#

#  Biomass-derived mesoporous core-shell Fe3C@graphene

1. **oxide nanospheres for electrochemical energy storage**

3

4

5

6

7 Xinli Yi,a,b Wen He,c\* Xudong Zhang,c Kwan San Huid and Wangwang Xua\*

8

9

10

11 a.College of Materials and Chemical Engineering, Key Laboratory of Inorganic

12

13 Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges

14

15 University, Yichang, 443002, P. R. China

16

17 b.Hubei Three Gorges Laboratory, Yichang, Hubei 443007, P. R. China.

18

19 c.Department of Materials Science and Engineering, Qilu University of Technology

20

21

22 (Shandong Academy of Sciences), Jinan, 250353, P. R. China.

23

24 d.School of Engineering, Faculty of science, University of East Anglia, Norwich, NR4

25

26 7TJ, United Kingdom.

27

28

29

30

31 **Abstract**

32

33

34 The biomass-derived mesoporous core-shell Fe3C@graphene oxide nanospheres

35

36 (mFe3C@GO NSs) was synthesized with high-quality lignins and applied for

37

38 electrochemical energy storage. The synthesis conditions of mFe3C@GO NSs are

39

40 optimized and its formation mechanism is proposed. The mFe3C@GO NSs

41

42 homogeneously dispersed in GO conductive network and maintained the structural

43

44 integrity of the electrode in the electrochemical process. Benefiting from the

45

46 advantages of the core-shell construction and graphene oxide network, the

47

48 mFe3C@GO NSs exhibits extensible exploration in electrochemical energy storage

49

50

51 (EES).

52

53 **Keywords**: mFe3C@GO NSs; Biomass-derived compounds; Nanostructured

54

55 electrode; Lithium-ion battery; Electrochemical energy storage

56

57

58

## 1 1. Introduction

2

3 By integrating Li-ion battery electrode and supercapacitor into one device is

4

5 expected to combine the advantages of the two energy storage mechanisms to

6

7 obtain a “double high” Li-ion battery (LIB) and supercapacitor (SC) hybrid

8

9

10 energy storage devices (LIB-SC HESDs), which are likely to be the future

11

12 power source for multi-function electronic equipment and electric/hybrid

13

14 vehicles [1, 2]. However, the performance of LIB-SC HESDs is limited by the

15

16 mismatched charge storage capacity and electrode kinetics between

17

18 battery-type and capacitive electrodes [1]. Therefore, the design of

19

20 high-performance electrode materials and understanding on the matching

21

22 theory between the positive and negative electrodes of LIB-SC HESDs face

23

24 overwhelming challenges [3].

25

26

27 Graphene (GN)-like two-dimensional (2D) materials have the potential in

28

29 applications due to their unique interfacial structure, attractive properties, facile

30

31 synthesis, and ease of functionalization [4, 5]. Numerous studies indicate that

32

33 the effective work function of carbon-based electrode was increased

34

35 significantly by inserting metal oxide nanoparticles [6-8]. The GN and iron

36

37 carbide (Fe3C) bifunctional oxygen electrocatalysts demonstrated synergistic

38

39 effects [9, 10]. Fe3C was applied in lithium-ion batteries (LIBs) as anode

40

41 material, the question remains, however, the structure collapse originating from

42

43 volume change during the continuous charge/discharge process and the poor

44

45

46 conductivity of Fe3C resulted in rapid capacity fading, particularly in high

47

48 current density [11]. Structure engineering and conductive network doping had

49

50 wide applicability to solve these problems [12-14]. Nevertheless, the

51

52 fabrication of core-cell carbon coating with different design strategies of large

53

54 specific surface area, excellent conductivity and mechanical flexibility lead to

55

56 restricted performance improvement [15]. In general, the core-shell structure is

57

58 desirable to realize synergism effect, but surprisingly little attention focus on

1 the utilization of lignin. Lignin emerges as a by-product from papermaking

2

3 industry by the degradation of the nature wood, which is suitable for

4

5 thermochemical reaction for its high yield of pyrolysis products and is

6

7 considered a promising feedstock for carbon materials production [16, 17]. Its

8

9 surfactant structure contains multifarious functional groups of carboxyl,

10

11 hydroxyl, benzyl alcohol, methoxyl, and trace elements (such as Si and S, etc),

12

13 providing lone pair electrons, nucleation sites and adsorb metal ions [18].

14

15 Here, the biomass-derived mesoporous core-shell Fe3C@graphene oxide

16

17 nanospheres (mFe3C@GO NSs) were fabricated by a simple wet chemical

18

19 route with high-quality lignins as the organic ligands of Fe(II)/Fe(III)-MOFs

20

21

22 precursor and the carbon source, and the synthesis mechanism was proposed.

23

24 The microstructure and chemical composition exhibits synergetic effects of fast

25

26 ion insertion/extraction, high electrolyte permeability, and electric conductivity

27

28 for lithium-ion battery and supercapacitor, respectively. More importantly, the

29

30 HESDs constructed with mFe3C@GO NSs and mesoporous Li3V2(PO4)3/C

31

32 microspheres (mLVP/C MSs) [19] exhibit highly matched capacity and

33

34 significant pseudocapacitive behavior.

35

36

## 37 2. Experiments sections

38

39

## 40 2.1. Synthesis of mFe3C@GO NSs

41

42 The Fe3O4-MOFs precursor was synthesized by a simple, low-cost and green method

43

44 of hydrothermal crystallization and reduction. Typically, 33 mL 1mol L−1 Fe3+

45

46 solution was slowly added into 50 mL lignin solution with magnetic stirring for 6 h at

47

48 room temperature to form a thick liquid. The pH value of the mixed solution was

49

50 reduced from 13 to 7. Subsequently, the mixed solution was shifted to a Teflon-sealed

51

52 autoclave and heat-treated for 48 h at 180°C. After the autoclave cooled down to room

53

54 temperature naturally, the precipitate was washed with deionized water for three times

55

56 and dried at 60 °C to obtain the Fe3O4-MOFs precursor. The mFe3C@GO NSs was

57

58 obtained by carbonizing Fe3O4-MOFs precursor at high temperature for 8 h in a tube

furnace with a heating rate of 5°C min−1 in nitrogen (N2) atmosphere. For comparison,

1

2 the GO blank sample was prepared without additional Fe3+ through similar conditions.

3

## 4 2.2. Characterizations

5

6 X-ray diffraction (XRD) was recorded on a LabX XRD-6100 with Cu-Kα radiation

7

8 (Shimadzu, λ= 1.5406 Å). X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+)

9

10 was carried out to characterize the elemental components and chemical states of

11

12 elements. Field emission scanning electron microscopy (FE-SEM) was used to

13

14

15 observe the morphological structure of sample by a ZEISS scanning electron

16

17 microscope equipped with an X-ray energy dispersive spectrometer (EDS) at 20 kV,

18

19 and the EDS images were captured for analysing the distribution of elements. The

20

21 JEF-2100F is a transmission electron microscopy (TEM) that performed the lattice

22

23 fringe images under the condition of 200 kV. Raman spectra were measured by a

24

25 Renishaw RM2000 Raman microscope with 514 nm excitation argon laser.

26

27 Differential scanning calorimetry (DSC-100H, Nanjingdazhan) was used to measure

28

29 the thermal change of Fe3O4-MOFs precursor. The N2 adsorption–desorption isotherm

30

31 and Barrett–Joyner–Halenda (BJH) pore size distribution were obtained at 77 K using

32

33 an automatic surface area analyzer (Micromeritics, Gemini V2380, USA).

34

## 35 2.3. Electrochemical measurements

36

37 **2.3.1 Li-ion batteries**

38

39 The electrochemical performances were characterized in a coin-type LIR2032 cell at

40

41 room temperature. The working electrode was prepared by mixing 80% mFe3C@GO

42

43 NSs, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) in N-methyl

44

45

46 pyrrolidone to prepare , and then the slurry was coated on copper foil surface

47

48 uniformly. After that, the electrode was dried at 60 °C in an electric thermostatic

49

50 drying oven and then dried at 110 °C for 10 h in vacuum drying oven. The electrode

51

52 was cut it into wafers with a diameter of 15 mm. The cells were assembled in a

53

54 high-purity argon-filled inert glove box with the synthesized electrode as anode and

55

56 polypropylene (PP) membrane as a separator, 1.0 M LiPF6 EC: DC: EMC (ethylene

57

58 carbonate: dimethyl carbonate: cthylene methyl carbonate = 1:1:1 ) as the electrolyte.

59

60 After assembling battery pack and ageing treatment, the electrochemical

characteristics were conducted. The charge-discharge and cyclic voltammetry (CV)

1

2 curves were measured by Channels battery analyzer (CT3008W) between 0.01–3.00 V.

3

4 Electrochemical impedance spectroscopy (EIS) tests were performed in the frequency

5

6 range from 100 KHz to 10 mHz. The CV and EIS measurements were recorded on a

7

8 PARSTAT 2263 electrochemical workstation. All the processes were measured at

9

10 room temperature.

11

12

## 13 2.3.2 Hybrid energy storage devices (HESDs)

14

15 Hybrid energy storage devices (HESDs) were constructed using mFe3C@GO NSs as

16

17 the anode and mLVP/C MSs as the cathode. The average mass loading of the mLVP/C

18

19 MSs cathode was about 1.35 mg cm−2. The charge-discharge curves were carried out

20

21 between 0.00–4.00 V. All the tests were performed at room temperature.

22

23 The average mass loading of the active material is shown in equation 1:

24

25 Mass load = m/A 1

26

27 Where m (mg) is the mass of active material, A (cm2) is the area of the electrode

28

29 sheet with a diameter of 15 mm.

30

31

## 32 3. Results and discussion

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53 **Fig. 1** (a-c) Schematic illustration for reaction of lignin with Fe3+. (d, e)

54

1. Secondary building units of Fe(III)-MOFs, Fe(II)/Fe(III)-MOFs and spiral
2. Fe3O4-MOFs (gray: C; voilet: FeO6 octahedron; blue: FeO4 tetrahedron). (f)

57

58 Structure illustrations of mFe3C@GO NSs after carbonization.

59

60

1 Fe3+ is an ideal metal ion to construct nodes of metal-organic frameworks

2

3 (MOFs) due to its low toxicity, abundance and hard Lewis acid, resulting in

4

5 stronger coordinating bonding with organic ligands, and therefore more stable

6

7 frameworks [20-22]. The in-situ synthesis of mFe3C@GO NSs is shown in Fig.

