Porous carbon spheres and monoliths: morphology controlling, pore size tuning and their applications as Li-ion battery anode materials

Aled D. Roberts[a,b], Xu Li[b] and Haifei Zhang*[a]*

a) Department of Chemistry, University of Liverpool, Liverpool, UK, L69 7ZD. Email: zhanghf@liv.ac.uk.

b) Institute of Materials Research and Engineering, A*STAR, Singapore, 117602. Email: x-li@imre.a-star.edu.sg

Electronic Supplementary Information

General Reviews on Porous Carbons, Carbon Nanotubes, Graphenes, and the Relevant Carbon-based Materials:

(1) A. Stein, Z. Wang, M. A. Fierke, Functionalization of Porous Carbon Materials with Designed Pore Architecture, *Adv. Mater.* 2009, **21**, 265-293

This review covers the preparation of template porous carbons, but focused on pore surface functionalization and attachment of nanoparticles onto pore surface.

(2) D. R. Rolison, J. W. Long, J. C. Lytle, A. E. Fischer, C. P. Rhodes, T. M. McEvoy, M. E. Bourq, A. M. Lubers, Multifunctional 3D nanoarchitectures for energy storage and conversion, *Chem. Soc. Rev.* 2009, **38**, 226-252.

This review deals with the design and fabrication of 3D multifunctional architectures for energy storage and conversion, e.g., assembled nanoarchitectures, ultraporous nanoarchitectures. It is however not focused on porous carbon materials.

(3) S. L. Candelaria, Y.Shao, W. Zhou, X. Li, J. Xiao, J. Zhang, Y. Wang, J. Liu, J. Li, G. Cao, Nanostructured carbon for energy storage and conversion, *Nano Energy* 2012, **1**, 195-220.

This review describes the synthesis and applications of nanoporous carbon as electrodes for supercapacitors and electrodes in Li-ion batteries, gas storage, supports for fuel cells, Li-S batteries, Li-O batteries. The carbon nanostructures are mainly carbon nanotubes, graphene-based materials, and carbon-based nanocomposites.

(4) X. Cao, Z. Yin, H. Zhang, Three-Dimensional Graphene Materials: Preparation, Structures and Application in Supercapacitors, *Energy Environ. Sci.* 2014, DOI: 10.1039/C4EE00050A

This review presents the current progress of 3D graphene materials, based on their different structures, their preparation methods, properties and applications, and the applications of such materials in supercapacitors.

(5) J. Zhu, D. Yang, Z. Yin, Q. Yan, H. Zhang, Graphene and Graphene-Based Materials for Energy Storage Applications, *Small*, 2014, DOI: 10.1002/smll.201303202

This Review summarizes the recent progress in graphene and graphene-based materials for four energy storage systems, *i.e.*, lithium-ion batteries, supercapacitors, lithium-sulfur batteries, and lithium-air batteries.

(6) G. Lu, H. Li, C. Liusman, Z. Yin, S. Wu, H. Zhang, Surface enhanced Raman scattering of Ag or Au nanoparticle-decorated reduced graphene oxide for detection of aromatic molecules, *Chem. Sci.* 2011, **2**, 1817-1821.

This paper describes a method for fabrication of an efficient surface enhanced Raman scattering (SERS) substrate by combination of metallic nanostructures and graphene, which shows dramatic Raman enhancement and efficient adsorption of aromatic molecules.

(7) J. Liu, Z. Lin, T. Liu, Z. Yin, X. Zhou, S. Chen, L. Xie, F. Boey, H. Zhang, W. Huang, Multilayer Stacked Low-Temperature-Reduced Graphene Oxide Films: Preparation, Characterization, and Application in Polymer Memory Devices, *Small* 2010, **6**, 1536-1542.

(8) X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, H. Zhang, Graphene-Based Materials: Synthesis, Characterization, Properties, and Applications, *Small* 2011, **7**, 1876-1902.

In this review, after a general introduction to graphene and its derivatives, the synthesis, characterization, properties, and applications of graphene-based materials are discussed.

(9) X. Zhou, F. Boey, H. Zhang, Controlled growth of single-walled carbon nanotubes on patterned substrates, *Chem. Soc. Rev.* 2011, **40**, 5221-5231.

This tutorial review describes the commonly used lithographic techniques to pattern catalysts used for controlled growth of single-walled carbon nanotubes (SWCNTs), specifically confined to the horizontal direction. Advantages and disadvantages of each method will be briefly discussed. Applications of the SWCNT arrays grown from the catalyst patterns will also be introduced.

