel
39 method for the synthesis of sustainable electrochemical materials.

40

41 RESULTS

42 Mineral Precipitation by *N. crassa* Grown in Urea- and MnCl_2 -amended Media

43 After 12 days incubation in media amended with 330 mM urea and 5 mM MnCl_2 , *N. crassa* biomass was
44 examined by scanning electron microscopy (Fig. 1A-F). It was found that most of the hyphae became
45 biomineralized and/or were enveloped by minerals in various formations. Fig. 1d shows a cross-section
46 of a hypha which was completely wrapped by a biomineral sheath ($\sim 2\text{-}3\ \mu\text{m}$) forming a hollow
47 biomineralized column. Three main types of mineral formation could be observed: acicular (Fig. 1a, b)
48 which clustered together with the hyphae (Fig. 1A), lamellar (Fig. 1D, E, F) which enveloped the hyphae
49 as a biomineralized sheath (Fig. 1D, E) and granular (Fig. 1C, E, F) which were mainly associated with
50 hyphal surfaces or the other lamellar minerals. EDXA showed that the main elements present in these
51 minerals were Mn, P, O and C (Inset Fig. 1A). XRD analysis revealed that six different Mn-containing
52 minerals were present: rhodochrosite (MnCO_3), switzerite $(\text{Mn, Fe})_3(\text{PO}_4)_2$, bixbyite $(\text{Mn, Fe})_2\text{O}_3$,
53 hausmannite $(\text{Mn}^{2+}\text{Mn}^{4+}_2\text{O}_4)$, pyrolusite (MnO_2) and manganosite (MnO) (Fig. 2A).

54 After treatment at high temperature (300°C) for 4 h, the biomass was carbonized although the
55 overall morphology did not show significant alteration (Fig. 1A, G). The carbonized hyphae were in a
56 biomineralized form but appeared to be more fragile. Compared with the extensive mineral deposition
57 shown in Fig. 1D, the heat-treated minerals around the hyphae became looser in their structure (Fig. 1I)
58 which may be due to the carbonization of the biomass and also the decomposition of carbonate
59 minerals at high temperature. Only lamellar minerals were observed (Fig. 1G, H, I) and the thickness of
60 these nanoscale minerals was around 20 nm. The main elements detected were still Mn, P, O and C
61 (inset Fig. 1G) but XRD showed that most minerals were amorphous which inhibited precise mineral
62 identification. FTIR was therefore used in an attempt to characterize these amorphous precipitates (Fig.
63 2B). According to FTIR, no carbonate-related peaks were detected in the sample with the peaks in the

64 regions of 1025 cm^{-1} and 588 cm^{-1} being due to the ν_3 and ν_4 vibrational modes of PO_4^{3-} . Taken together,
65 EDXA (Inset Fig. 1G) and FTIR results (Fig. 2B) therefore indicate that the amorphous minerals left after
66 heat treatment comprised manganese phosphate and manganese oxides (MnO_x), with the valency of
67 Mn in the mineral necessitating identification by X-ray photoelectron spectroscopy (XPS) (Fig. 3).

68 XPS was employed to determine the surface chemical properties of the sample, and the fully
69 scanned spectrum of the sample showed three main peaks, at 283.2 eV, 530.2 eV, and 640.5 eV,
70 corresponding to C 1s, O 1s, and Mn 2p, respectively (Fig. 3). The minor peaks located at 132.0 and
71 398.0 eV are assigned to P 2p, N 1s respectively, the phosphorus and nitrogen mainly arising from the
72 phosphate and ammonium present in the medium (Fig. 3A). The asymmetric Mn $2p_{3/2}$ main peak is
73 found at 640.5 eV with a $2p_{3/2}$ to $2p_{1/2}$ splitting of 11.9 eV (Fig. 3B) which is in accordance with previous
74 data for Mn $2p_{3/2}$ and Mn $2p_{1/2}$ in MnO and Mn_2O_3 [25-28]. The fitted multiplet structure of Mn $2p_{3/2}$
75 and Mn $2p_{1/2}$ with binding energies of 644.6 eV and 656.8 eV (Fig. 3B), respectively, are related to the
76 binding energy of Mn^{4+} in MnO_2 [25]. After carbonization, some MnO_x was anchored to the surface of
77 the carbonized mycelium. Due to the poor conductivity of the carbonized mycelium, the C-C peak
78 shifted to 283.2 eV [29]. In addition C-O/C-O-C and O-C=O were observed at 286.7 eV and 290 eV
79 respectively: partial thermal decomposition of the carbonized mycelium and manganese carbonate may
80 contribute to these peaks. Fig. 3D shows the O1s photoemission spectra of the prepared Mn-containing
81 sample. The spectrum was deconvoluted into three contributions with binding energies of 527.9 eV,
82 530.1 eV and 532.6 eV (Fig. 3D). The first two lines can be attributed to oxygen atoms bound to
83 manganese atoms in higher and lower oxidation states (527.9 eV, 530.2 eV) as represented by Mn-O-Mn
84 and Mn-O-H bond configurations, which correspond to the Mn(IV) in MnO_2 , Mn(II) in MnO and/or Mn(III)
85 in Mn_2O_3 , respectively [25, 26, 30]. The latter peak is assigned to oxygen from water molecules (H-O-H
86 bonds). These results indicate that manganese atoms in lower Mn(II) oxidation states occupy a large
87 proportion of the sample.