8

9 1. Benefiting from Fe3+ ions and functional groups in lignin, the nucleation and

10

11 growth of the lyotropic liquid crystals (LLCs) is determined (Fig. S1a).

12

13 Moreover, the factor affecting the spontancous chelation and depolymerization

14

15 is electrophilic attack of lignins (Fig. 1a). The nucleation and growth of Fe3+

16

17 ions are correlated with the functional groups and highly hydrophilic groups on

18

19 lignin surface (Fig. 1b). When Fe3+ ions are deficient, the Fe/lignin chelates

20

21

22 tend to curl in some directions because of electrostatic attraction (Fig. 1c). The

23

24 hydrothermal crystallization behaviour of Fe(III)-MOFs in connection with the

25

26 self-assembly of Fe/lignin chelates. Surplus functional groups were pulled away

27

28 from the lignin structure and donated electron, causing the oxidation-reduction

29

30 reactions of Fe3+ ions and forming the Fe(II)/Fe(III)-MOFs, and ultimately the

31

32 spiral Fe3O4-MOFs (Fig. 1d and e). In the synthesis process, Fe3O4 produce

33

34 chemisorption to the π bond of unsaturated hydrocarbons in lignin,

35

36 consequently weakening the bond energy of lignin and prompting the cleavage

37

38

39 of organo-functional groups (C-H and C-O bonds). Meanwhile, the lignins

40

41 provide carbon-rich matrix and abundant free carbon atoms. The mFe3C@GO

42

43 NSs was obtained by carbonizing Fe3O4-MOFs at 800 °C for 8 h in an nitrogen

44

45 atmosphere. Fe3C nanospheres that coated by graphene oxide are dispersed in

46

47 the conductive network of GO nanosheet homogeneously (Fig. 1f).

48

49 X-ray diffraction (XRD) patterns of the samples synthesized with the

50

51 different addition amounts of Fe3+ were displayed in Fig. S2, demonstrating the

52

53 optimal volume ratio 0.66 of 1mol L−1 Fe3+ solution and the liquid containing

54

55 the lignin. The semi-transparent 3D visualisation image in Fig. 2a shows the

56

57

58 layered skeleton structure and open interlinking pores of Fe3O4-MOFs with

59

60 oversize connected pores (0.5–1.0 μm) (Fig. S3). The X-ray diffraction (XRD)

1 pattern demonstrates the crystal structure of Fe3O4-MOFs (Fig. 2b). The

2

3 diffraction peaks at 5-30° correspond to the simulated MIL-53(Fe), while the

4

5 peaks at 30-80° relate to the Fe3O4 crystalline phase (JCPDS, No. 89-3854) [23,

6

7 24]. The synthetic temperature of Fe3C range from 750 to 850 °C was

8

9 confirmed by differential scanning calorimeter (DSC, Fig. S4). The

10

11 mFe3C@GO NSs synthesized at 800 °C for 8 h is well indexed to orthorhombic

12

13 phase of Fe3C (PDF#65-2413) and graphene oxide, while the samples

14

15 synthesized at 750 °C and 900 °C contain impurity phase (Fig. 2c). The

16

17 graphene oxide with a high degree of disorder is evidenced by a wide reflection

18

19 2θ range from 20 to 30°, with a strong peak characteristic at 2θ=25°. Raman

20

21

22 spectra (Fig. 2d) indicate the intensity ratio (IG/ID=1.87) of mFe3C@GO NSs is

23

24 higher than that of GO (IG/ID=1.06), demonstrating the higher graphitization

25

26 degree of graphene oxide in mFe3C@GO NSs. Furthermore, the sharper shape

27

28 and stronger intensity of 2D peak for mFe3C@GO NSs shifted to lower

29

30 frequency obviously, which may be result from the catalytic effect of Fe ions on

31

32 the cross-linking reaction of lignins and the graphitization of graphene in the

33

34 synthesis process.

35

36 X-ray photoelectron spectroscopy (XPS) was carried out to characterize

37

38

39 the elemental components and chemical states of mFe3C@GO NSs (Fig. S5a).

40

41 High resolution XPS spectrum of Fe 2p present two signals at 711.5 eV (Fe

42

43 2p2/3) and 726.0 eV (Fe 2p1/2), declaring that Fe is in a CFe6 octahedron

44

45 environment with +1 valency (Fig. S5b) [13, 14]. The typical C-C peak and

46

47 C=C peak at 284.8 eV and 285.4 eV can be ascribed to the GO layer (Fig. S5c).

48

49 The high-ordered GO nanosheets was formed by cross-linking condensation

50

51 polymerization of lignin molecules during the heat treatment process.

52

53 The blank sample demonstrates the existence of GO and microcomponent

54

55 of SiC (Fig. 2c), in conjunction with a porous sponge structure (Fig. S6), in

56

57

58 which graphene oxide nanosheet interwined closely with amorphous carbon

59

60 (AC) and graphite carbon nanofibers (GCNFs). The 3D honeycomb structure of

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

1. **Fig. 2** (a) Local semi-transparent 3D visualisation image and (b) XRD patterns
2. of Fe3O4-MOFs precursor and simulated MOF-53(Fe). (c) XRD patterns. (d)

21

1. Raman spectra. (e) TEM image and (f) the elemental mapping image of Fe
2. element. (g) TEM image and TEM-EDS line scan curves along the diameter

24

25 (the yellow line) of the mFe3C@GO NSs nanoparticle.

26

27

28

29 mFe3C@GO NSs (Fig. S7) composed of overlap nanosheets and nanospheres

30

31 exhibits similar morphology to Fe3O4-MOFs, illustrating the structure

32

33 stabilization without collapse during calcination process owing to its

34

35 thermostability. TEM images (Fig. S8a-c) show different size of Fe3C core-shell

36

37 (10-100 nm) with a shell thickness of approximately 4.0 nm embedded in GO

38

39 nanosheets uniformly. The lattice spacings of 0.20 and 0.24 nm are in

40

41 conformity to the (031) and (210) planes of Fe3C, respectively (Fig. S8d and e).

42

43

44 The elemental mapping image of mFe3C@GO NSs indicate the weight

45

46 percentage of Fe is approximately 43% (Fig. 2e and f). The elemental line

47

48 scanning (Fig. 2f) reveal that the Fe element reduced gradually from core to

49

50 surface along the diameter of mFe3C@GO NSs nanosphere, further verifying

51

52 the inner core of Fe3C NPs are well coated by GO shells and homogeneously

53

54 dispersed in the conductive network of GO nanosheet (Fig. S9). Furthermore,

55

56 the increased intensity of ordered hierarchical mesopores conduces to improve

57

58 physical and chemical properties of mFe3C@GO NSs. Most notably, the

59

60

1 mFe3C@GO NSs exhibit an ultra-high BET surface area of 639.1 m2 g−1,

2

3 promoting the permeability of electrolyte and resulting in an excellent

4

5 electrochemical performance (Fig. S10).

6

7 Particularly, the mFe3C@GO NSs synthesized at 800 °C delivers an

8

9 ultrahigh initial discharge capacity of 1800 mAh g−1 at the current density of 1

10

11 A g−1 and and remains at 800 mAh g−1 even at a high current density of 10 A g−1,

12

13 displaying superior high rate capability than that of other anodes for lithium-ion

14

15 battery (Fig. 3a). Charge/discharge voltage profiles of mFe3C@GO NSs at 1 A

16

17 g−1 remain the same and stable after 2nd cycle (Fig. S11), in conjunction with

18

19 the long term cycling performance at 10 A g−1 displayed in Fig. 3b. After 1000

20

21

22 cycles, the reversible capacity retention of mFe3C@GO NSs decreases to about

23

24 715 mAh g−1 and closes to the coulombic efficiency of 100%, demonstrating

25

26 the outstanding cycling stability. The unique core-shell structure of

27

28 mFe3C@GO NSs is conductive to provide abundant sites and flexible buffer

29

30 space for Li+ storage. The prominent decreased peak intensity at 0.8 V after

31

32 1000th cycle and the disappeared peak at 1.5 V can be related to the irreversible

33

34 side reactions and the solid electrolyte interface (SEI) formation, respectively

35

36 (Fig. 3c). The charge transfer resistance (Rct) of mFe3C@GO NSs after 1000th

37

38

39 cycle indicates the improved ions and electrolyte transport properties (Fig. S12),

40

41 in accordance with the electronic conductivity.

42

43 The hybrid energy storage devices (HESDs) were assembled by

44

45 mFe3C@GO NSs (anode) and mLVP/C MSs (cathode) to reveal the potential

46

47 application. The anode/cathode prelithiation is carried out to overcome the

48

49 electrolyte-consuming problem, tuning the electrochemical performance and

50

51 achieving remarkable energy and high power density [25, 26]. By contrast, the

52

53 luminosity of LED bulb driven by HESDs after prelithiation (Fig. 3e) is

54

55 significantly higher than that of LED bulb before prelithiation (Fig. 3d). The

56

57

58 HESDs after prelithiation exhibit better rate capability (Fig. 3f). The initial

59

60 charge and discharge capacities after prelithiation are 544.7 and 528.1 mAh g−1

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

1. **Fig. 3** (a) Rate capability of electrodes synthesized at different temperature. (b)
2. Cycling performance and Columbic efficiency of mFe3C@GO NSs. (c) Cyclic
3. voltammogran curves at the scan rate of 0.1 mV s−1. Electrochemical

28

1. performance evaluation of HESDs with the optimal mass ratio of
2. mpositive/mnegative=4.15. (d, e) Brightness contrast photos of LED bulb driven by
3. HESDs, (f) Rate performance, (g) Long-term cycling performance, (h) Nyquist

32

33 plots and (i) Ragone plots.

34

35

36

37 at 0.1 A g−1, respectively. The HESDs after prelithiation delivers excellent rate

38

39 performance at the rates from 1 to 5 A g−1, and the discharge capacity of 217.8

40

41 mAh g−1 can be remained at 5 A g−1. The long-term cycling performance of

42

43 HESDs after prelithiation is improved tremendously (Fig. 3g) in contrast to that

44

45 of HESDs before prelithiation, which can be attributed to lower Rct (152.7 Ω)

46

47

48 (Fig. 3h) and the enhanced contribution of pseudocapacitive behavior (Fig.

