RSC Advances

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Graphic Abstract

Interface Chemistry Engineering in Electrode Systems for Electrochemical Energy Storage

Lei Yu, Zhongyu Qian, Nannan Shi, Qi Liu, Jun Wang and Xiaoyan Jing
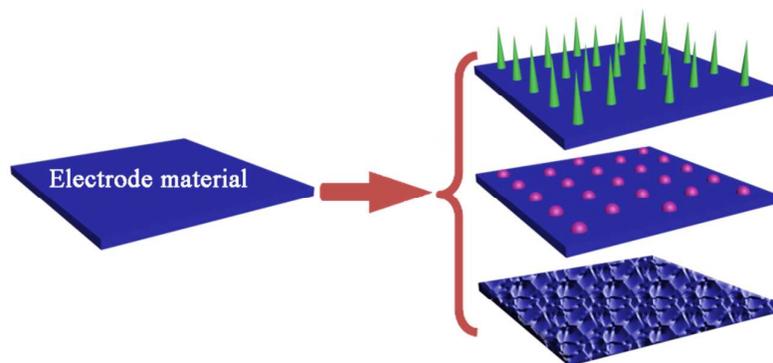
In this review, we introduce two powerful strategies for well-controlled interface (step-by-step nano-architectures grown on substrates and nanoscale building blocks with spatial precision). Interface chemistry engineering in electrode systems for electrochemical energy storage needs to integrate individual materials components to interface design and optimization. Step-by-step growing provides robust contact between working materials and substrates. Nanoscale building blocks as solution-processable precursors are potentially low cost alternative and promising for the bulk production. Flexible step-by-step assembly by combining interfacial self-assembly with nanoscale building blocks may be a powerful way for interface chemistry of electrochemical energy storage.

ARTICLE TYPE

Interface Chemistry Engineering in Electrode Systems for Electrochemical Energy Storage

Lei Yu,[a] Zhongyu Qian,[a] Nannan Shi,[a] Qi Liu,*[a] Jun Wang*[a,b] and Xiaoyan Jing[a]

Although high power electrochemical capacitors and high energy batteries have some differences in the charge storage mechanism, high-efficiency energy storage requires an excellent interface between the electronic-transporting phase (electrode) and the ionic-transporting phase (electrolyte). Considerable amounts of attentions have been paid to interface and entire electrode system to solve all kinds of
10 technological challenges for the development. We introduce two powerful strategies for well-controlled interface (step-by-step nano-architectures grown on substrates and nanoscale building blocks with spatial precision). Then, some recent advances are focused on the interface design of current collectors and highlight the interfacial bonding between electrochemically active materials and conductive substrates. Interface chemistry engineering in electrode systems for electrochemical energy storage needs to integrate
15 individual materials components to interface design and optimization. Step-by-step growing provides robust contact between working materials and substrates. Nanoscale building blocks as solution-processable precursors are potentially low cost alternative and promising for the bulk production. Flexible step-by-step assembly by combining interfacial self-assembly with nanoscale building blocks may be a powerful way for interface chemistry of electrochemical energy storage.

20 1. Introduction

Electrochemical power sources, as a secure and sustainable energy supply, have been intensively investigated in technological development and standard of living.[1] High power electrochemical capacitors (ECs) and high energy lithium ion
25 batteries (LIBs) are at the forefront of these, to meet the higher requirements of future systems.[2] Although they have some difference in the charge storage mechanism (ECs store charges at surface or in a thin layer of active materials in reversible processes, while, LIBs store charges by the intercalation of Li^+
30 ions from the surface to the bulk of active materials),[3] developing new materials and advancing architecture designs of the electrochemical interfaces assign equally importance to them for future energy storage systems.[4,5]

The high-efficiency energy storage requires an excellent
35 interface between the electronic-transporting phase (electrode) and the ionic-transporting phase (electrolyte).[6] Nanostructured materials with a shortened ion diffusion pathway benefit high energy devices, high power performance relies on enhanced electron transport related with electronic conductivity and
40 mobility.[4] The hybrid or composite materials integrate several types of functional materials and make them synergistically enhance the properties of each component. 3D-architecture design of materials shortens the transport lengths for ions and increases the contact area between the electrode and the
45 electrolyte[5]. Heterostructured nanoarchitectures have achieved notable success in scrupulous design of smart hybridization and controllable microstructure for electrochemical energy storage.

Lei Yu received his BSc degree in the College of Material Science and Chemical Engineering, Harbin Engineering University in 2012. His research interests focus on the design and synthesis of nanomaterials, as well as their applications for energy conversion and storage devices.

Jun Wang received his PhD from the College of Material Science and Chemical Engineering, Harbin Engineering University under the supervision of Prof. Milin Zhang. He was appointed as a full professor at the College of Material Science and Chemical Engineering in 2007. His research interests include synthesis of new nanostructured materials and nanocomposites, and their application in energy storage and environment areas, such as supercapacitors, corrosion prevention, and adsorption of U (VI) ion.