88

89 **Electrochemical Properties of the MycMnO_x/C Electrode in a Supercapacitor**

90 The electrochemical characteristics of MycMnO_x/C were investigated using an asymmetrical hybrid
91 supercapacitor. There were large differences in current densities between the two electrolytes at a scan
92 rate of 10 mV s⁻¹ (Fig. 4A), which were due to the electrode material (MycMnO_x/C) being unstable in
93 alkaline conditions and easily performing redox reactions. According to Fig. 4B, at a scan rate of 10 mV s⁻¹,
94 the specific capacitance of MycMnO_x/C in KOH was 483 F g⁻¹, while in Na₂SO₄ it was 119 F g⁻¹. If the
95 scan rate was increased to 500 mV s⁻¹, the specific capacitance decreased to 244.5 F g⁻¹ and 38 F g⁻¹,
96 respectively. This may be because the hyphae could facilitate the dispersion of the electrolyte ions
97 which could then better react with the active sites. When the MycMnO_x/C electrode was charged at 1 A
98 g⁻¹ current density in 5.4 M KOH, a voltage plateau was observed around 0.3 V which corresponded to
99 the redox peak in the positive scanning cyclic voltammetry (CV) curve (Fig. 4C). Therefore, the
100 MycMnO_x/C electrode was tested at 1 A g⁻¹ for 200 cycles and the initial capacity of MycMnO_x/C in 5.4
101 M KOH was 362 F g⁻¹ (Fig. 4d, see also Table S1). During the discharge cycling test, the capacitance
102 retention of the electrode was 36.7% in 5.4 M KOH and 98.5% in 1 M Na₂SO₄ after 200 cycles (Fig. 4D).

103

104 **Electrochemical Properties of the MycMnO_x/C Electrode in a Lithium-ion Battery**

105 The electrochemical lithium storage capability of MycMnO_x as an anode material in lithium-ion batteries
106 was evaluated by assembling CR2025 coin-type cells. Figure 4E shows CV curves at a scan rate of 0.5 mV
107 s⁻¹. During the first cathode cycle, the sharp reduction peak close to 0.1 V corresponded to reduction of
108 MnO_x to Mn⁰ and the formation of Li₂O and the solid electrolyte interface (SEI) [31, 32]. It is worth
109 noting that the pair of redox peaks for MnO_x/C at 0.6 and 1.8 V stabilized after the first cycle. This
110 phenomenon occurred in the amorphous MycMnO_x/C electrode in the lithium-ion battery which means

111 that the Mn (II) in amorphous MycMnO_x/C could be re-oxidized to a higher oxidation state. The
112 conversion reaction may be written as follows:



114 The charge/discharge curves of the MycMnO_x/C battery at a current density of 0.1 A g⁻¹
115 between 0.01 and 3 V are shown in Fig. 4F. During the first discharge process, a sustained voltage
116 plateau at 0.5 V was observed which was attributed to the reduction of MnO_x to Mn⁰ [33], which then
117 decreased gradually to 0.01 V delivering a discharge capacity of 911 mA h g⁻¹. In the subsequent cycling
118 process, the discharge plateau increased to about 1.0 V which could be partially related to the improved
119 kinetics of the reactants which consume less energy to be activated after the first discharge process [33,
120 34]. The initial columbic efficiency was 46.7 %. The irreversible capacity in the first few cycles could be
121 mainly due to the large capacity loss in the first cycle, which was mainly attributed to the formation of a
122 solid electrolyte interface (SEI) layer due to chemical reactions between electrolyte and the anode
123 material.

124 To further investigate the electrochemical performance of the MycMnO_x/C hybrid, the rate
125 capability of the sample was tested (Fig. 4G). When the current density reached 0.5 A g⁻¹, the specific
126 capacity of the MycMnO_x/C hybrid still remained about 200 mA h g⁻¹ (Fig. 4g). Fig. 4H shows the
127 discharge/charge cycling performance of the MycMnO_x/C hybrid at a current density of 100 mA g⁻¹ for
128 200 cycles. It is interesting to find that the reversible capacity dropped slowly over the first 50 cycles and
129 then increased with cycling and remained at 92% of its initial specific capacity after 200 cycles (See also
130 Table S2). It has been reported that electrolyte degradation will result in the formation of a polymeric
131 gel-like film around MycMnO_x particles, and growth of this polymeric layer will increase the capacity of
132 the metal oxide with further cycling [35].