49

50 S13). Extraordinarily, the HESDs after prelithiation still display a discharge

51

52 capacity of 136 mAh g−1 and a retention rate of 91.6% after 1200 cycles at 5 A

53

54 g−1. The HESDs after prelithiation present ultrahigh energy and power densities

55

56 (Fig. 3i), exhibiting exceptionally matched faradaic capacity and kinetics.

57

58

59

60

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20 **Fig. 4** (a) CV curves, (b) Plots of log (sweep rate) versus log (peak current) and

21

1. (c) Capacitive contribution of HESDs after prelithiation at various sweep rates.
2. (e) Schematic diagram of energy storage mechanisms of HESDs after

24

1. prelithiation. Schematic representation of the microstructure of (d) batter-type
2. mLVP/C MSs electrode and (f) mFe3C@GO NSs pseudocapacitive electrode.

27

28

29

30 The synergy effect between cathode and anode was further investigated to

31

32 explore the energy storage mechanism. CV curves of the HESDs after

33

34 prelithiation in a voltage window of 1.5-3.0 V with changing scanning rate from

35

36 0.2 to 5 mV s−1 was recorded to identify the battery and pseudocapacitive

37

38 behavior. The reversible redox peaks (2.35/1.89 V at 0.2 mV s−1) corresponds to

39

40

41 the phase transition during Li+ intercalation/de-intercalation, indicating the

42

43 charge storage mechanism depends on the diffusion-controlled reaction (Fig.

44

45 4a). The area of CV curves increases with the increases of scanning rate,

46

47 accompanied by positive voltage shifts of anodic potential and negative voltage

48

49 shifts of cathodic potential, respectively. Consequently, the well-matching

50

51 concept of electrodes contributes to the conspicuous position repeatability of

52

53 CV peaks and electrochemical reversibility of the electrode reaction [25]. The

54

55 calculated-*b* values ranging from 0.5 to 1.0 indicate the “transition” area

56

57

58 between the surface-controlled process of pseudocapacitive materials and the

59

60 diffusion-controlled process of battery-type materials, and the capacitive

1 contribution increases with the increasing of *b*-values [27, 28]. The higher

2

3 *b*-value of anode (0.73) and cathode (0.61) reflect a mixed contribution of

4

5 diffusion-controlled and the surface-controlled process (Fig. 4b). The higher

6

7 capacity contribution (approximately 53.4%) (Fig. 4c) of HESDs after

8

9 prelithiation at a high scanning rate of 5 mV s−1 can be attributed to the

10

11 pseudocapacitive behavior of mFe3C@GO NSs. Hence, the charge storage

12

13 mechanism of mFe3C@GO NSs supercapacitor is predominantly the

14

15 surface-controlled process. This is done by adsorbing and electrostatic

16

17 accumulating charges in hierarchical mesoporous conductive network of GO

18

19 nanosheet, resulting in higher energy density without the sacrifice of power

20

21

22 density of HESDs after prelithiation. During the charging/discharging process,

23

24 Li+ ions extracted/inserted from/into batter-type mLVP/C MSs electrode and

25

26 inserted/extracted into/from the mFe3C@GO NSs pseudocapacitive electrode

27

28 by the mechanisms of adsorption and electrostatic accumulation (Fig. 4e). The

29

30 LVP NPs promote the fast Li+ solid-state transportation effectively (Fig. 4d) and

31

32 achieve a high diffusion rate and energy density of batter-type mLVP/C MSs

33

34 electrode, which may be related to the well contacts of the interconnected

35

36 mesoporous NPs and the electrolyte. The flexible GO shell maintains the

37

38

39 structural integrity and elastic buffer, resulting in high power density, excellent

40

41 rate capability and cycle performance (Fig. 4f). In addition, the active

42

43 biocarbon network possesses good electronic conductivity. Therefore, selecting

44

45 and optimizing the active material and electrode architecture benefit to acquire

46

47 ultrahigh energy and power densities of HESDs after prelithiation, which has

48

49 great potential for significantly improving fast and efficient energy storage in

50

51 the future.

52

53

## 54 4. Conclusions

55

56

57 In summary, multifunctional mesoporous core-shell mFe3C@GO NSs was

58

59 prepared by hydrothermal synthesis and high-temperature calcination with

1 high-quality lignins as the organic ligands of Fe(II)/Fe(III)-MOFs precursor and

2

3 the carbon source. The functional groups of lignins and Fe ions catalyze the

4

5 cross-linking of lignins and the formation of GO nanosheet, and the synthesis

6

7 mechanism was proposed. The mFe3C@GO NSs homogeneously dispersed in

8

9 GO conductive network and maintained the structural integrity of the electrode

10

11 in the electrochemical process, which exhibited high reversible specific

12

13 capacity, excellent rate capability and cycling stability. This elaborate work

14

15 encourages the investigation of biomass waste conversion and utilization and

16

17 the extensible exploration of multifunctional materials for rechargeable

18

19 batteries.

20

21

## 22 Declaration of competing interest

23

24

25 The authors declare no conflict of interest.

26

27

## 28 Acknowledgements

29

30

31 This work is supported by the National Natural Science Foundation of China

32

33 (No. 61368007), the Natural Science Foundation of Shandong Province (Grant

34

35 No. ZR2019MEM053), and the Project (D20015).

36

37

38 **References**

39

40

41 1 Su F, Qin J, Das P, Zhou F, Wu ZS. A high-performance rocking-chair

42

43 lithium-ion battery-supercapacitor hybrid device boosted by doubly matched

44

45 capacity and kinetics of the faradaic electrodes. Energy Environ Sci 2021; 14:

46

47 2269-2277. https://doi.org/10.1039/D1EE00317H

48

49 2 Tie D, Huang S, Wang J, Ma J, Zhang J, Zhao Y. Hybrid energy storage

50

51 devices: advanced electrode materials and matching principles. Energy Stor

52

53 Mater 2019; 21: 22-40. https://doi.org/10.1016/j.ensm.2018.12.018

54

55 3 Sharma R, Kumar H, Kumar G, Sharma S, Aneja R, Sharma AK, Kumar R,

56

57

58 Kumar P. Progress and challenges in electrochemical energy storage devices:

1 fabrication, electrode material, and economic aspects. Chem Eng J 2023; 468:

2

3 143706. https://doi.org/10.1016/j.cej.2023.143706

4

5 4 Wei H, Huang W, Luo K, Huang Y, Zhong S, Yan D. PVP-assisted synthesis

6

7 of hollow Ni0.75Zn0.25Fe2O4 nanospheres for lithium-ion batteries. Int J

8

9 Hydrogen Energy 2023; 48: 20208-20215.

10

11 https://doi.org/10.1016/j.ijhydene.2023.01.303

12

13 5 Qin G, Jia Z, Li A, Sun S, Liu Z, Zhuang CL, Chen J. Nitrogen-rich

14

15 carbon/SiO2 nanotubes composites prepared by self-assembly as

16

17 high-performance anode lithium-ion battery. Int J Hydrogen Energy 2023; 48:

18

19 20208-20215. https://doi.org/10.1016/j.ijhydene.2023.09.201

20

21

22 6 Zhang S, Wang K, Chen H, Liu H, Yang L, Chen Y, Li H. ZIF-67 derived

23

24 in-situ grown NeCo3S4-GN/CNT interlinked conductive networks for

25

26 high-performance especially cycling stable supercapacitors. Carbon 2022; 194:

27

28 10-22. https://doi.org/10.1016/j.carbon.2022.03.054

29

30 7 Huang X, Qi X, Boey F, Zhang H. Graphene-based composites. Chem Soc Rev

31

32 2012; 41: 666–686. https://doi.org/10.1039/C1CS15078B

33

34 8 Solís-Fernández P, Bissett M, Ago H, Synthesis, structure and applications of

35

36 graphene-based 2D heterostructures. Chem Soc Rev 2017; 46: 4572–4613.

37

38

39 https://doi.org/10.1039/C7CS00160F

40

41 9 Shi J, Wang Y, Du W, Hou Z. Synthesis of graphene encapsulated Fe3C in

42

43 carbon nanotubes from biomass and its catalysis application. Carbon 2016; 99:

44

45 330–337. https://doi.org/10.1016/j.carbon.2015.12.049

46

47 10 Fan X, Peng Z, Ye R, Zhou H, Guo X. M3C (M: Fe, Co, Ni) nanocrystals

48

49 encased in graphene nanoribbons: an active and stable bifunctional

50

51 electrocatalyst for oxygen reduction and hydrogen evolution reactions. ACS

52

53 Nano 2015; 9: 7407–7418. https://doi.org/10.1021/acsnano.5b02420

54

55 11 Zhang J, Wang K, Xu Q, Zhou Y, Cheng F, Guo S. Beyond yolk-shell

56

57

58 nanoparticles: Fe3O4@Fe3C core@shell nanoparticles as yolks and carbon

1 nanospindles as shells for efficient lithium ion storage. ACS Nano 2015; 9:

2

3 3369–3376. https://doi.org/10.1021/acsnano.5b00760

4

5 12 Tan Y, Zhu K, Li D, Bai F, Wei Y, Zhang P. N-doped graphene/Fe–Fe3C

6

7 nano-composite synthesized by a Fe-based metal organic framework and its

8

9 anode performance in lithium ion batteries. Chem Eng J 2014; 258: 93–100.

10

11 https://doi.org/10.1016/j.cej.2014.07.066

12

13 13 [Zheng](https://pubmed.ncbi.nlm.nih.gov/?term=Zheng%2BJ&cauthor_id=34382971) J, [Kong](https://pubmed.ncbi.nlm.nih.gov/?term=Kong%2BF&cauthor_id=34382971) F, [Tao](https://pubmed.ncbi.nlm.nih.gov/?term=Tao%2BS&cauthor_id=34382971) S, [Qian](https://pubmed.ncbi.nlm.nih.gov/?term=Qian%2BB&cauthor_id=34382971) B. A Fe2O3-Fe3C heterostructure encapsulated

14

15 into a carbon matrix for the anode of lithium-ion batteries. Chem Commun

16

17 2021; 57: 8818-8821. https://doi.org/10.1039/D1CC03945H

18

19 14 Chen R, Zhou Y, Li X. Cotton-derived Fe/Fe3C-encapsulated carbon nanotubes

20

21

22 for high-performance lithium-sulfur batteries. Nano Lett 2022; 22: 1217–1224.