ARTICLE TYPE

Superior to traditional core/shell nanostructure or 3D-architecture design, interface chemistry engineering leads to long cycle life, low cost, and a relatively larger energy density. In addition, hybrid interface can modification of each other with
[5] reinforcements and fewer inherent limitations.[7-9] A range of nanoscale building blocks, such as electric double-layer capacitive (EDLC) graphene or carbon nanotube materials (high-power but relatively low-energy, reasonably high conductivity and relatively high surface-area),[10-12] moderate electrochemical
[10] conducting polymers,[13-15] and pseudocapacitive transition-metal-based oxides or hydroxides (TMOs) or battery materials (high-energy, volume change during electrochemical process and poor electric conductivity),[16-18] have gained prominence with high specific surface area and small dimensions. Besides, interface
[15] between current collectors and active materials has also attracted increasing interests.[19,20]

Most traditional research focused on active materials and synthesis, as it has been widely accepted that interface of electrode materials plays a key role during electrochemical
[20] process, considerable amounts of attentions have been paid on interface and entire electrode system to solve all kinds of technological challenges for the development.[21] Practical applications require balance between capacity and specific capacity. Electrodes should have a large mass loading towards
[25] green grid,[22-24] and interface should be designed with an optimal physical space.[7] Nanocomposites could be achieved with well-controlled interface by two powerful strategies: step-by-step nano-architectures grown on substrates[3,25,26](desirable to integrate these hybrid nanocomposites and substrates with robust interface,
[30] but is not sufficient in nanoscale spatial precision with limited synthetic methods) and nanoscale building blocks with spatial precision[27-29](the fabrication is more flexible, but often lacks suitable interfacial bonding with the substrates by using slurry-pasting). We first review the two promoting ways of fabricating
[35] hybrid electrode materials. After that, some recent advances are focused on interface design of current collectors. Next, we highlight the interfacial bonding between electrochemically active materials and conductive substrates. The concluding section is focused on several promising research trends in the
[40] electrode architecture design with an outlook.

2. Step-by-step nano-architectures grown on substrates

Step-by-step growing avoids additives and provides robust contact between working materials and substrates, the interval
[45] space formed between neighboring makes easy diffusion of ionic-transporting region.[26] Some efforts have also been directed at the search from metal oxide materials-conductive matrix to hybrid mixed metal oxides,[3,25,26] primary structure grown on substrates should be electrochemically stable and good electrical
[50] conductivity, compared with the subsequent structure. Hybrid mixed metal oxides exhibit better in high energy for fast ion transport, but worse electronic-transporting than carbon-based structures.[27-39] Step-by-step growing is concordant with interface design of current collectors, poor electronic-transporting phase
[55] may rely on the interface of current collectors more,[27-39] interface design of current collectors will be discussed later.
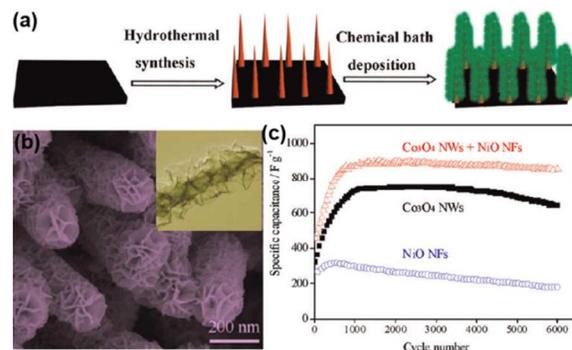

Fig. 1 (a) Schematic illustration of the two-step synthesis of metal oxide core/shell nanowire arrays directly on various substrates. (b) Scanning
[60] electron micrograph and transmission electron micrograph (inset) of metal oxide core/shell nanowire arrays. (c) Cycling performances of Co_3O_4/NiO nanowire arrays. (Reproduced from *Acs Nano*, 2012, **6**, 5531-5538. Copyright 2012, American Chemical Society.[31])

Heterostructured core/shell nanowire arrays may be one of the
[65] most scientific and technological interests. Fabrication of core nanowire arrays with well-defined morphologies is critical, which is often achieved by electrodeposition,[32-34] vapor deposition[35-37] and hydrothermal synthesis.[38,39] Currently, tremendous efforts have been devoted to developing cost-effective and simple
[70] methods. For example, Xia et al. presented a simple two-step solution-based method to synthesize transition metal oxide core/shell nanoarrays by combining hydrothermal synthesis and chemical bath deposition, core nanowires could act as backbones to guide the shell materials preferentially deposited, and the
[75] core/shell nanoarrays lead to enhanced electrochemical properties (452 F/g and 1.35 F/cm^2 at 2 A/g).[31] (Fig. 1)
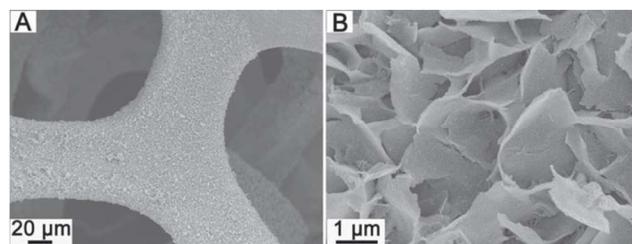

