

Electronic Supplementary Information (ESI)

MnO₂ Nanostructures with Three-dimensional (3D) Morphology Replicated from Diatoms for High-Performance Supercapacitors

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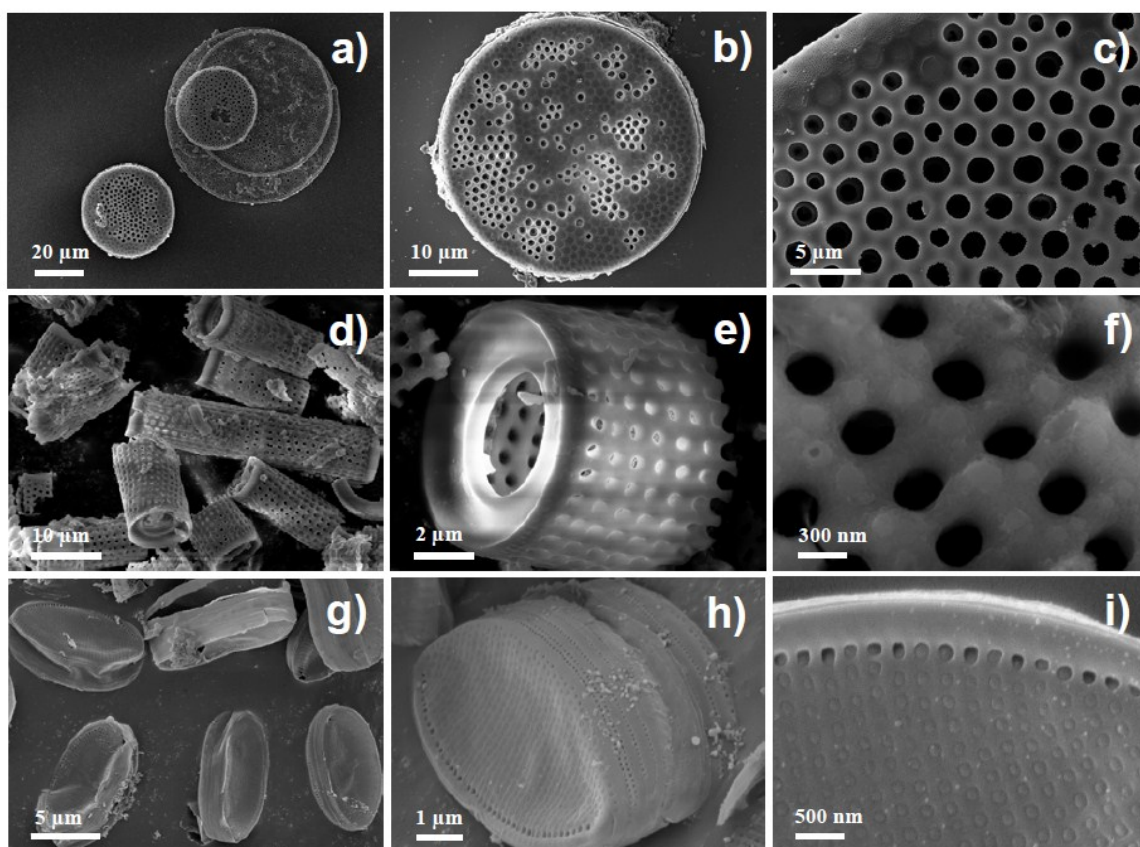
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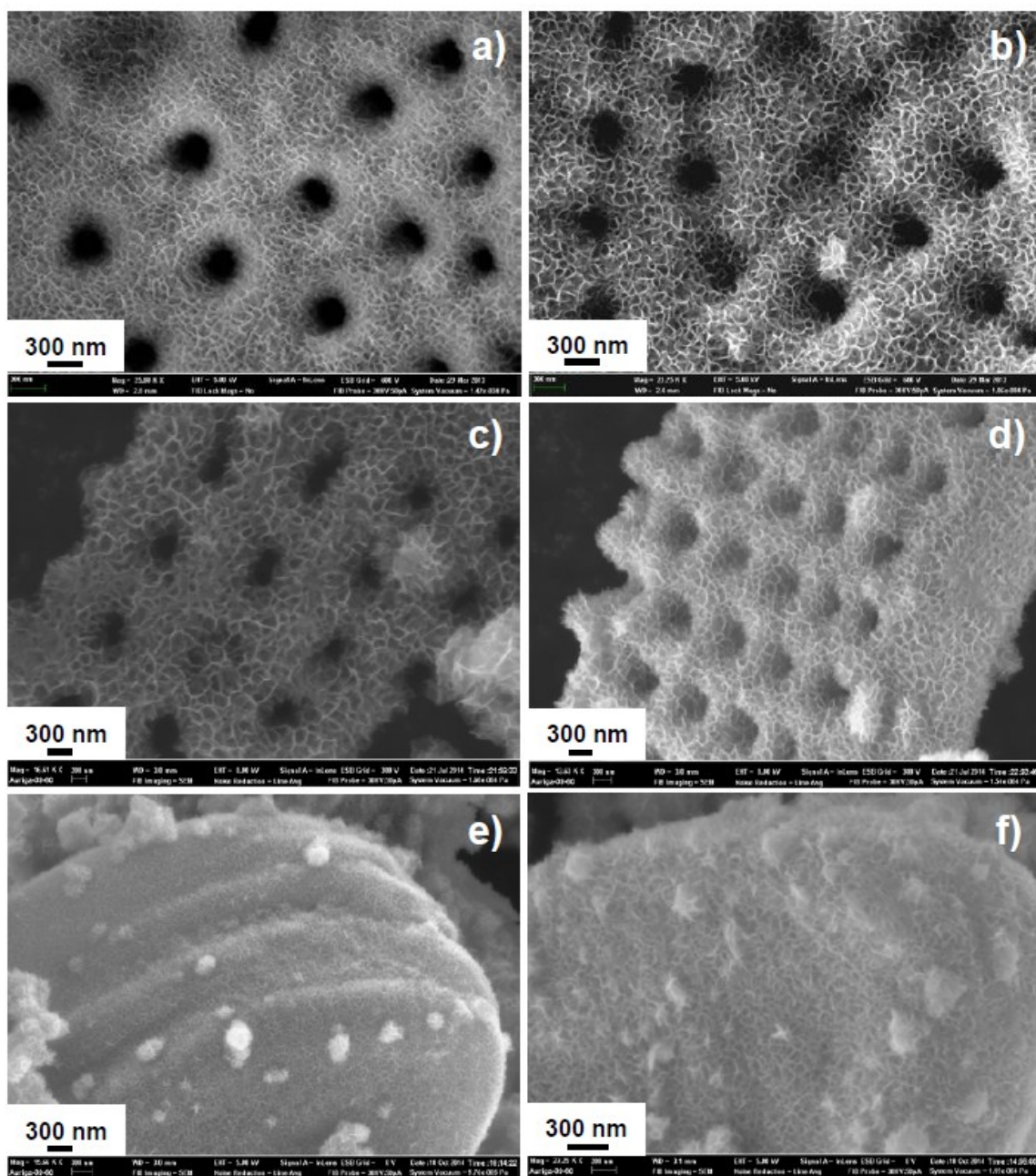