23

24 https://doi.org/10.1021/acs.nanolett.1c04380

25

26 15 Shen W, Kou W, Liu Y, Dai Y, Zheng W, He G, Wang S, Zhang Y, Wu X,

27

28 Fan S, Li X. Fe3C-doped asymmetric porous carbon membrane binder-free

29

30 integrated materials as high performance anodes of lithium-ion batteries. Chem

31

32 Eng J 2019; 368: 310–320. https://doi.org/10.1016/j.cej.2019.02.199

33

34 16 Schlee P, Hosseinaei O, O' Keefe CA, Mostazo-Lopez MJ, Cazorla-Amoros D,

35

36 Herou S, Tomani P, Grey CP, Titirici MM. Hardwood versus softwood Kraft

37

38

39 lignin-precursor-product relationships in the manufacture of porous carbon

40

41 nanofibers for supercapacitors. J Mater Chem A 2020; 8: 23543.

42

43 https://doi.org/10.1039/D0TA09093J

44

45 17 Schutyser W, Renders T, Bosch SV, Koelewijn SF, Beckham GT, Sels BF.

46

47 Chemicals from lignin: an interplay of lignocellulose fractionation,

48

49 depolymerisation, and upgrading. Chem Soc Rev 2018; 47: 852–908.

50

51 https://doi.org/10.1039/C7CS00566K

52

53 18 Xu YH, Zhou Q, Li MF, Bian J, Peng F. Tetrahydro-2-furanmethanol

54

55 pretreatment of eucalyptus to enhance cellulose enzymatic hydrolysis and to

56

57

58 produce high-quality lignin. Bioresour Technol 2019; 280: 489–492.

59

60 https://doi.org/10.1016/j.biortech.2019.02.088

1 19 Du X, He W, Zhang X, Yue Y, Liu H, Zhang X, Min D, Ge X, Du Y.

2

3 Enhancing the electrochemical performance of lithium ion batteries using

4

5 mesoporous Li3V2(PO4)3/C microspheres. J Mater Chem 2012; 22: 5960–5969.

6

7 https://doi.org/10.1039/C1JM14758G

8

9 20 Fei Y, Liang M, Yan L, Chen Y, Zou H. Co/C@cellulose nanofiber aerogel

10

11 derived from metal-organic frameworks for highly efficient electromagnetic

12

13 interference shielding. Chem Eng J 2020; 392: 124815.

14

15 https://doi.org/10.1016/j.cej.2020.124815

16

17 21 Liu C, Huang X, Liu J, Wang J, Chen Z, Luo R, Wang C, Li J, Wang L, Wang

18

19 J, Yu C. A general approach to direct growth of oriented metal-organic

20

21

22 framework nanosheets on reduced graphene oxides. Adv Sci 2020; 7: 1901480.

23

24 https://doi.org/10.1002/advs.201901480

25

26 22 Han D, Zhao Z, Xu Z, Wang H, He Z, Wang H, Shi J, Zheng L. Metal organic

27

28 frameworks enabled multifunctional poly(ethylene oxide)-based solid polymer

29

30 electrolytes with high lithium-ion conductivity and excellent stability. ACS

31

32 Appl Energy Mater 2022; 5: 8973–8981.

33

34 https://doi.org/10.1021/acsaem.2c01461

35

36 23 Zhang C, Hu W, Jiang H, Chang JK, Zheng M, Wu QH, Dong Q.

37

38

39 Electrochemical performance of MIL-53(Fe)@RGO as an organic anode

40

41 material for li-ion batteries. Electrochim Acta 2017; 246: 528–535.

42

43 https://doi.org/10.1016/j.electacta.2017.06.059

44

45 24 Liang R, Shen L, Jing F, Qin N, Wu L. Preparation of MIL-53(Fe)-reduced

46

47 graphene oxide nanocomposites by a simple self-assembly strategy for

48

49 increasing interfacial contact: efficient visible-light photocatalysts. ACS Appl

50

51 Mater Interfaces 2015; 7: 9507–9515.

52

53 <http://dx.doi.org/10.1021/acsami.5b00682>

54

55 25 Zhang H, Cheng J, Liu H, Li D, Zeng Z, Li Y, Ji F, Guo Y, Wei Y, Zhang S,

56

57

58 Bai T, Xu X, Peng R, Lu J, Ci L. Prelithiation: a critical strategy towards

1 practical application of high-energy-density batteries. Adv Energy Mater 2023;

2

3 13: 2300466. https://doi.org/10.1002/aenm.202300466

4

5 26 Wang F, Wang B, Li J, Wang B, Zhou Y, Wang D, Liu H, Dou S. Prelithiation:

6

7 a crucial strategy for boosting the practical application of next-generation

8

9 lithium ion battery, ACS Nano 2021; 15: 2197–2218.

10

11 https://doi.org/10.1021/acsnano.0c10664

12

13 27 Liu J, Wang J, Xu C, Jiang H, Li C, Zhang L, Lin J, Shen JL. Advanced energy

14

15 storage devices: basic principles, analytical methods, and rational materials

16

17 design. Adv Sci 2018; 5: 170032. https://doi.org/10.1002/advs.201700322

18

19 28 Zhang L, Zhang X, Tian G, Zhang Q, Knapp M, Ehrenberg H, Chen G, Shen Z,

20

21

22 Yang G, Gu L, Du F. Lithium lanthanum titanate perovskite as an anode for

23

24 lithium ion batteries. Nat Commun 2020; 11: 3490.

25

26 https://doi.org/10.1038/s41467-020-17233-1

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

Revised Manuscript (Clean, unmarked, FINAL version) [Click here to view linked References](https://www2.cloud.editorialmanager.com/he/viewRCResults.aspx?pdf=1&docID=123526&rev=3&fileID=3367152&msid=3e7ef597-23e0-4be2-98df-ce8bd9bb1c23)

# Biomass-derived mesoporous core-shell Fe3C@graphene

1. **oxide nanospheres for electrochemical energy storage**

3

4 Xinli Yi,a,b Wen He,c\* Xudong Zhang,c Kwan San Huid and Wangwang Xua\*

5

1. a.College of Materials and Chemical Engineering, Key Laboratory of Inorganic
2. Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges
3. University, Yichang, 443002, P. R. China
4. b.Hubei Three Gorges Laboratory, Yichang, Hubei 443007, P. R. China.
5. c.Department of Materials Science and Engineering, Qilu University of Technology
6. (Shandong Academy of Sciences), Jinan, 250353, P. R. China.
7. d.School of Engineering, Faculty of science, University of East Anglia, Norwich, NR4
8. 7TJ, United Kingdom.

14

## Abstract

1. The biomass-derived mesoporous core-shell Fe3C@graphene oxide nanospheres
2. (mFe3C@GO NSs) was synthesized with high-quality lignins and applied for
3. electrochemical energy storage. The synthesis conditions of mFe3C@GO NSs are
4. optimized and its formation mechanism is proposed. The mFe3C@GO NSs
5. homogeneously dispersed in GO conductive network and maintained the structural
6. integrity of the electrode during the electrochemical process. Benefiting from the
7. advantages of the core-shell construction and graphene oxide network, the
8. mFe3C@GO NSs exhibits extensible exploration in electrochemical energy storage
9. (EES).
10. **Keywords**: mFe3C@GO NSs; Biomass-derived compounds; Nanostructured
11. electrode; Lithium-ion battery; Electrochemical energy storage

27

28

## 1. Introduction

1. Energy storage technology is a frontier research orientation, which efficiently
2. eliminates greenhouse gas emissions, reduces petroleum reliance and facilitates
3. the sustainable utilization of energy. In order to enhance the competitiveness of
4. the rechargeable batteries-based electric vehicles (EVs), some barriers of high
5. energy/power density, cost, fast charging capability and compatible sizes need
6. to overcome to consummate power sources [1-3]. The integrated device
7. combined with the advantages of two energy storage mechanisms, lead to a
8. “double high” Li-ion battery (LIB) and supercapacitor (SC) hybrid energy
9. storage devices (HESDs), further providing possible power source for
10. multi-function electronic equipment and electric/hybrid vehicles [4, 5].
11. However, the mismatches of charge storage capacity and electrode kinetics
12. between battery-type and capacitive electrodes lead to a relatively restricted
13. performance of LIB-SC HESDs. [4]. Therefore, the design of high-performance
14. electrode materials and understanding on the matching theory between the
15. positive and negative electrodes of LIB-SC HESDs face overwhelming
16. challenges [6].
17. In the pursuit of high-performance energy storage devices,
18. biomass-derived carbon materials and its hybrids have been regarded as the
19. potential candidate electrodes owing to the inexpensive feedstock, nontoxicity
20. and diverse sources of renewable biomass source [7, 8]. The utilization of
21. biomass contributes to achieve a zero-waste circular bioeconomy and greener
22. energy storage. Furthermore, the chemical/physical properties and structural
23. advantages have an effect on fabricating biomass-derived activated carbon
24. during the following carbonization and activation, resulting in high specific
25. surface area, pore structure, and high graphitization [9, 10]. Especially
26. graphene (GN)-like two-dimensional materials, has draws significant attentions
27. owing to the unique interfacial structure, attractive properties, facile synthesis,
28. and ease of functionalization [11-13]. Numerous studies indicate that the
29. effective work function of carbon-based electrode was increased significantly
30. by inserting metal oxide nanoparticles [14-19]. The graphitic carbon and iron
31. carbide (Fe3C) bifunctional oxygen electrodes demonstrated synergistic effects
32. [20, 21]. For Fe3C anode materials used in LIBs, particularly in high current
33. density, there is an urgent need to restrain the structure collapse originated from
34. volume change during the continuous charge/discharge process and the poor
35. conductivity of Fe3C, which results in rapid capacity fading [22]. Structure
36. engineering and conductive network had wide applicability to solve these
37. problems [23-25]. Nevertheless, the core-cell carbon coating featured with large
38. specific surface area, excellent conductivity and mechanical flexibility can be
39. fabricated through different design strategies, further contributes to restricted
40. performance improvement [26]. In general, the core-shell structure is desirable
41. to realize synergism effect, but surprisingly little attention focus on the
42. utilization of lignin. Lignin emerges as a by-product from papermaking industry
43. by the degradation of the nature wood, which is suitable for thermochemical
44. reaction for its high yield of pyrolysis products and is considered a promising
45. feedstock for carbon materials production [27, 28]. Its surfactant structure
46. contains multifarious functional groups (carboxyl, hydroxyl, benzyl alcohol,
47. methoxyl e.g.) and trace elements (such as Si and S, etc), providing lone pair
48. electrons, nucleation sites and adsorb metal ions [29].
49. Here, the biomass-derived mesoporous core-shell Fe3C@graphene oxide
50. nanospheres (mFe3C@GO NSs) were fabricated by a simple wet chemical
51. route with high-quality lignins as the organic ligands and the carbon source, and
52. the synthesis mechanism was proposed. The structure of mFe3C@GO NSs
53. exhibits effects on fast ion insertion/extraction, high electrolyte permeability,
54. and electric conductivity for lithium-ion battery and supercapacitor,
55. respectively. More importantly, the HESDs constructed with mFe3C@GO NSs
56. and mesoporous Li3V2(PO4)3/C microspheres (mLVP/C MSs) [30] exhibit
57. highly matched capacity and significant pseudocapacitive behavior.