Fig. 2 Scanning electron micrographs of the $NiCo_2O_4$ nanosheets on Ni
[80] foam after cycling for 3000 cycles with a current density of 25 mA cm^{-2}. (Reproduced from *Adv. Mater.*, 2013, **25**, 976-979. Copyright 2013, Wiley-VCH.[53])

Hydrothermal approaches may be facile for one-dimensional (1D) nanoarrays directly on various substrates and be spoke self-
[85] assembled structures.[40-43] As another point of view, it is a kind of technique for tailoring the interface of the matrix. Nanowire arrays are designed to guarantee a fast ion and electron transfer, so there still exists some nano-architectures may be promising for electrochemical energy storage, such as nanoflake arrays and
[90] networked nanocoatings.[44-47] More high-effective interfaces should be explored with three-dimensional porous structures and robust interface from self-assembled nanomaterials.[48-52] Nanoflake arrays seem to exhibit poor microstructures compared with nanowire arrays, but the fabrication is flexible and easy to
[95] scale up. Zhang et al. presented a simple template-free solution-based method combined with a post annealing treatment, it is successfully developed to grow interconnected mesoporous

$NiCo_2O_4$ nanosheets on various conductive substrates, the integrated electrodes exhibit an ultrahigh specific capacitance (1743.4 F/g and 2.09 F/cm^2 at 8.5 mA/cm^2) and excellent cycling stability at a high charge /discharge current density (17.1% loss,
5 3000 cycles,at 25 mA/cm^2).[53] (Fig. 2) $NiCo_2O_4$ has better electrical conductivity and higher electrochemically activity compared with NiO and Co_3O_4, it could be good backbones to guide the shell materials grown.
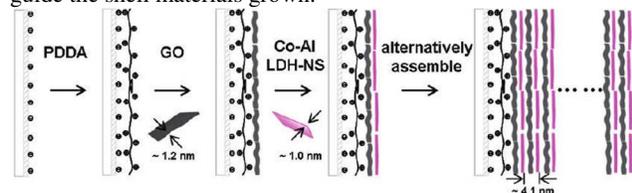

10 Fig. 3 Schematic of layer-by-layer assembly process for multilayer films of positively charged Co-Al LDH nanosheets and negatively charged graphene oxide nanosheets. (Reproduced from *Langmuir*, 2012, **28**, 293-298. Copyright 2012, American Chemical Society.[55])

Step-by-step growing promotes a binder- and conductive
15 agent-free robust adhesion. However, these electrodes often have a small mass loading compared with slurry-pasting,[42,43,53] the technique needs to be considered with interface design of current collectors to integrate the interface of electrodes system. Whether growing or not is not the foremost, robust adhesion with
20 substrates should be considered first. It can be achieved by electrostatic sequential adsorption, such as layer-by-layer (LBL) assembly, Langmuir-Blodgett and electrophoretic deposition.[54] Dong et al. reported the fabrication of flexible films of Co-Al layered double hydroxide (LDH) nanosheets/graphene oxide via
25 LBL assembly process (1204 F/g and 90 F/cm^2 at 5 mV/s, 40 bilayers; over 99% after 2000 cycles, at 20 A/g).[55] LBL assembly is a powerful tool to build well organized layered films with finely controlled film thickness and uniformity, but it may be difficult for a large mass loading. However, it is desirable for
30 step-by-step to grow developing towards more flexible step-by-step assembly. It can be inferred from the related discussion that the first step is difficult and limited, but the second step is various and flexible.

3. Nanoscale building blocks with spatial precision

35 ### 3.1 Planar or graphene-based nanostructures

Flexible solution-based methods have scrupulous design of nanoarchitectures and smart hybridization. Graphene oxide (GO), as a promising solution-processable precursor for the bulk production of reduced graphene oxide (rGO) and potentially low
40 cost alternative, is derivative by functional groups for growth of inorganic nanoparticles to afford strongly coupled hybrids.[56-58] High energy active materials, such as TMOs, exhibit electrochemically active with electrolyte, but poor electronic-transporting. During an electrochemical process, phase change is
45 estimated from surface to bulk entirely towards high energy. For better electronic-transporting, electrochemically stable phase is needed. Strongly coupled TMOs-graphene hybrid materials achieve these with graphene acted as stable electric conductive phase and TMOs acted as active materials for high energy. The
50 self-assembly of nanoparticles anchored on GO nanosheets could be directed with surfactants-assisted,[59-61] (Fig. 4) solvent-assisted