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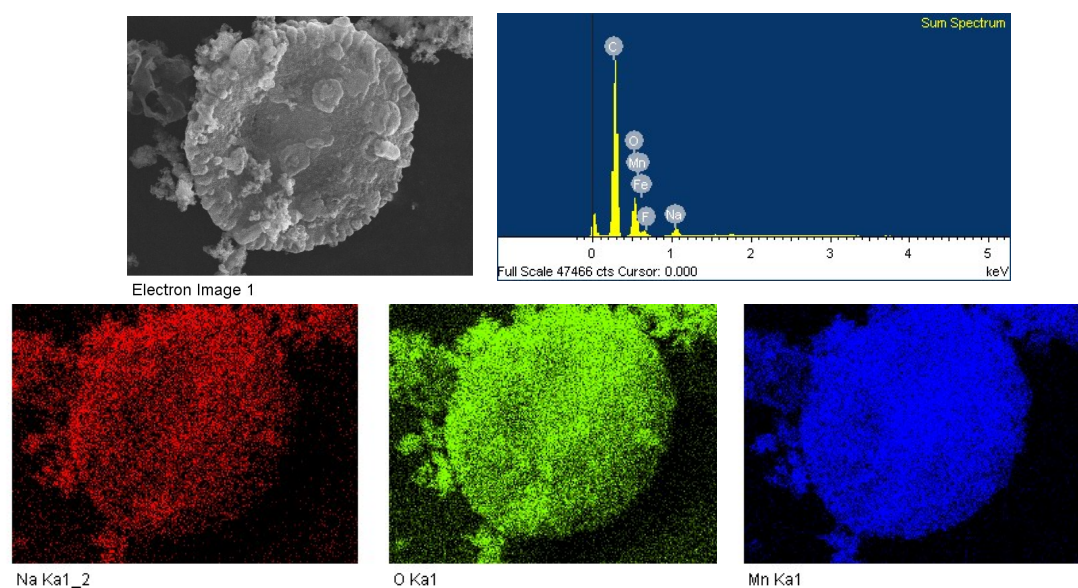
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SI-1 SEM images of diatom structure obtained from three species with different morphologies: (a, b, c), *Coscinodiscus* diatoms from fossilized DE, (d, e, f) *Melosira* diatoms from fresh water fossilised DE and (g, h, i), *Navicula* from cultured diatoms