## 2. Experiments sections

1. **2.1. Synthesis of mFe3C@GO NSs**
2. The Fe-species composite precursor was synthesized by a simple, low-cost and green
3. method of hydrothermal crystallization and reduction. 0.89 g FeCl3·6H2O powder was
4. dissolved in 33 mL deionized water with continuous stirring to form a uniform
5. solution. Then, the solution was slowly added into 50 mL lignin solution (pH ≈ 13)
6. with magnetic stirring for 6 h at room temperature to form a thick liquid (pH ≈ 7).
7. Subsequently, the thick liquid was then transformed into a Teflon-sealed autoclave
8. and heated at 180°C for 48 h. After the autoclave cooled down to room temperature
9. naturally, the precipitate was washed with deionized water for three times and dried at
10. 60 °C to obtain the Fe-species composite precursor (including Fe3O4 and MIL-53(Fe)).
11. Finally, the Fe-species composite precursor was placed in a tube furnace and then
12. heated at 800 °C for 8 h with a heating rate of 5°C min−1 under nitrogen (N2)
13. atmosphere. The mFe3C@GO NSs was obtained. For comparison, the GO blank
14. sample was prepared by calcination treatment of dried lignin solution at 800 °C under
15. N2 for 8 h.

## 2.2. Characterizations

1. The crystalline characteristics of materials were identified by X-ray diffraction (XRD,
2. LabX XRD-6100) with Cu-Kα radiation (Shimadzu, λ= 1.5406 nm) at a scanning rate
3. of 5° min−1. The elemental composition and chemical states of elements was carried
4. out by X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+). The binding
5. energies were calibrated to the C 1s peak (284.6 eV). The morphologies and surface
6. microstructures of materials were observed by Field emission gun (FEG) scanning
7. electron microscopy (SEM) (Quanta 200F) using an operating voltage of 20 kV with
8. an X-ray energy dispersive spectrometer (EDS) and a ZEISS scanning electron
9. microscope. The EDS images were captured at the positions emerged in the TEM
10. images, providing the distribution of elements. The crystallographic structure of
11. materials were investigated by transmission electron microscopy (TEM, JEF-2100F)
12. under the condition of 200 kV. The high-revolution TEM images associated with line
13. scanning TEM-EDS profiles indicated the element distribution across the diameter of
14. a single nanoparticle. Raman spectra were measured by a Renishaw RM2000 Raman
15. microscope with 514 nm excitation argon laser. Differential scanning calorimetry
16. (DSC-100H, Nanjingdazhan) was used to measure the thermal change of Fe-species
17. composite precursor. Gravimetric analysis is a quantitative chemical method for
18. accurately determining the element contents of the materials. The N2 adsorption–
19. desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution curves
20. were obtained at 77 K using an automatic surface area analyzer (Micromeritics,
21. Gemini V2380, USA).

## 2.3. Electrochemical measurements

1. **2.3.1 Electrode preparation for LIBs and electrochemical measurements**
2. The electrochemical performances were characterized in a coin-type LIR2032 cell at
3. room temperature. The working electrode was prepared by mixing 80% mFe3C@GO
4. NSs, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) in N-methyl
5. pyrrolidone, then stirring to prepare the slurry and coating it on copper foil surface
6. uniformly. After that, the electrode was dried at 60 °C in an electric thermostatic
7. drying oven and then dried at 110 °C for 10 h in vacuum drying oven. The electrode
8. was cut it into wafers with a diameter of 15 mm. The average mass loading of the
9. mFe3C@GO NSs electrode was about 1.2 mg cm−2 (Table S1). The cells were
10. assembled in a high-purity argon-filled inert glove box with the synthesized electrode
11. as anode and polypropylene (PP) membrane as a separator, 1.0 M LiPF6 EC: DC:
12. EMC (ethylene carbonate: dimethyl carbonate: cthylene methyl carbonate = 1:1:1 ) as
13. the electrolyte. After assembling battery pack and ageing treatment, the
14. electrochemical characteristics were conducted. The charge-discharge and cyclic
15. voltammetry (CV) curves were measured by Channels battery analyzer (CT3008W)
16. between 0.01–3.00 V. Electrochemical impedance spectroscopy (EIS) tests were
17. performed in the frequency range from 100 KHz to 10 mHz. The CV and EIS
18. measurements were recorded on a PARSTAT 2263 electrochemical workstation. All
19. the processes were measured at room temperature.

## 2.3.2 Electrochemical measurements of HESDs

1. HESDs were constructed using mFe3C@GO NSs as the anode and mLVP/C MSs as
2. the cathode. The experimental process of prelithialization in form is similar to the
3. structure of the common half-cell. Before the construction of full battery, the electrode
4. materials (anode and cathode) were activated respectively in corresponds half-cell
5. systems through electrochemical prelithialization. Afterwards, the half-cell was
6. disassembled respectively, and then the anode and cathode electrodes were
7. reassembled to construct a new full-cell without washing. The average mass loading
8. of the mLVP/C MSs cathode was about 1.35 mg cm−2. The charge-discharge curves
9. were carried out between 0.00–4.00 V. All the tests were performed at room
10. temperature.
11. The average mass loading of the active material is shown in equation 1:
12. Mass load = m/A 1
13. Where m (mg) is the mass of active material, A (cm2) is the area of the electrode
14. sheet with a diameter of 15 mm.

## 3. Results and discussion

1. Lignin carbon-based composites employ as electrode materials for
2. electrochemical because of their inherited outstanding properties [31, 32].
3. Lignin exhibits advantages for carbon-based composites such as
4. environmentally friendly, good biocompatibility, and high carbon content [33].
5. Particularly, the functional groups of lignin play key roles in the formation of
6. Fe-species precursor. The in-situ synthesis of mFe3C@GO NSs is shown in Fig.
7. 1. Benefiting from Fe3+ ions and functional groups in lignin, the nucleation and
8. growth of the lyotropic liquid crystals is determined (Fig. S1a). Moreover, the
9. factor affecting the spontancous chelation and depolymerization is electrophilic
10. attack of lignins (Fig. 1a). The nucleation and growth of Fe3+ ions are correlated

1

1. **Fig. 1** (a-c) Schematic illustration for reaction of lignin with Fe3+. (d, e)
2. Secondary building units of Fe(III)-precursor, Fe(II)/Fe(III)-precursor and
3. Fe-species composite precursor (gray: C; voilet: FeO6 octahedron; blue: FeO4
4. tetrahedron). (f) Structure illustrations of mFe3C@GO NSs after carbonization.

6

1. with the functional groups and highly hydrophilic groups on lignin surface (Fig.
2. 1b). When Fe3+ ions are deficient, the Fe/lignin chelates tend to curl in some
3. directions because of electrostatic attraction (Fig. 1c). The hydrothermal
4. crystallization behaviour of Fe(III)-precursor is associated with the
5. self-assembly of Fe/lignin chelates. Surplus functional groups were pulled away
6. from the lignin structure and donated electron, causing the oxidation-reduction
7. reactions of Fe3+ ions and forming the Fe(II)/Fe(III)-precursor, and ultimately
8. formed the intermediate Fe-species composite precursor (including Fe3O4 and
9. MIL-53(Fe)) (Fig. 1d and e). In the synthesis process, the Fe3O4 produces
10. chemisorption to the π bond of unsaturated hydrocarbons in lignin,
11. consequently weakening the bond energy of lignin and prompting the cleavage
12. of organo-functional groups (C-H and C-O bonds). Meanwhile, the lignins
13. provide carbon-rich matrix and abundant free carbon atoms. The mFe3C@GO
14. NSs was obtained by carbonizing Fe-species composite precursor at 800 °C for
15. 8 h in N2 atmosphere. Fe3C nanospheres that coated by graphene oxide are

22

1

1. **Fig. 2** (a) Local semi-transparent 3D visualisation image and (b) XRD patterns
2. of Fe-species composite precursor (black) and simulated MIL-53(Fe) (red). (c)
3. XRD patterns of calcined samples at different temperatures. (d) Raman spectra
4. of mFe3C@GO NSs and blank GO samples. (e) TEM image and (f) the
5. elemental mapping image of Fe element. (g) TEM image and TEM-EDS line
6. scan curves along the diameter (the yellow line) of the mFe3C@GO NSs
7. nanoparticle.

