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Fungal Biomineralization of Manganese as a Novel Source of Electrochemical Materials

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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 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

RESULTS

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

After 12 days incubation in media amended with 330 mM urea and 5 mM $MnCl_2$, *N. crassa* biomass was examined by scanning electron microscopy (Fig. 1A-F). It was found that most of the hyphae became biomineralized and/or were enveloped by minerals in various formations. Fig. 1d shows a cross-section of a hypha which was completely wrapped by a biomineral sheath (~2-3 μm) forming a hollow biomineralized column. Three main types of mineral formation could be observed: acicular (Fig. 1a, b) which clustered together with the hyphae (Fig. 1A), lamellar (Fig. 1D, E, F) which enveloped the hyphae as a biomineralized sheath (Fig. 1D, E) and granular (Fig. 1C, E, F) which were mainly associated with hyphal surfaces or the other lamellar minerals. EDXA showed that the main elements present in these minerals were Mn, P, O and C (Inset Fig. 1A). XRD analysis revealed that six different Mn-containing minerals were present: rhodochrosite ($MnCO_3$), switzerite $(Mn, Fe)_3(PO_4)_2$, bixbyite $(Mn, Fe)_2O_3$, hausmannite ($Mn^{2+}Mn^{4+}_2O_4$), pyrolusite (MnO_2) and manganosite (MnO) (Fig. 2A).

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

3

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

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^{-}

94 ^{1}, the specific capacitance of MycMnO$_x$/C in KOH was 483 F g^{-1}, while in Na$_2$SO$_4$ 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 Na$_2$SO$_4$ after 200 cycles (Fig. 4D).

103

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 Mn^0 and the formation of Li$_2$O 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:

113   MnO$_x$ + 2xLi $\longleftrightarrow$ Mn + xLi$_2$O

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 Mn^0 [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

DISCUSSION

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

Previous research has demonstrated that the urease-positive fungus *Neurospora crassa* is an excellent candidate for $CaCO_3$ biomineralization, and more than 90% of supplied calcium (50 mM) could be precipitated as calcite [24]. Such performance of ureolytic fungi in urea-supplemented media suggested a useful method for the synthesis of calcite as well as other metal-containing carbonates. For example, ~50% of supplied $CdCl_2$ (0.5 M) was precipitated as pure otavite ($CdCO_3$) by the culture supernatant obtained after growth of *N. crassa* in urea-supplemented medium [24]. Other urease-positive fungi (*Pestalotiopsis* sp. and *Myrothecium gramineum*) isolated from calcareous soil were also found to be able to precipitate $CaCO_3$ and $SrCO_3$ as well as olekminskite ($Sr(Sr, Ca)(CO_3)_2$) and Sr-containing vaterite (($Ca_xSr_{1-x})CO_3$) [21]. In this work, *N. crassa* was cultured in urea- and $MnCl_2$-modified media, and various mineral morphologies were observed to be accreted around the hyphae and $MnCO_3$ was identified by XRD. With thermal treatment of the biomass-mineral composite at 300°C for 4 h, MnO_x containing different oxidation states of Mn resulted and the fungal biomass was carbonized to provide a coal-like material which was used as a carbon precursor. Biological material, such as biomass from fungi [8, 11, 12], microalgae [9, 14], or bacteria [23], has been used previously as sustainable carbon precursors for energy storage devices [36]. Long et al. [12] previously obtained a porous layered carbonaceous material from hydrothermally treated fungal biomass which possessed a high surface area,

7

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 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 (~400 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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312   supercapacitor with high energy and power density. Adv. Mater. *25*, 4746-4752.

313

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 $MnCl_2$. (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 $MnCl_2$. (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 Na_2SO_4 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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