SI-2 SEM images of diatomite @ MnO₂ with different morphologies prepared using different diatoms: (a, b), *Coscinodiscus* (c, d), *Melosira* and (e, f), *Navicula*



SI-3 the scanning electron microscope (SEM) images and the corresponding energy dispersive X-ray spectrometry (EDS) elemental mapping of the MnO₂ structure showing the uniform distribution of O, K and Mn elements. images of diatomite @ MnO₂ with different morphologies prepared using different diatoms: (a, b), *Coscinodiscus* (c, d), *Melosira* and (e, f), *Navicula*

Table S1 The percentages of MnO₂ in diatoms @ MnO₂.

<i>Samples</i>	<i>M₁</i>	<i>M₂</i>	<i>percentage</i>
Coscinodiscus- diatom@MnO ₂	40 mg	22.4 mg	56.0%
Melosira- diatom@MnO ₂	40 mg	27.7 mg	69.25%
Navicula- diatom@MnO ₂	40 mg	31.3 mg	78.25%

Table S2 BJH Adsorption Pore Distribution of MnO₂ patterns by replica molding from diatom with different morphologies: (a) Melosira-diatom, (b) Coscinodiscus-diatom, and (c) Navicula-diatom, respectively.

<i>(a) Pore Diameter</i>	<i>Average</i>	<i>Incremental</i>
<i>Range (nm)</i>	<i>Diameter (nm)</i>	<i>Pore Volume</i>
<i>Melosira-diatom</i>		<i>(cm³/g)</i>
481.2 - 47.8	51.6	0.136963
47.8 - 27.3	32.1	0.034350
27.3 - 18.9	21.5	0.016338
18.9 - 14.4	16.0	0.008749
14.4 - 11.7	12.7	0.005078
11.7 - 9.8	10.6	0.003094
9.8 - 8.4	9.0	0.001838
8.4 - 7.4	7.8	0.001228
7.4 - 6.6	6.9	0.000687
6.6 - 5.9	6.2	0.000342
5.9 - 5.3	5.6	0.000237
5.3 - 4.9	5.1	0.000005
4.9 - 1.7	1.7	0.000125
<i>(b) Pore Diameter</i>	<i>Average</i>	<i>Incremental</i>
<i>Range (nm)</i>	<i>Diameter (nm)</i>	<i>Pore Volume</i>
<i>Coscinodiscus-diatom</i>		<i>(cm³/g)</i>
169.1 - 46.8	54.9	0.075436
46.8 - 26.8	31.5	0.034028
26.8 - 18.7	21.3	0.015838
18.7 - 14.4	16.0	0.008481
14.4 - 11.6	12.7	0.005410
11.6 - 9.8	10.5	0.003436

9.8 - 8.5	9.0	0.002299
8.5 - 7.4	7.9	0.001717
7.4 - 6.6	7.0	0.001037
6.6 - 5.9	6.2	0.000759
5.9 - 5.4	5.6	0.000541
5.4 - 4.9	5.1	0.000319
4.9 - 4.5	4.7	0.000206
4.5 - 4.2	4.3	0.000077
4.2 - 3.6	3.7	0.000133
3.6 - 3.1	3.2	0.000075
3.1 - 2.9	3.0	0.000043
2.9 - 2.7	2.8	0.000010
2.7 - 2.5	2.6	0.000145
2.5 - 2.2	2.2	0.000080
2.2 - 2.0	2.1	0.000275
2.0 - 1.8	1.9	0.000325
1.8 - 1.7	1.7	0.000596

<i>(c) Pore Diameter</i>	<i>Average</i>	<i>Incremental</i>
<i>Range (nm)</i>	<i>Diameter (nm)</i>	<i>Pore Volume</i>
<i>Navicula-diatom</i>		<i>(cm³/g)</i>
168.6 - 48.0	56.5	0.077591
48.0 - 27.1	31.9	0.031409
27.1 - 18.7	21.3	0.014995
18.7 - 14.4	15.9	0.007878
14.4 - 11.7	12.7	0.004759
11.7 - 9.8	10.6	0.002992
9.8 - 8.5	9.0	0.001886

8.5 - 7.4	7.9	0.001146
7.4 - 6.6	7.0	0.000739
6.6 - 5.9	6.2	0.000279
5.9 - 5.4	5.6	0.000122
5.4 - 4.9	5.1	0.000148
4.9 - 3.3	3.4	0.000040
3.3 - 3.1	3.2	0.000117
3.1 - 2.9	3.0	0.000263
2.9 - 2.7	2.8	0.000107
2.7 - 2.5	2.6	0.000236
2.5 - 2.3	2.4	0.000194
2.3 - 2.2	2.2	0.000270
2.2 - 2.0	2.1	0.000305
2.0 - 1.8	1.9	0.000378
1.8 - 1.7	1.7	0.000476

Table S3 Comparison of specific capacitances between the reported MnO₂ electrodes and the present work. All values are measured using the three-electrode system.