(10) X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, Graphene-based electrodes, *Adv. Mater.* 2012, **24**, 5979-6004.

In this review, after a short introduction to the properties and synthetic methods of graphene and its derivatives, the importance of graphene-based electrodes, their fabrication techniques, and application areas are discussed.

(11) X. Huang, X. Qi, F. Boey, H. Zhang, Graphene-based composites, *Chem. Soc. Rev.* 2012, **41**, 666-686.

This review presents and discusses the current development of graphene-based composites. The review focuses on the description of various methods to synthesize graphene-based composites, especially those with functional polymers and inorganic nanostructures. Particular emphasis is placed on strategies for the optimization of composite properties. Lastly, the advantages of graphene-based composites in applications such as the Li-ion batteries, supercapacitors, fuel cells, photovoltaic devices, photocatalysis, as well as Raman enhancement are described.

(12) H. Jiang, P. S. Lee and C. Li, 3D carbon based nanostructures for advanced supercapacitors, *Energy Environ. Sci.*, 2013, **6**, 41-53.

The carbon nanostructures comprise of CNTs-based networks, graphene-based architectures, hierarchical porous carbon-based nanostructures and other even more complex carbon-based 3D configurations. Their advantages and disadvantages for supercapacitors are compared and summarized.

(13) A. Vu, Y. Qian, A. Stein, Porous Electrode Materials for Lithium-Ion Batteries – How to Prepare Them and What Makes Them Special, *Adv. Energy. Mater*. 2012, **2**, 1056-1085.

This review highlights methods of synthesizing porous electrode materials by templating and template-free methods and discusses how the structural features of porous electrodes influence their electrochemical properties.

Some review papers about emulsion-templating:

(1) H. Zhang and A.I. Cooper, Synthesis and applications of emulsion-templated porous materials*Soft Matter*, 2005, **1**, 107-113. Review paper.

(2) M. S. Silverstein, PolyHIPEs: Recent advances in emulsion-templated porous polymers, *Prog. Polym. Sci.* 2014, **39**, 199-234. Review paper.

Some review papers and research papers about ice templating.

(1) H. Zhang and A. I. Aligned porous structures by directional freezing. *Adv. Mater.* 2007,19, 1529-1533. Research news paper.

(2) M. C. Gutierrez, L. Ferrer and F. del Monte , Ice-templated materials : sophisticated structures exhibiting enhanced functionalities obtained after unidirectional freezing and ice-segregation-induced self-assembly, *Chem. Mater.* 2008, **20**, 634–648. Review paper.

(3) S. Deville, Ice-tempating, freeze casting: Beyond materials processing, *J. Mater. Res.,* 2013, **28**, 2202-2219. Review paper.

(4) M. Barrow, A. Eltmimi, A. Ahmed, P. Myers, H. Zhang, Frozen polymerization for aligned porous structures with enhanced mechanical stability, conductivity, and as stationary phase for HPLC, *J. Mater. Chem.* 2012, **22**, 11615-11620. Research paper.

Some review papers and research papers about hydrothermal carbonization.

(1) B. Hu, K. Wang, L. Wu, S.H. Yu, M. Antonietti, M. M. Titirici, Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass, *Adv. Mater.* 2010, **22**, 813-828. Review paper.

(2) S. Kang, X. Li, J. Fan, J. Chang, Hydrothermal conversion of lignin: A review, *Renewable and Sustainable Energy Reviews*, 2013, **27**, 546-558.

(3) E. Uner, S. Brutti, S. Panero, B. Scrosati, Nanoporous carbons from hydrothermally treated biomass as anode materials for lithium ion batteries, *Micropor. Mesopor. Mater.* 2013, **172**, 25-33. Research paper

(4) S. A. Wohlgemuth, F. Vilela, M. M. Titirici and M. Antonietti, A one-pot hydrothermal synthesis of tunable dual heteroatom-doped carbon microspheres, *Green Chem.* 2012, **14**, 741-749. Research paper.

Some reviews about metal-organic frameworks (MOFs)

(1) H. -C. Zhou, J. R. Long, and O. M. Yaghi, Introduction to Metal–Organic Frameworks, *Chem. Rev.*, 2012, **112**, 673-674.

General reviews about metal-organic frameworks. This issue of Chemical Reviews is a special issue about all aspects of metal organic frameworks.

(2) W. Chaikittisilp, K. Ariga and Y. Yamauchi, A new family of carbon materials: synthesis of MOF-derived nanoporous carbons and their promising applications, *J. Mater. Chem. A*, 2013, **1**, 14-19.