133

134 DISCUSSION

135 Much research has been carried out on the synthesis of advanced materials, using a biological template,
136 with nano- or microscale structures and unique properties [11, 23]. Compared to conventional methods,
137 minerals precipitated by a biomineralization process may contain an inorganic/organic hierarchical
138 structure which can show excellent physico-chemical attributes as well as biological properties [36]. In
139 this work, we have focussed on the synthesis of manganese oxide (MnO_x) by a fungal biomineralization
140 system, and have investigated its potential application as an electrode material in supercapacitors and
141 lithium ion batteries.

142 Previous research has demonstrated that the urease-positive fungus *Neurospora crassa* is an
143 excellent candidate for CaCO_3 biomineralization, and more than 90% of supplied calcium (50 mM) could
144 be precipitated as calcite [24]. Such performance of ureolytic fungi in urea-supplemented media
145 suggested a useful method for the synthesis of calcite as well as other metal-containing carbonates. For
146 example, ~50% of supplied CdCl_2 (0.5 M) was precipitated as pure otavite (CdCO_3) by the culture
147 supernatant obtained after growth of *N. crassa* in urea-supplemented medium [24]. Other urease-
148 positive fungi (*Pestalotiopsis* sp. and *Myrothecium gramineum*) isolated from calcareous soil were also
149 found to be able to precipitate CaCO_3 and SrCO_3 as well as olekminskite ($\text{Sr}(\text{Sr}, \text{Ca})(\text{CO}_3)_2$) and Sr-
150 containing vaterite ($(\text{Ca}_x\text{Sr}_{1-x})\text{CO}_3$) [21]. In this work, *N. crassa* was cultured in urea- and MnCl_2 -modified
151 media, and various mineral morphologies were observed to be accreted around the hyphae and MnCO_3
152 was identified by XRD. With thermal treatment of the biomass-mineral composite at 300°C for 4 h,
153 MnO_x containing different oxidation states of Mn resulted and the fungal biomass was carbonized to
154 provide a coal-like material which was used as a carbon precursor. Biological material, such as biomass
155 from fungi [8, 11, 12], microalgae [9, 14], or bacteria [23], has been used previously as sustainable
156 carbon precursors for energy storage devices [36]. Long et al. [12] previously obtained a porous layered
157 carbonaceous material from hydrothermally treated fungal biomass which possessed a high surface area,

158 bulk density and a multilayer cross-linked framework. When used as an electrode material in
159 supercapacitors, it showed a high volumetric capacitance and excellent cycling stability. Due to rapid
160 and reversible redox reactions between the different oxidation states, theoretical high energy storage
161 capacity and low cost, MnO_x have been used as an electrode material in supercapacitors [29, 37],
162 lithium ion batteries [38, 39] and lithium air batteries [39]. However, pure MnO_x has poor electronic
163 conductivity, exhibits a rapid decrease in storage capacity of Li^+ , and ion diffusion during the
164 charge/discharge processes [38]. Many efforts have been made in an attempt to solve these problems
165 such as using conductive additives and carbon coatings [38]. Reddy et al. [38] combined coaxial MnO_2
166 nanotubes with conducting carbon nanotubes (CNT) to improve the performance of lithium ion batteries
167 and showed that such MnO_2/CNT hybrid nanotubes enhanced the electronic conductivity and reversible
168 capacity of the electrode. To improve the energy and power density of a supercapacitor, bacterial
169 cellulose derived carbon nanofibers loaded with MnO_2 were used as the anode, and this cost-effective
170 device delivered a high energy density ($32.91 \text{ W h kg}^{-1}$) and excellent cycling stability after 2000 cycles
171 [40]. Though much research has been carried out on the synthesis or capability enhancement of
172 electrode materials, little attention has been paid to the construction of novel electrode materials using
173 fungal biomineralization products. After thermal treatment, the MycMnO_x derived from thermal
174 decomposition of the biomineralized MnCO_3 , comprised an outer shell with the conducting carbonized
175 fungal biomass in the inner core. Compared with conventional physico-chemical methods, our
176 experiments illustrate a facile and novel procedure for preparation of MycMnO_x/C materials. The
177 biomineralization process of MnCO_3 by an ureolytic fungus not only provided the carbon precursor but
178 also a source of manganese oxide which can be used directly as an electrode material after heat
179 treatment. When used as an electrode material in a supercapacitor, compared with manganese oxide
180 synthesized by other methods, the MycMnO_x/C exhibited a good specific capacitance of 362 F g^{-1} at a
181 current density of 1 A g^{-1} (See also Table S1). The fungal mycelium provides a framework for the