dispersion of graphene-based material or hydrothermal,[62-64] which opens a promising avenue for replacing the framework carbon atoms of graphene.[65] Wang et al. coerced multiple phases of SnO_2
55 and graphene into deterministic nanostructured materials by self-assembly (760 mAh/g, at 80 mA/g).[59]
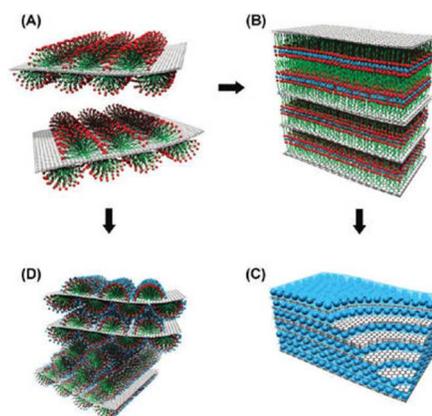

Fig. 4 Schematic illustrations of the ternary self-assembly approach to
60 ordered metal oxide/graphene nanocomposites. (A) Adsorption of surfactant hemimicelles on the surfaces of the graphene causes its dispersion in surfactant micelles in an aqueous solution. (B) The self-assembly of anionic sulfonate surfactant on the graphene surface with oppositely charged metal cation species and the transition into the lamella
65 mesophase nanocomposites. (C) Metal oxide/graphene layered nanocomposites composed of alternating layers of metal oxide nanocrystals and graphene stacks after crystallization of metal oxide and removal of the surfactant. (D) Self-assembled hexagonal nanostructure of metal oxide precursor with nonionic surfactants on graphene stacks.
70 (Reproduced from *Acs Nano*, 2010, **4**, 1587-1595. Copyright 2010, American Chemical Society.[59])

Stable, single and few-atom-thick two-dimensional (2D) nanomaterials beyond graphene have been one of the most extensively studied to exhibit fascinating and technologically
75 useful properties, such as charge transport confined to a plane and high electron mobility.[66] Liquid exfoliation of layered compounds are now considered to be excellent candidates for future electronic applications.[67,68] For example, positively charged layered double hydroxide nanosheets and some negatively
80 charged oxide nanosheets could be obtained by using formamide and quaternary amine ion, respectively.[69-72] Time-consuming and possible surface residues of foreign ions are quite unfavorable, Feng et al. took advantage of an intermediate intercalated compound precursor of $VS_2 \cdot NH_3$ (4.76 F/cm^2 and 317 F/cm^3 at
85 0.2 A/m^2, area: 11.52 cm^2, thickness: 150 nm).[73] Besides, "Bottom Up" strategies process a efficient route for liquid exfoliation.[74-76] Flocculation occurs when electrolytes (counterions) added to colloidal nanosheets.[67] Directed assembly of positively and negatively charged nanosheets can be achieved
90 to construct sandwich lamellar systems, it is possible to tailor superlattice-like assemblies by incorporating 2D nanocrystal building blocks.[67,77]

3.2 Interpenetrating networks of 1D nanomaterials

1D carbon nanotubes (CNTs) can be viewed as graphene sheets
95 rolled up into nanoscale tubes.[78] CNTs have gained prominence as nanoscale building blocks for dispersing the active materials to prevent them from agglomerating, interpenetrating networks of 1D CNT-based nanomaterials also afford an efficient electronic

pathway to provide better electrical contacts.[4,79] Hierarchical interconnected pore channels can be also achieved by hybrid CNTs and V_2O_5 nanowires (792 F/g, 3.8 mg/cm^2 for lithium ion ECs; ~400 F/g, 1-3 mg/cm^2 for sodium ion ECs).[80,81] (Fig. 5) High-power CNTs and high energy V_2O_5 are intertwined with each other, the network ensures fast and efficient electronic-transporting.[11]
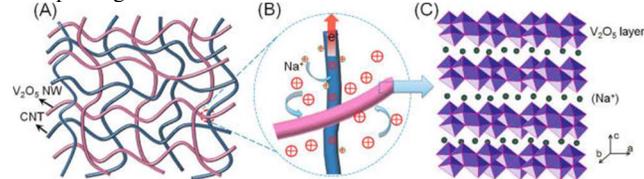

Fig. 5 Schematic of (A) a nanocomposite consisting of interpenetrating networks of V_2O_5 nanowires and CNTs, (B) intimate contacts between the V_2O_5 nanowire and CNTs facilitating charge transport, and (C) Na$^+$ intercalation within the V_2O_5 layer structure. (Reproduced from *Acs Nano*, 2012, **6**, 4319-4327. Copyright 2012, American Chemical Society.[81])