This is a highlight paper about the use of metal-organic frameworks as templates to prepare nanoporous carbons.

More examples showing the influence of morphology and incorporation of nanoparticles on materials properties and LIB anode performance:

(1) X. W. Lou, C.M. Li and L.A. Archer, Designed Synthesis of Coaxial SnO_2@carbon Hollow Nanospheres for Highly Reversible Lithium Storage, *Adv. Mater.*, 2009, **21**, 2536-2539.

(2) Z.C. Yang, M. Wang, A. M. Yong, S. Y. Wong, X.H. Zhang, H. Tan, A. Y. Chang, X. Li, and J. Wang, Intrinsically fluorescent carbon dots with tunable emission derived from hydrothermal treatment of glucose in the presence of monopotassium phosphate, *Chem. Commun.* 2011, **47**, 11615-11617.

By simple incorporation of precursor metal-salts or prepared colloidal nanoparticles into the glucose solution prior to carbonization, metal nanoparticles-encapsulated carbon spheres were produced. Such a process may be translated to other materials in order to fabricate various carbon-composite spheres with novel properties for various applications.

The synthesis of coaxial SnO_2@carbon hollow nanospheres by Lou *et al.* is another attempt to overcome the shortcomings associated with Li-alloy forming anode materials.[(1)] By employing SiO_2 as a hard template, carbon-coated hollow SnO_2 spheres, with diameters of about 250 nm, were prepared, displaying impressive LIB anode performance – a stable C_{rev} of about 500 mAh g^{-1} after 200 cycles at a moderate current density of 200 mA g^{-1}.

(3) A. F. Gross and A. P. Nowak, Hierarchical Carbon Foams with Independently Tunable Mesopore andMacropore Size Distributions, *Langmuir*, 2010, **26**, 11387-11383.

An example of using RF solution as carbon precursor to produce emulsion-templated carbon is given here: The RF solution was emulsified by blending with silicone oil and sodium dodecylbenzenesulfonate as surfactant. The O/W emulsion in a closed jar was aged for 72 h at 85 ^{o}C to form a bright orange foam monolith. After solvent exchange and drying in air, the foam was pyrolyzed at 1200 ^{o}C under flowing nitrogen. Pore volumes up to 5.26 cm^3 g^{-1} and electrical conductivities of 0.34 S cm^{-1} were obtained for the carbon material.

(4) A. J. Amali, J. K. Sun and Q. Xu, From assembled metal–organic framework nanoparticles to hierarchically porous carbon for electrochemical energy storage, *Chem. Commun.*, 2014, **50**, 1519-1522.

Simple carbonization of assembled ZIF-8 nanoparticles in Ar yielded a hierarchically porous carbon framework with micro-, meso-, and macro-pores.

(5) X. Cao, Y. Shi, W. Shi, X. Rui, Q. Yan, J. Kong and H. Zhang, Preparation of MoS_2 -Coated Three-Dimensional Graphene Networks for High-Performance Anode Material in Lithium-Ion Batteries, *Small*, 2013, **9**, 3433-3438.

MoS_2 has a similar structure to graphite. Its layered structure and the weak van der Waals interaction between the layers enable easy intercalation of Li^+ ions without a significant increase in volume (theoretical capacity ~ 670 mAh g^{-1}). However, their cyclic stability and rate performance are quite poor. As an anode material for LIBs, the MoS_2-coated 3D graphene network composite exhibited reversible capacities of 877 and 665 mAh g^{-1} during 50 cycles of charging-discharging process at current densities of 100 and 500 mA g^{-1}, respectively. At a much higher current density of 4 A g^{-1}, a 10^{th}-cycle capacity of 466 mAh g^{-1} was observed.

(6) N. D. Petkovich, S. G. Rudisill, B. E. Wilson, A. Mukherjee and A. Stein, Control of TiO_2 Grain Size and Positioning in Three-Dimensionally Ordered Macroporous TiO_2/C Composite Anodes for Lithium Ion Batteries, *Inorg. Chem.* 2014, **53**, 1100-1112.

Apart from improving performance, the incorporation of nanoparticles may also improve safety, which is a very important aspect but is not covered in this review. In this paper, TiO_2 offers a safety advantages compared to graphite anodes due to its higher potential for lithium intercalation. TiO_2 grain size and position in 3D ordered macroporous TiO_2/carbon composites have been investigated as anodes for Li-ion battery. The materials delivered a stable capacity (> 170 mAh g^{-1} at the rate of C/2) over 100 cycles.