9

1. dispersed in the conductive network of graphitic carbon nanosheet
2. homogeneously (Fig. 1f).
3. X-ray diffraction (XRD) patterns of the samples synthesized with the
4. different addition amounts of Fe3+ were displayed in Fig. S2, demonstrating the
5. optimal volume ratio 0.66 of 1mol L−1 Fe3+ solution and the lignin liquid. The
6. semi-transparent 3D visualisation image in Fig. 2a shows the layered skeleton
7. structure and open interlinking pores of Fe-species composite precursor with
8. oversize connected pores (0.5–1.0 μm) (Fig. S3). As shown in Fig. 2b, the
9. phase constitution of the product after hydrothermal treatment was performed
10. by X-ray diffraction (XRD). The diffraction peaks at 5-30° correspond to the
11. simulated MIL-53(Fe), while the peaks at 30-80° relate to the Fe3O4 crystalline
12. phase (JCPDS, No. 89-3854) [34, 35]. The synthetic temperature of Fe3C range
13. from 750 to 850 °C was confirmed by differential scanning calorimeter (DSC,
14. Fig. S4). The mFe3C@GO NSs synthesized at 800 °C for 8 h is well indexed to
15. orthorhombic phase of Fe3C (PDF#65-2413) and graphene oxide, while the
16. samples synthesized at 750 °C and 900 °C contain impurity phase (Fig. 2c).
17. The graphene oxide with a high degree of disorder is evidenced by a wide
18. reflection 2θ range from 20 to 30°, in conjunction with a strong peak
19. characteristic at 2θ=25°. The Raman spectra of the mFe3C@GO NSs and blank
20. GO samples are revealed in Fig. 2d, which offer more insight into the carbon
21. structures and the degree of graphitization. Two prominent characteristic D and
22. G peaks for at 1354/1351 cm−1 and 1578/1599 cm−1 are observed, and the
23. intensity ratio of *ID/IG* are 0.54 and 0.94 for the mFe3C@GO NSs and blank GO
24. samples, respectively. The relative lower intensity ratio (*ID/IG*) of mFe3C@GO
25. NSs demonstrates a higher graphitization degree of carbon [36]. Furthermore,
26. the intense 2D band at 2969 cm−1 corresponds to the two phonons lattice
27. vibration, indicating the characteristic of graphene oxide. These results revealed
28. the successful carbonization and graphitization of lignins during the
29. carbonization process [37].
30. X-ray photoelectron spectroscopy (XPS) was carried out to characterize
31. the elemental components and chemical states of mFe3C@GO NSs (Fig. S5a).
32. High resolution XPS spectrum of Fe 2p present two signals at 711.5 eV (Fe
33. 2p2/3) and 726.0 eV (Fe 2p1/2), declaring Fe (+1) is in a CFe6 octahedron
34. environment (Fig. S5b) [24, 25]. The typical C-C peak and C=C peak at 284.8
35. eV and 285.4 eV can be ascribed to the GO layer (Fig. S5c). The high-ordered
36. GO nanosheets was formed by cross-linking condensation polymerization of
37. lignin molecules during the heat treatment process.
38. The blank sample demonstrates the existence of GO and microcomponent
39. of SiC (Fig. 2c), in conjunction with a porous sponge structure (Fig. S6), in
40. which graphene oxide nanosheet interwined closely with amorphous carbon
41. and graphite carbon nanofibers. The 3D honeycomb structure of mFe3C@GO
42. NSs (Fig. S7) composed of overlap nanosheets and nanospheres exhibits
43. similar morphology to Fe-species composite precursor, illustrating the structure
44. stabilization without collapse during calcination process owing to its
45. thermostability. TEM images (Fig. S8a-c) confirm the dispersed distribution of
46. Fe3C nanosphere (10-100 nm), in a typical core-shell configuration that the
47. thickness of graphene oxide shell is approximately 4.0 nm. The lattice fringe
48. (0.33 nm) of the outer layer of mFe3C@GO NSs relates to the (110) plane of
49. graphene oxide, which is in consistent with the results of XRD and Raman
50. spectra (Fig. S8d). Moreover, the lattice spacings of 0.20 and 0.24 nm are in
51. conformity to the (031) and (210) planes of Fe3C, respectively (Fig. S8e and f).
52. The elemental mapping images of mFe3C@GO NSs indicate the weight
53. percentage of Fe is approximately 43% (Fig. 2e and f). Similar results was
54. conducted by the gravimetric method, with Fe and C contents of 43.4 wt.% and
55. 52.2 wt.%, respectively (Table S2). The elemental line scanning (Fig. 2g)
56. reveals that the Fe element reduced gradually from core to surface along the
57. diameter of mFe3C@GO NSs nanosphere, further verifying the inner core of
58. Fe3C NPs are well coated by GO shells and homogeneously dispersed in the
59. conductive network of GO nanosheet (Fig. S9). Furthermore, the increased
60. intensity of ordered hierarchical mesopores conduces to improve physical and
61. chemical properties of mFe3C@GO NSs. Most notably, the mFe3C@GO NSs
62. exhibit an ultra-high BET surface area of 639.1 m2 g−1, promoting the
63. permeability of electrolyte and resulting in an excellent electrochemical
64. performance (Fig. S10).
65. Particularly, the mFe3C@GO NSs synthesized at 800 °C delivers an
66. ultrahigh initial discharge and charge capacities of 1800 mAh g−1 and 698.8
67. mAh g−1 with initial coulombic efficiency of 38.8% at the current density of 1 A
68. g−1 (Fig. S11). The mFe3C@GO NSs electrode delivers relatively stable
69. discharge/charge capacities and Coulombic efficiency of approximately 93%
70. from 20th to 50th cycles, demonstrating its excellent cycling stability (Table

1

1. **Fig. 3** (a) Rate capability of electrodes synthesized at different temperature. (b)
2. Cycling performance and Columbic efficiency of mFe3C@GO NSs. (c) Cyclic
3. voltammogran curves at the scan rate of 0.1 mV s−1. Electrochemical
4. performance evaluation of HESDs with the optimal mass ratio of
5. mpositive/mnegative=4.15. (d, e) Brightness contrast photos of LED bulb driven by
6. HESDs, (f) Rate performance, (g) Long-term cycling performance, (h) Nyquist
7. plots and (i) Ragone plots.

9

1. S3). TEM images in Fig. S12 demonstrate the structural integrity and dispersion
2. of mFe3C@GO NSs after 50 cycles. From the structural view, the graphene
3. oxide outer layer contributes to restrain excessive side reactions and cushion the
4. structural changes during the charging/discharging process, resulting in
5. structural integrity. As shown in Fig. 3a, the mFe3C@GO NSs demonstrates
6. superior rate capability than that of other anodes for lithium-ion battery.
7. Furthermore, the mFe3C@GO NSs exhibits high capacity retention rate after
8. 1000 cycles (715 mAh g−1) and approximately 100% Coulombic efficiency
9. even at a high current density of 10 A g−1 (Fig. 3b), demonstrating the
10. outstanding cycling stability. Fortunately, the mFe3C@GO NSs exhibits
11. comparable electrochemical performance with the recently reported Fe3C-based
12. electrode materials (Table S4) and Fe-based materials with
13. nanosphere-structure (Table S5). The electrochemical performance of
14. mFe3C@GO NSs can be attributed to the following factors: (1) The ultra-high
15. BET surface area provides abundant active sites and flexible buffer space for
16. Li+ storage, and the core-shell structure cushions the volume expension
17. effectively [38]; (2) The conductive channel between Fe3C and graphitic carbon
18. layer improves the electrical conductivity; (3) The graphene oxide outer layer is
19. conducive to the adsorption of lithium ion [39].
20. The prominent decreased peak intensity at 0.8 V after 1000th cycle and the
21. disappeared peak at 1.5 V can be related to the irreversible side reactions and
22. the solid electrolyte interface (SEI) formation, respectively (Fig. 3c). The EIS
23. plots of mFe3C@GO NSs electrode before and after cycling, and the
24. corresponding equivalent circuit are shown in Fig. S13. The semicircle at
25. high-frequency areas is relevant to the charge transfer resistance (Rct) on the
26. electrode/electrolyte interface, which is parallel to the interface capacitance
27. (CPE). The oblique line at low-frequency areas presents the Lithium-ion
28. diffusion impedance (Warburg impedance, Zw). Obviously, the smaller
29. semicircular diameters of mFe3C@GO NSs electrode after 1000th cycles
30. indicates the effectively improved electron/ion transport properties, in
31. accordance with the electronic conductivity [40-42].
32. The HESDs were assembled by mFe3C@GO NSs (anode) and mLVP/C
33. MSs (cathode) to reveal the potential application. The anode/cathode
34. prelithiation is carried out to overcome the electrolyte-consuming problem,
35. tuning the electrochemical performance and achieving remarkable energy and
36. high power density [43, 44]. By contrast, the luminosity of LED bulb driven by
37. HESDs after prelithiation (Fig. 3e) is significantly higher than that of LED bulb
38. before prelithiation (Fig. 3d). The HESDs after prelithiation exhibit better rate
39. capability (Fig. 3f). The initial charge and discharge capacities after
40. prelithiation are 544.7 and 528.1 mAh g−1 at 0.1 A g−1, respectively. The
41. HESDs after prelithiation deliver excellent rate performance from 1 to 5 A g−1,
42. and the discharge capacity of 217.8 mAh g−1 can be remained at 5 A g−1. The
43. long-term cycling performance of HESDs after prelithiation is improved
44. significantly (Fig. 3g) in contrast to that of HESDs before prelithiation, which
45. can be attributed to the lower Rct (152.7 Ω) (Fig. 3h) and the enhanced
46. contribution of pseudocapacitive behavior (Fig. S14). Extraordinarily, the
47. HESDs after prelithiation still display a discharge capacity of 136 mAh g−1 and
48. a retention rate of 91.6% after 1200 cycles at 5 A g−1. The HESDs after
49. prelithiation present ultrahigh energy and power densities (Fig. 3i), exhibiting
50. exceptionally matched faradaic capacity and kinetics.
51. The synergy effect between cathode and anode was further investigated to
52. explore the energy storage mechanism. CV curves of the HESDs after
53. prelithiation was recorded in a voltage window of 1.5-3.0 V with changing
54. scanning rate from 0.2 to 5 mV s−1 to identify the battery and pseudocapacitive
55. behavior. The reversible redox peaks (2.35/1.89 V at 0.2 mV s−1) corresponds to
56. the phase transition during Li+ intercalation/de-intercalation, indicating the
57. charge storage mechanism depends on the diffusion-controlled reaction (Fig.
58. 4a). The area of CV curves increases with the increasing of scanning rate,
59. accompanied by positive voltage shifts of anodic potential and negative voltage
60. shifts of cathodic potential, respectively. Consequently, the well-matching
61. concept of electrodes contributes to the conspicuous position repeatability of
62. CV peaks and electrochemical reversibility of the electrode reaction [43]. The
63. calculated-*b* values ranging from 0.5 to 1.0 indicate the “transition” area
64. between the surface-controlled process of pseudocapacitive materials and the
65. diffusion-controlled process of battery-type materials, and the capacitive
66. contribution increases with the increasing of *b*-values [45, 46]. The higher
67. *b*-value of anode (0.73) and cathode (0.61) reflect a mixed contribution of

1

1. **Fig. 4** (a) CV curves, (b) Plots of log (sweep rate) versus log (peak current) and
2. (c) Capacitive contribution of HESDs after prelithiation at various sweep rates.
3. (e) Schematic diagram of energy storage mechanisms of HESDs after
4. prelithiation. Schematic representation of the microstructure of (d) batter-type
5. mLVP/C MSs electrode and (f) mFe3C@GO NSs pseudocapacitive electrode.