Samples	C _s (F g ⁻¹)	Electrolyte	Test condition	References
Hollow MnO ₂ microsphere	90	1 M Na ₂ SO ₄	10 mV s ⁻¹	1
Amorphous MnO ₂	110	2 M NaCl	5 mV s ⁻¹	2
α-MnO ₂ hollow urchins	123	0.5 M Na ₂ SO ₄	2 mV s ⁻¹	3
Ambigel MnO ₂	130	2 M NaCl	5 mV s ⁻¹	4
α-MnO ₂ nanorod	152	1 M Na ₂ SO ₄	5 mV s ⁻¹	5
α-MnO ₂ hollow sphere	167	1 M Na ₂ SO ₄	2.5 mA cm ⁻²	6
Birnessite hollow MnO ₂	169	1 M Na ₂ SO ₄	0.25 A g ⁻¹	7
MnO ₂ spherical particle	170.8	0.5 M K ₂ SO ₄	0.5 A g ⁻¹	8
MnO ₂ nanowire	176	1 M Na ₂ SO ₄	5 mV s ⁻¹	9
MnO ₂ nanosheet	182	0.1 M Na ₂ SO ₄	0.1 A g ⁻¹	10
MnO ₂ microsphere	190	1 M Na ₂ SO ₄	0.5 A g ⁻¹	11
α-MnO ₂ sphere	200	0.25 M Na ₂ SO ₄	1 A g ⁻¹	12
Amorphous MnO ₂ ·nH ₂ O	200	2 M KCl	5 mV s ⁻¹	13
MnO ₂ nanosheet array	201	1 M Na ₂ SO ₄	1 A g ⁻¹	14
MnO ₂ -pillared layered MnO ₂	206	1 M Na ₂ SO ₄	5 mV s ⁻¹	15

Birnessite MnO ₂ nanosphere	210	1 M Na ₂ SO ₄	1 A g ⁻¹	16
Mesoporous MnO ₂	221	1 M Na ₂ SO ₄	5 mV s ⁻¹	17
Core-corona MnO ₂	226	0.5 M Li ₂ SO ₄	0.2 A g ⁻¹	18
γ-MnO ₂ film	240	0.1 M Na ₂ SO ₄	1 mA cm ⁻²	19
α-MnO ₂ nanorod	245	1 M KOH	1 A g ⁻¹	20
Amorphous MnO ₂ particle	251	1 M Na ₂ SO ₄	2 mV s ⁻¹	21
α-MnO ₂ spherical-like particle	258.7	1 M Na ₂ SO ₄	0.1 A g ⁻¹	22
Layered δ-MnO ₂	265	1 M Na ₂ SO ₄	5 mV s ⁻¹	23
Mesoporous α-MnO ₂ network	283	1 M Na ₂ SO ₄	2 mV s ⁻¹	24
Mesoporous MnO ₂ nanoparticle	284.2	1 M Li ₂ SO ₄	1 mV s ⁻¹	25
α-MnO ₂ spherical aggregate	297	0.1 M Na ₂ SO ₄	20 mV s ⁻¹	26
MnO ₂ nanowire	300	1 M Na ₂ SO ₄	5 mV s ⁻¹	27
Nanoscale MnO ₂	305	1 M Na ₂ SO ₄	2 mV s ⁻¹	28
MnO ₂ tubular nanostructure	315	1 M Na ₂ SO ₄	0.2 A g ⁻¹	29
α-MnO ₂ nanoflake film	328	1 M Na ₂ SO ₄	5 mV s ⁻¹	30
α-MnO ₂ ultralong nanowire	345	0.5 M Na ₂ SO ₄	1 A g ⁻¹	31
MnO ₂ nanoflower	347	1 M Na ₂ SO ₄	5 mV s ⁻¹	32
MnO ₂ hollow structure	366	1 M Na ₂ SO ₄	5 mV s ⁻¹	33
Clew-like MnO ₂ particle	404.1	1 M Na ₂ SO ₄	2 mV s ⁻¹	34
MnO ₂ nanofiber	412	0.1 M Na ₂ SO ₄	2 mV s ⁻¹	35
Melosira-type MnO ₂	371.2	1 M Na ₂ SO ₄	0.5 A g ⁻¹	This work

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