One dimension nanomaterials are easy to build networks with short ion diffusion paths and better utilization.[11] Among various methods, template-directed and hydrothermal synthesis has been a powerful route with simplicity and great variability in controlling the chemical composition and morphology in both lateral and longitudinal dimensions.[82-84] Macroscopic-scale assembled nanowires thin films promote the interface-induced and external fields assisted technology, for example, Langmuir-Blodgett Technique, evaporation-induced, microfluidic flow, bubble-blowing, electrospinning, magnetic field-assisted.[85]

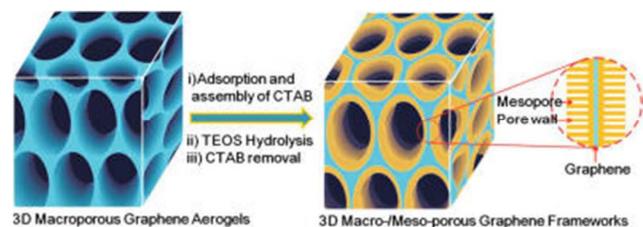### 3.3 Three-dimensional gel frameworks

Fig. 6 Fabrication of hierarchical macro- and mesoporous GAs-SiO$_2$ frameworks: (i) electrostatic adsorption and assembly of ofcetyltrimethyl ammonium bromide (CTAB) on the surface of 3D GAs, (ii) tetraethoxysilane hydrolysis for nucleation and growth of mesoporous silica on the surface of CTA$^+$-adsorped GAs, and (iii) CTAB removal through ethanol washing, drying, and thermal annealing. (Reproduced from *J. Am. Chem. Soc.*, 2012, **134**, 19532-19535. Copyright 2012, American Chemical Society.[91])

Three-dimensional (3D) graphene gel frameworks can be cheaply produced on a large scale from graphene oxide by hydrothermal or additives,[86-89] The 3D structures provide high specific surface areas, strong mechanical strengths and fast mass and electron transport kinetics.[90] Hierarchical macro- and mesoporous graphene aerogels (GAs) can be also fabricated, the macropores can act as a bulk buffering reservoir for electrolytes diffusion, while the mesopores can provide a larger accessible active surface area, and micropores can continuously increase charge accommodation.[91] (Fig. 6) Hierarchical porous structures also benefit TMOs, large pores increase ion transport, small pores increase volumetric energy densities.[92] Hydrogel interpenetrates

solid-state with liquid-state, that is to say, it interpenetrates efficient ion and electron transport.

In addition, Worsley et al. utilized carbon to knit together graphene sheets into a macroscopic 3D structure with superior electrical conductivity. Graphene aerogel synthesis was carried out by sol-gel polymerization of resorcinol and formaldehyde, followed by pyrolysis.[93] 3D Graphene-based compounds can be prepared in situ reduced with self-assembly and embedding of components.[94-96] Hydrothermal carbonization and pyrolysis are rising techniques for the synthesis of porous carbonaceous materials.[97-99] Hence, an innovative approach is to incorporate metal oxide nanoparticles to the porous carbon materials.[8,100,101]

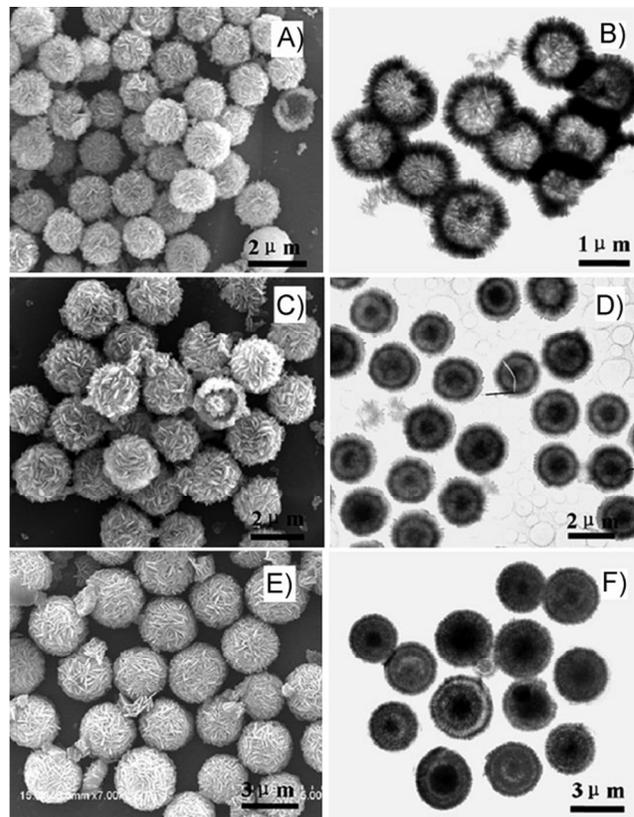### 3.4 Nanomaterials-assembled hierarchical microstructures