7

1. diffusion-controlled and the surface-controlled process (Fig. 4b). The higher
2. capacity contribution (approximately 53.4%) (Fig. 4c) of HESDs after
3. prelithiation at a high scanning rate of 5 mV s−1 can be attributed to the
4. pseudocapacitive behavior of mFe3C@GO NSs. Hence, the charge storage
5. mechanism of mFe3C@GO NSs supercapacitor is predominantly the
6. surface-controlled process. This is done by adsorbing and electrostatic
7. accumulating charges in hierarchical mesoporous conductive network of GO
8. nanosheet, resulting in higher energy density without the sacrifice of power
9. density of HESDs after prelithiation. During the charging/discharging process,
10. Li ions extracted/inserted from/into batter-type mLVP/C MSs electrode and
11. inserted/extracted into/from the mFe3C@GO NSs pseudocapacitive electrode
12. by the mechanisms of adsorption and electrostatic accumulation (Fig. 4e). The
13. LVP NPs promote the fast Li+ solid-state transportation effectively (Fig. 4d) and
14. achieve a high diffusion rate and energy density of batter-type mLVP/C MSs
15. electrode, which may be related to the well contacts of the interconnected
16. mesoporous NPs and the electrolyte. The flexible GO shell maintains the
17. structural integrity and elastic buffer, resulting in high power density, excellent
18. rate capability and cycle performance (Fig. 4f). In addition, the active
19. biomass-derived carbon layer network possesses good electronic conductivity.
20. Therefore, selecting and optimizing the active material and electrode
21. architecture benefit to acquire ultrahigh energy and power densities of HESDs
22. after prelithiation, which has great potential for significantly improving fast and
23. efficient energy storage in the future. The insights gained from studying button
24. cell-type electrochemical cells contribute to advancements in energy density,
25. efficiency, safety, and longevity, which are crucial for powering electric
26. vehicles with heavy motors. Improving the performance of these smaller cells
27. can lead to advancements in larger battery technologies, making them more
28. reliable, cost-effective, and suitable for high-demand applications like electric
29. vehicles.
30. Consequently, we explored the methods to fabricate biomass-derived
31. electrode materials and its utilization in energy storage devices. The regulation
32. of experimental conditions (such as raw material dosage, carbonization
33. temperature) has enabled development of high performance electrode materials
34. from biomass energy source. This holds tremendous potential for harvesting
35. green electrode materials with high performance, in conjunction with
36. reutilization process and cost inexpensive. However, despite these unique
37. structural characteristics and high electrochemical performance of
38. biomass-derived electrode materials, significant questions and challenges
39. remain. The chemical composition, impurities and structure of biomass
40. feedstock are affected by the natural changes, consequently resulting in
41. inconstant internal structure. Assume that these factors associate with
42. performance, further explorations associated with technologies and limitations
43. are needed for large-scale applications in energy storage devices.

## 4. Conclusions

1. In summary, multifunctional mesoporous core-shell mFe3C@GO NSs was
2. prepared by hydrothermal synthesis and high-temperature calcination with
3. high-quality lignins as the organic ligands of the intermediate precursor and the
4. carbon source. During the carbonization process, the lignins were successfully
5. graphitized, and the synthesis mechanism of mFe3C@GO NSs was simulated
6. and proposed. The mFe3C@GO NSs homogeneously dispersed in GO
7. conductive network and maintained the structural integrity of the electrode
8. during the electrochemical process, resulting in high reversible specific capacity,
9. excellent rate capability and cycling stability. This elaborate work encourages
10. the investigation of biomass waste conversion and utilization and the extensible
11. exploration of multifunctional materials for rechargeable batteries.

## Declaration of competing interest

1. The authors declare no conflict of interest.

## Acknowledgements

1. This work is supported by the National Natural Science Foundation of China
2. (No. 61368007), the Natural Science Foundation of Shandong Province (Grant
3. No. ZR2019MEM053), and the Project (D20015).

## Declaration of generative AI and AI-assisted technologies

1. The use of generative artificial intelligence (AI) or AI-assisted technologies in
2. this article is not permitted in academic writing process.

## CRediT authorship contribution statement

1. Xinli Yi designed and proceed the experiments, performed the analysis, drafted the
2. manuscript and designed the figures. Wen He and Wangwang Xu contributed to the
3. design and implementation of the research, to the analysis of the results and to the
4. reviewing & editing of the manuscript. Xudong Zhang was involved in planing and
5. supervised the work. Kwan San Hui aided in interpreting the results and contributed
6. to the final version of the manuscript. All authors discussed the results and contributed
7. to the final manuscript.

## References

1. 1. Deng J, Bae C, Denlinger A, Miller T. Electric vehicles batteries: requirements and

9 challenges. Joule 2020; 4: 509-515. <https://doi.org/10.1016/j.joule.2020.01.013>

1. 2. Kumar H, Sharm R, Yadav A, Kumar R. Recent advancement made in the field of
2. reduced graphene oxide-based nanocomposites used in the energy storage devices: A

12 review. J Energy Storage 2021; 33: 102032. <https://doi.org/10.1016/j.est.2020.102032>

1. 3. He W, Li C, Zhao B, Zhang X, Hui K S, Zhu J. Metal Ti quantum chain-inlaid 2D
2. NaSn2(PO4)3/H-doped hard carbon hybrid electrodes with ultrahigh energy storage

15 density. Chem Eng J 2021; 403: 126311. https://doi.org/10.1016/j.cej.2020.126311

1. 4. Su F, Qin J, Das P, Zhou F, Wu ZS. A high-performance rocking-chair lithium-ion
2. battery-supercapacitor hybrid device boosted by doubly matched capacity and kinetics
3. of the faradaic electrodes. Energy Environ Sci 2021; 14: 2269-2277.

19 <https://doi.org/10.1039/D1EE00317H>

1. 5. Tie D, Huang S, Wang J, Ma J, Zhang J, Zhao Y. Hybrid energy storage devices:
2. advanced electrode materials and matching principles. Energy Stor Mater 2019; 21:

22 22-40. <https://doi.org/10.1016/j.ensm.2018.12.018>

1. 6. Sharma R, Kumar H, Kumar G, Sharma S, Aneja R, Sharma AK, Kumar R, Kumar
2. P. Progress and challenges in electrochemical energy storage devices: fabrication,
3. electrode material, and economic aspects. Chem Eng J 2023; 468: 143706.

26 <https://doi.org/10.1016/j.cej.2023.143706>

1. 7. Jin C, Nai J, Sheng O, Yuan H, Zhang W, Tao X, Lou X. Biomass-based materials
2. for green lithium secondary batteries. Energy Environ Sci 2021; 14: 1326.

3 https://doi.org/10.1039/d0ee02848g

1. 8. Baskar A V., Singh G, Ruban A M., Davidraj J M., Bahadur R, Sooriyakumar P,
2. Kumar P, Karakoti A, Yi J, Vinu A. Recent progress in synthesis and application of
3. biomass-based hybrid electrodes for rechargeable batteries. Adv Funct Mater 2023; 33:

7 2208349. <https://doi.org/10.1002/adfm.202208349>

1. 9. Liang J, Liu X, Zhang T, Yu K, Liang C. Hemp straw carbon and Ni/NiO
2. embedded structure composites as anode materials for lithium ion batteries. J Alloys

10 Compd 2021; 889: 161776. <https://doi.org/10.1016/j.jallcom.2021.161776>

1. 10. Park S, Song J, Lee W C, Jang S, Lee J, Kim J, Kim H-K, Min K. Advances in
2. biomass-derived electrode materials for energy storage and circular carbon economy.

13 Chem Eng J 2023; 470: 144234. <https://doi.org/10.1016/j.cej.2023.144234>

1. 11. Wei H, Huang W, Luo K, Huang Y, Zhong S, Yan D. PVP-assisted synthesis of
2. hollow Ni0.75Zn0.25Fe2O4 nanospheres for lithium-ion batteries. Int J Hydrog Energy

16 2023; 48: 20208-20215. <https://doi.org/10.1016/j.ijhydene.2023.01.303>

1. 12. Qin G, Jia Z, Li A, Sun S, Liu Z, Zhuang CL, Chen J. Nitrogen-rich carbon/SiO2
2. nanotubes composites prepared by self-assembly as high-performance anode
3. lithium-ion battery. Int J Hydrog Energy 2023; 48: 20208-20215.

20 [https://doi.org/10.1016/j.ijhydene.2023.09.20](https://doi.org/10.1016/j.ijhydene.2023.09.201)1

1. 13. Yadav A, Kumar H, Sharm R, Kumari R, Singh D, Hamed O A.. Metal oxide
2. decorated polyaniline based multifunctional nanocomposites: An experimental and
3. theoretical approach. Results in Engineering 2023; 18: 101161.

24 <https://doi.org/10.1016/j.rineng.2023.101161>

1. 14. Zhang S, Wang K, Chen H, Liu H, Yang L, Chen Y, Li H. ZIF-67 derived in-situ
2. grown NeCo3S4-GN/CNT interlinked conductive networks for high-performance
3. especially cycling stable supercapacitors. Carbon 2022; 194: 10-22.

28 <https://doi.org/10.1016/j.carbon.2022.03.054>

1 15. Huang X, Qi X, Boey F, Zhang H. Graphene-based composites. Chem Soc Rev

2 2012; 41: 666–686. <https://doi.org/10.1039/C1CS15078B>

1. 16. Solís-Fernández P, Bissett M, Ago H, Synthesis, structure and applications of
2. graphene-based 2D heterostructures. Chem Soc Rev 2017; 46: 4572–4613.

5 <https://doi.org/10.1039/C7CS00160F>

1. 17. Kumar H, Luthra M, Punia M, Singh D. Ag2O@PANI nanocomposites for
2. advanced functional applications: A sustainable experimental and theoretical approach.
3. Colloids Surf A Physicochem Eng Asp 2022; 640: 128464.

9 [https://doi.org/10.1016/j.colsurfa.2022.12846](https://doi.org/10.1016/j.colsurfa.2022.128464)4

1. 18. Kumari R, Kumar H, Sharma R, Yadav A, Kumar G, Tundwal A, Dhayal A,
2. Sharma A. Highly sensitive amperometric food sensor for Sudan-I dye using
3. nanocomposites modified working electrode. Microchem J 2023; 193: 109078.