182 deposition of minerals, and also evenly distributes the electrolyte ions which facilitates redox reactions
183 in solution. Compared with other reported MnO_x materials in lithium ion batteries (See also Table S2),
184 the MycMnO_x/C did not show a very good capacity ($\sim 400 \text{ mA h g}^{-1}$) at a current density of 100 mA g^{-1}
185 which might be due to the low concentration of Mn^{2+} added to the medium. However, it is worth noting
186 that the MycMnO_x/C had an outstanding cycling stability and 91% of capacity was retained after 200
187 cycles. According to XRD analysis, most of the decomposed minerals derived from fungal
188 bioprecipitation were amorphous while some were present in nanoscale-sheets. Compared with
189 crystalline MnO_x/C , the amorphous MycMnO_x/C nanosheets had a lower volume change during the
190 redox reactions and this could also enhance the structural stability of the MycMnO_x/C . During the
191 process of biomineralization, the hyphae provide a template for nucleation, growth and deposition of
192 minerals, and the thermal decomposition of the biogenic MnCO_3 and carbonization of fungal biomass
193 results in a large specific surface area of the MycMnO_x/C . This is the first report of the application of
194 fungal-derived MnO_x as an electrode material in supercapacitors and lithium ion batteries, with the
195 MycMnO_x/C showing good electrochemical properties, especially in cycling stability in lithium ion
196 batteries. Fungal biomineralization methods for the synthesis of mycogenic MnO_x/C could therefore be
197 a useful and **alternative** strategy for the preparation of novel electrochemical materials.

198

199 **AUTHOR CONTRIBUTIONS**

200 Conceptualization, Q.L., D.L. and G.M.G.; Methodology, Q.L., D.L. and G.M.G.; Investigation, Q.L. and D.L.;
201 Writing - Original Draft, Q.L. and D.L.; Writing - Review & Editing, Q.L. and G.M.G.; Funding Acquisition,
202 G.M.G.; Resources, G.M.G., Z.J. and L.C.; Supervision, G.M.G.

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313

314 **Figure Legends**

315 Fig. 1. Scanning electron microscopy (SEM) of *N. crassa* incubated in liquid media amended with 330
316 mM urea and 5 mM MnCl₂. (a-f) Before and (g-i) after heat treatment at 300°C for 4 h. Insets show
317 energy dispersive X-ray analysis (EDXA) of the minerals precipitated by *N. crassa* (a) before and (g) after
318 the heat treatment. Scale bars: (a) = 50 μm, (b, c) = 5 μm, (d, e, f, i) = 2 μm, (g) = 100 μm, (h) = 10 μm. All
319 samples were incubated for 12 days at 25°C in the dark. Typical images are shown from many similar
320 examples.

321 Fig. 2. Identification of minerals precipitated by *N. crassa* grown for 12 days at 25°C in the dark in liquid
322 media amended with 330 mM urea and 5 mM MnCl₂. (a) X-ray diffraction (XRD) analysis; (b) Fourier
323 transform infrared spectroscopy (FTIR) of minerals precipitated by *N. crassa* after heat treatment at
324 300°C for 4 h. Typical spectra are shown from one of several determinations.

325 Fig. 3. X-ray photoelectron spectroscopy (XPS) of carbonized fungal biomass with Mn-containing
326 minerals. (a) Total XPS spectra. Insets are the XPS spectra of N 1s and P 2p, respectively. The spectral
327 peaks contributing to the spectrum are labeled and the near-horizontal line is the background. The
328 jagged line is the raw spectra data, and the smooth curve is the best fit spectrum; (b) XPS Mn 2p spectra;
329 (c) C 1s and (d) O 1s spectra. Symbols and curves are as in (a). Typical spectra are shown from one of
330 several determinations.

331 Fig. 4. Electrochemical measurements of a MycMnO_x/C electrode in a (a-d) supercapacitor (e-h) LiB: (a)
332 Cyclic voltammetry (CV) curves; (b) specific capacitances at various scan rates in different electrolytes; (c)
333 galvanostatic charge/discharge curves of the MycMnO_x/C with 1 A g⁻¹ current density in an electrolyte of
334 5.4 M KOH and 1 M Na₂SO₄ after 20 cycles; (d) cycling performance of biomass material electrode at a
335 current density of 1 A g⁻¹ for 200 cycles. Inset shows the first 10 charge/discharge cycles; (e) cyclic
336 voltammetry (CV) curves at a scan rate of 0.5 mV/s; (f) charge/discharge curves at 0.1 A g⁻¹; (g)
337 charge/discharge capacity of MycMnO_x/C at different current densities; (h) cycling performance and

338 coulombic efficiency at a 0.5 A g^{-1} current density. Typical patterns are shown from one of several
339 determinations.

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