Fig. 7 Scanning electron micrographs (A,C,E) and transmission electron micrographs (B,D,F) images of the three samples: A,B) single-shelled Co_3O_4 hollow spheres, C,D) double-shelled spheres, and E,F) triple-shelled spheres. (Reproduced from *Adv. Funct. Mater.*, 2010, **20**, 1680-1686. Copyright 2010, Wiley-VCH.[109])

Various methodologies have been developed to achieve self-assemblied special nanostructure to make easy diffusion of ionic-transporting region.[102-107] Recently, multishelled hollow structures have received more attention from potential applications.[102,108] Multishell hollow Co_3O_4 spheres composed of oriented self-assembled nanosheets were synthesized via a hydrothermal method, double-shelled spheres benefits superior electrical conductivity and high structural stability with superior void-space-utilizing rate during volume change during Li$^+$ insertion–extraction.[109] Besides, Wang et al. reported a facile "pumpkin-carving" strategy for the production of single-crystal $CoSn(OH)_6$ nanoboxes with a uniform size.[102]

Hydrotalcite-like compounds consist of positively charged

brucite-like host layers and charge balancing anions in the interlayer, α-hydroxides are reported to be isostructural with hydrotalcite-like compounds, which have a larger interlayer than that of the brucite-like structure.[110,111] The intercalated
5 anions are exchangeable, thus making it possible to adjust the interlayer spacing.[110] Wang et al. reported a novel strategy of fabricating conical structures be formed by the rolling-up of layered α-cobalt hydroxide materials, the lower size limit of accessible hollow spaces in cobalt hydroxide-based
10 electrochemical capacitors through an anion exchange reaction studying.[112,113] Nanomaterials-assembled hierarchical microstructures construct an excellent interface for ionic-transport, but fail to provide robust adhesions with matrixes, which lead to a poor electron-transporting phase.

15 **3.5 Surface coating**

Coating the surface of the electrode material is a common technique used for improving the functionality and performance of the electrode material. For the lithium ion batteries, carbon coating is one of the most popular means of easily enhancing the
20 electronic conductivity of electrode materials, and can also stabilize SEI films.[114-116] Moreover, surface coatings onto cathode material with oxides (NiO or MnO_2) can essentially shield from direct exposure to the electrolyte solution, improving the structural integrity of the cathode material and suppressing phase
25 transitions.[117,118] For the supercapacitors, a conducting polymer such as polypyrrole (PPy) usually is used to coat the surface of the electrode materials to, which lead to significantly improved electron transport within every nanostructures. PPy was chosen not only because it has greater density and better degree of
30 flexibility, but also itself can undergo a fast redox reaction to store charge.[119]

4. Interface design of current collectors
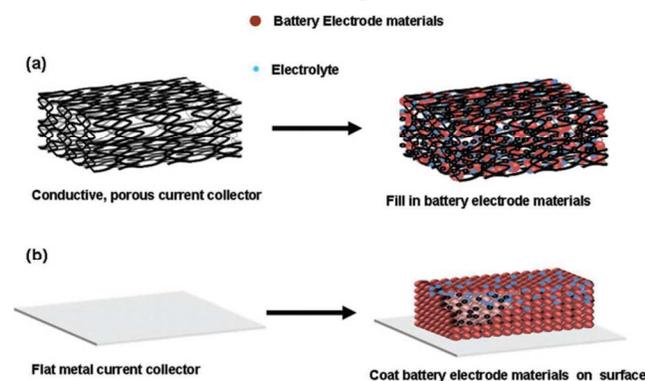
4.1 Microstructured interface design

35 Fig. 8 Design and fabrication of 3D porous current collectors filled with the battery electrode material. (a) (left): Highly conductive fibrous network after coating polyester fibers with carbon nanotubes and (right): Porous conductor filled with battery materials, where the conductive polyester fiber network functions as an effective current collector and the
40 organic electrolyte penetrates throughout the entire structure effectively. (b) By comparison, the battery electrode material is coated on the surface of the flat current collector in the traditional architecture. (Reproduced from *Adv. Energ. Mater.*, 2011, **1**, 1012-1017. Copyright 2011, Wiley-VCH.[120])

45 3D porous current collectors have excellent interfaces between the electronic-transporting phase and the ionic-transporting phase,