13 [https://doi.org/10.1016/j.microc.2023.10907](https://doi.org/10.1016/j.microc.2023.109078)8

1. 19. Yadav A, Kumar H, Sharma R, Kumari R, Kumar G, Tundwal A, Dhayal A, Yadav
2. A, Singh D. Mixed metal oxide decorated polypyrrole nanocomposites for
3. multifunctional applications. Inorg. Chem Commun 2023; 158: 111701.

17 <https://doi.org/10.1016/j.inoche.2023.111701>

1. 20. Shi J, Wang Y, Du W, Hou Z. Synthesis of graphene encapsulated Fe3C in carbon
2. nanotubes from biomass and its catalysis application. Carbon 2016; 99: 330–337.

20 <https://doi.org/10.1016/j.carbon.2015.12.049>

1. 21. Fan X, Peng Z, Ye R, Zhou H, Guo X. M3C (M: Fe, Co, Ni) nanocrystals encased
2. in graphene nanoribbons: an active and stable bifunctional electrocatalyst for oxygen
3. reduction and hydrogen evolution reactions. ACS Nano 2015; 9: 7407–7418.

24 <https://doi.org/10.1021/acsnano.5b02420>

1. 22. Zhang J, Wang K, Xu Q, Zhou Y, Cheng F, Guo S. Beyond yolk-shell
2. nanoparticles: Fe3O4@Fe3C core@shell nanoparticles as yolks and carbon
3. nanospindles as shells for efficient lithium ion storage. ACS Nano 2015; 9: 3369–

28 3376. <https://doi.org/10.1021/acsnano.5b00760>

1. 23. Tan Y, Zhu K, Li D, Bai F, Wei Y, Zhang P. N-doped graphene/Fe–Fe3C
2. nano-composite synthesized by a Fe-based metal organic framework and its anode
3. performance in lithium ion batteries. Chem Eng J 2014; 258: 93–100.

4 <https://doi.org/10.1016/j.cej.2014.07.066>

1. 24. [Zheng](https://pubmed.ncbi.nlm.nih.gov/?term=Zheng%2BJ&cauthor_id=34382971) J, [Kong](https://pubmed.ncbi.nlm.nih.gov/?term=Kong%2BF&cauthor_id=34382971) F, [Tao](https://pubmed.ncbi.nlm.nih.gov/?term=Tao%2BS&cauthor_id=34382971) S, [Qian](https://pubmed.ncbi.nlm.nih.gov/?term=Qian%2BB&cauthor_id=34382971) B. A Fe2O3-Fe3C heterostructure encapsulated into a
2. carbon matrix for the anode of lithium-ion batteries. Chem Commun 2021; 57:

7 8818-8821. <https://doi.org/10.1039/D1CC03945H>

1. 25. Chen R, Zhou Y, Li X. Cotton-derived Fe/Fe3C-encapsulated carbon nanotubes for
2. high-performance lithium-sulfur batteries. Nano Lett 2022; 22: 1217–1224.
3. <https://doi.org/10.1021/acs.nanolett.1c04380>
4. 26. Shen W, Kou W, Liu Y, Dai Y, Zheng W, He G, Wang S, Zhang Y, Wu X, Fan S,
5. Li X. Fe3C-doped asymmetric porous carbon membrane binder-free integrated
6. materials as high performance anodes of lithium-ion batteries. Chem Eng J 2019; 368:

14 310–320. <https://doi.org/10.1016/j.cej.2019.02.199>

1. 27. Schlee P, Hosseinaei O, O' Keefe CA, Mostazo-Lopez MJ, Cazorla-Amoros D,
2. Herou S, Tomani P, Grey CP, Titirici MM. Hardwood versus softwood Kraft
3. lignin-precursor-product relationships in the manufacture of porous carbon nanofibers
4. for supercapacitors. J Mater Chem A 2020; 8: 23543.

19 <https://doi.org/10.1039/D0TA09093J>

1. 28. Schutyser W, Renders T, Bosch SV, Koelewijn SF, Beckham GT, Sels BF.
2. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation,
3. and upgrading. Chem Soc Rev 2018; 47: 852–908.

23 <https://doi.org/10.1039/C7CS00566K>

1. 29. Xu YH, Zhou Q, Li MF, Bian J, Peng F. Tetrahydro-2-furanmethanol pretreatment
2. of eucalyptus to enhance cellulose enzymatic hydrolysis and to produce high-quality
3. lignin. Bioresour Technol 2019; 280: 489–492.

27 <https://doi.org/10.1016/j.biortech.2019.02.088>

28 30. Du X, He W, Zhang X, Yue Y, Liu H, Zhang X, Min D, Ge X, Du Y. Enhancing

1. the electrochemical performance of lithium ion batteries using mesoporous
2. Li3V2(PO4)3/C microspheres. J Mater Chem 2012; 22: 5960–5969.

3 <https://doi.org/10.1039/C1JM14758G>

1. 31. N Izaguirre, M Alberro, X Erdocia, J Labidi. Kraft and organosolv
2. lignin-activated carbon composites for supercapacitor electrode materials. J Energy

6 Storage 2024; 80: 110386. <https://doi.org/10.1016/j.est.2023.110386>

1. 32. M Zhu, H Liu, Q Cao, H Zheng, D Xu, H Guo, S Wang, Y Li, J Zhou. Electrospun
2. lignin-based carbon nanofibers as supercapacitor electrodes. ACS Sustainable Chem.

9 Eng. 2020, 8: 12831–12841. https://doi.org/10.1021/acssuschemeng.0c03062

1. 33. Y She, X Li, Y Zheng, D Chen, X Rui, X Lin, Y Qin. Natural Lignin: A
2. sustainable and cost-effective electrode material for high-temperature Na-ion battery.
3. Energy Environ Mater 2022, 0: e12538. <https://doi.org/10.1002/eem2.12538>
4. 34. Zhang C, Hu W, Jiang H, Chang JK, Zheng M, Wu QH, Dong Q. Electrochemical
5. performance of MIL-53(Fe)@RGO as an organic anode material for li-ion batteries.

15 Electrochim Acta 2017; 246: 528–535. <https://doi.org/10.1016/j.electacta.2017.06.059>

1. 35. Liang R, Shen L, Jing F, Qin N, Wu L. Preparation of MIL-53(Fe)-reduced
2. graphene oxide nanocomposites by a simple self-assembly strategy for increasing
3. interfacial contact: efficient visible-light photocatalysts. ACS Appl Mater Interfaces

19 2015; 7: 9507–9515. <http://dx.doi.org/10.1021/acsami.5b00682>

1. 36. Gong Y, Li D, Luo C, Fu Q, Pan C. Highly porous graphitic biomass carbon as
2. advanced electrode materials for supercapacitors. Green Chem 2017: 19: 4132.

22 <https://doi.org/10.1039/c7gc01681f>

1. 37. W Qu, X Han, J Liu, L Yin, C Liang, P Hu. Unlocking the graphitization potential
2. of lignin: insights into its transformation through hot pressing and carbonization.

25 Green Chem 2023, 25: 9873-9883. <https://doi.org/10.1039/D3GC03642A>

1. 38. Li H, Peng J, Wu Z, Liu X, Liu P, Chang B, Wang X. Constructing novel SiO*x*
2. hybridization materials by a double-layer interface engineering for high-performance
3. lithium-ion batteries. Chem Eng J 2023; 462: 142172.

1 <https://doi.org/10.1016/j.cej.2023.142172>

1. 39. Li W, Peng J, Li H, Wu Z, Chang B, Guo X, Chen G, Wang X. Architecture and
2. performance of Si/C microspheres assembled by nanoSi via electro-spray technology
3. as stability-enhanced anodes for lithiumion batteries. J Alloys Compd 2022; 903:

5 163940. <https://doi.org/10.1016/j.jallcom.2022.163940>

1. 40. Luo S, Peng L, Xie Y, Cao X, Wang X, Liu X, Chen T, Han Z, Fan P, Sun H, Shen
2. Y, Guo F, Xia Y, Li K, Ming X, Gao C. Flexible large‑ area graphene films of 50–600
3. nm thickness with high carrier mobility. Nano-Micro Lett 2023; 15: 61.

9 <https://doi.org/10.1007/s40820-023-01032-6>

1. 41. Peng L, Han Y, Wang M, Cao X, Gao J, Liu Y, Chen X, Wang B, Wang B, Zhu C,
2. Wang X, Cao K, Huang M, Cunning B V., Pang J, Xu W, Ying Y, Xu Z, Fang W, Lu Y,
3. Ruoff R S., Gao C. Multifunctional macroassembled graphene nanofilms with high

13 crystallinity. Adv Mater 2021; 33: 2104195. <https://doi.org/10.1002/adma.202104195>

1. 42. Zhang M, Guan K, Ji Y, Liu G, Jin W, Xu N. Controllable ion transport by
2. surface-charged graphene oxide membrane. Nat Commun 2019; 10: 1253.

16 <https://doi.org/10.1038/s41467-019-09286-8>

1. 43. Zhang H, Cheng J, Liu H, Li D, Zeng Z, Li Y, Ji F, Guo Y, Wei Y, Zhang S, Bai T,
2. Xu X, Peng R, Lu J, Ci L. Prelithiation: a critical strategy towards practical
3. application of high-energy-density batteries. Adv Energy Mater 2023; 13: 2300466.

20 <https://doi.org/10.1002/aenm.202300466>

1. 44. Wang F, Wang B, Li J, Wang B, Zhou Y, Wang D, Liu H, Dou S. Prelithiation: a
2. crucial strategy for boosting the practical application of next-generation lithium ion

23 battery, ACS Nano 2021; 15: 2197–2218. <https://doi.org/10.1021/acsnano.0c10664>

1. 45. Liu J, Wang J, Xu C, Jiang H, Li C, Zhang L, Lin J, Shen JL. Advanced energy
2. storage devices: basic principles, analytical methods, and rational materials design.

26 Adv Sci 2018; 5: 170032. <https://doi.org/10.1002/advs.201700322>

1. 46. Zhang L, Zhang X, Tian G, Zhang Q, Knapp M, Ehrenberg H, Chen G, Shen Z,
2. Yang G, Gu L, Du F. Lithium lanthanum titanate perovskite as an anode for lithium

1 ion batteries. Nat Commun 2020; 11: 3490.

2 <https://doi.org/10.1038/s41467-020-17233-1>