while, flat current collectors are difficult for electrolyte penetration.[120] (Fig. 8) 3D porous conductive materials, such as carbon paper and carbon cloth, are promising for high-
50 performance flexible electrodes.[121-124] Similar to EC materials, for current collectors with high electronic conductivity and mobility, only surface or a thin layer around the electrode/electrolyte interface play a key role, microstructured interface design of current collectors is vital for meet the
55 requirements of short transport lengths and large energy capacities with an optimal physical space.[7,125] When slurry-pasting is discussed, low specific capacity caused by the extra weight of additives and dead volume is obvious drawbacks.[26] these can be also caused by a poor interfacial design of current
60 collectors. Zhang et al. reported a self-assembled bicontinuous bulk electrode concept consisting of an electrolytically active material sandwiched between the electrolyte and the current collectors with polystyrene spheres template-assisted electrodeposition.[126] Gowda et al. reported 3D nanoporous Au
65 nanowire current collectors for thin film micro batteries, vertically aligned gold-silver nanotube arrays were fabricated using a template-assisted electrodeposition technique followed by treated with concentrated nitric acid.[127] Chemical-ecthing with nitric acid is a powerful way for nanoporous electrodes.[128,129]
70 Ideal electrode architectures provide three-dimensional interpenetrating efficient ion and electron transport.[126] Attempts at novel electrode design have been extensively made from conductive matrixes to integrate materials hybrid nanostructures.[30] Step-by-step growing is concordant with the
75 microstructured interface design of current collectors to assign to bridge the performance for electrode design. Step-by-step growing of battery materials is suitable for high-energy devices, while, microstructured interface design of current collectors may benefit high-power devices.[130]

80 **4.2 Surface modification and functionalization**

Textile fibers have a hierarchical structure with complicated surface morphology, each fiber is comprised of multiple individual cotton fibrils, which are in turn composed of multiple microfibrils bundled, functional groups cause the fibers to swell
85 in polar solutions. Flexible and porous textiles are used as supporters to make nanosystems electrodes,[132] and provide an effective three-dimensional (3D) framework for a large mass loading of electrochemical active materials. Porous conductors could be made with carbon nanotube or graphene coated,[131-134]
90 the fabrication process is simple and scalable, similar to those widely used for dyeing fibers and fabrics in the textile industry. (Fig. 9) Cotton T-shirt textiles could be converted into activated carbon textiles for energy storage applications.[135] Inspired of these, hierarchical macroporous sponges and flexible paper have
95 been designed to conductive substrates.[136-139] Polypyrrole-coat papers could be fabricated by a simple "soak and polymerization".[140] Hu et al. demonstrated highly conductive paper for energy-storage devices with single-walled CNTs and Ag nanowires integrated by solution-based processes.[141]
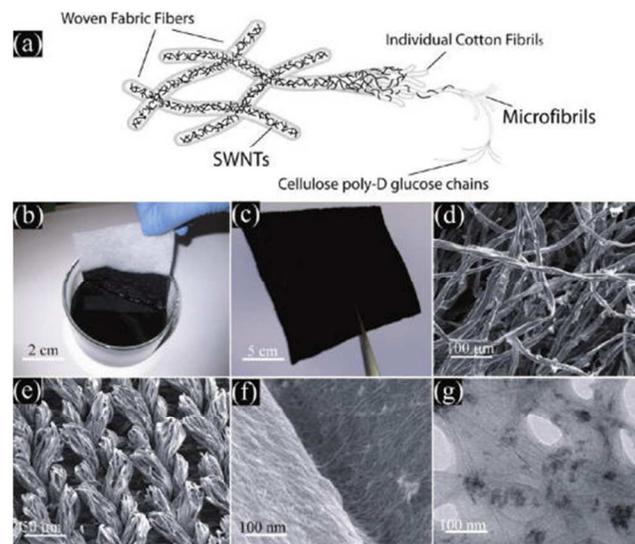
Fig. 9 Porous textile conductor fabrication. (a) Schematic of SWNTs wrapping around cellulose fibers to form a 3D porous structure. (b) Conductive textiles are fabricated by dipping textile into an aqueous CNT ink followed by drying in oven at 120 °C for 10 min. (c) A thin, 10 cm × 10 cm textile conductor based on a fabric sheet with 100% cotton and Rs of 4 Ω/sq. (d) SEM image of coated cotton reveals the macroporous structure of the cotton sheet coated with CNTs on the cotton fiber surface. (e) SEM image of fabric sheet coated with CNTs on the fabric fiber surface. (f) High-magnification SEM image shows the conformal coating of CNT covering and bridging between the fabric fibers. (g) TEM image of CNTs on cotton fibers. (Reproduced from *Nano Lett.*, 2010, **10**, 708-714. Copyright 2010, American Chemical Society.[131])

Alignments of nanocrystalline phases with different morphologies and microstructures show substantial differences in electrochemical performances, substrate dependent self-organization of mesoporous cobalt oxide nanowires with remarkable pseudocapacitance were reported.[142] Interfacial designs for electron and ion transfer are affected by chemical and physical properties of substrates, it implies the importance surface modification and functionalization.[143-145] A high mass loading of active materials usually leads to an increased electrode resistance. To solve these critical problems, Yu et al. developed a "3D conductive wrapping" method.[146]
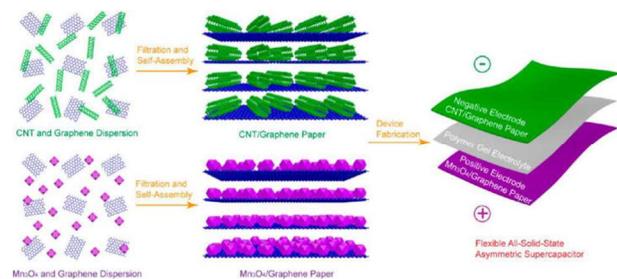
4.3 Self-supporting materials

Fig. 10 Illustration of the fabrication process for flexible all-solid-state asymmetric supercapacitors based on polymer gel electrolyte and free-standing paper electrodes. (Reproduced from *ACS Appl. Mater. Inter.*, 2012, **4**, 7020-7026. Copyright 2012, American Chemical Society.[153])

Papers are excellent candidates for substrates of flexible energy-storage applications and miniature devices, carbon nanotube/cellulose papers could be used in all-solid-state flexible supercapacitors.[147-149] Flexible CNT or graphene thin films could be prepared by filtration,[149-151] incorporating these with transition metal oxides or conductive polymers is a promising approach to further achieve better electrochemical performances of devices.[152,153] (Fig. 10) Recently, macroscopic GO membranes were prepared by evaporating GO at a liquid/air interface.[154] Electrochemically active materials serve as current collectors in self-supporting electrodes, no additional conductive matrix exists. Portable electronic devices develop in the trend of being small, thin, lightweight, flexible and even roll-up, flexible and lightweight devices need to provide much higher energy and power with less device mass, these could be achieved by combining thin films electrodes and polymer gel electrolytes.[141-148]

Ultralight and highly porous CNT or graphene aerogels may be another exciting candidates for electrically conducting aerogels,[155,156] the fabrication could be incorporated with transition metal oxides or conductive polymers for enhanced electrochemical performances.[157-159] Folded structured graphene paper from 3D graphene aerogels is also adaptable for high performance electrode materials.[160] Inspired by wearable electronic devices with textiles, easily woven fibrous electrodes could be prepared with CNT yarn infiltrated with polyaniline nanowire arrays.[161] Wet-spinning assemblies of macroscopic graphene fibers may be fabricated the same as fiber springing in the future.[162-164] Flexible and conductive fibers make wearable electrochemical storage devices feasible by utilizing nanotechnology, if integrated with stretchable energy generation to a self-powering nanosystem, wearable electrochemical storage devices could work when we walk and move.[165-168]

5. Interfacial bonding between working materials and substrates.
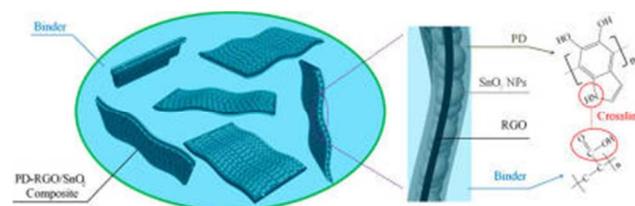
5.1 Binders and additives

Fig. 11 Illustration of the system-level strategy of the fabrication of rGO/SnO_2 composite-based anode for lithium ion battery. (Reproduced from *Nano Lett.*, 2013, **13**, 1711-1716. Copyright 2013, American Chemical Society.[20])

Slurry-pasting of active materials, conductive additives and polymeric binders onto the current collector is a traditional treatment for electrodes, however, random distribution of the constitutive phases has obvious drawbacks including poor electron transport and extra weight of additives.[26] Acitve materials ensure high energy, conductive additives guarantee high electron transport and power, binders keep structural stability during the electrochemical process. Selecting binders should be considered with interfacial bonding and high performance. For example, sodium alginate may be a good binder compared with polyvinylidene fluoride for lithium ion battery.[169] The excellent electrode performance caused by the sodium alginate is not only owing to without react between sodium alginate and electrolyte, but also electrode porosity. Sarkar et al. synthesized $NH_4V_4O_{10}$

along with CMC/alginate binder.[170] It delivers discharge capacity of 200 mAh/g at very high current rate of 1000 mA/g and completely retains its original discharge state at low current rate of 100 mA/g rate, whereas PVDF-based cathode delivers discharge capacity of 125 mAh/g at same current rate. Liu et al. prepared an alginate hydrogel binder which leads to a remarkable improvement in the electrochemical performance of the Si/C anode of a Li-ion battery.[171] Besides, conductive binders combine conductive additives with polymeric binders to tailor the conduction band and improve the mechanical binding force.[172,173] Wang et al. built a cross-link reaction between active materials coated with polydopamine and polyacrylic acid to form a robust network of covalent bonds in electrodes.[20] (Fig. 11)

Sometimes, additives may improve the performance. For instance, sodium alginate could direct nanofiber networks of polyaniline,[174] coating constituents phase-separate from battery materials could lead to a high-power performance,[175] polyvinyl alcohol gel could stabilize vanadium oxide nanowire for pseudocapacitors.[176] Heat treatments in air for binders burn-out and active materials sintered may be a powerful binder-free technique for porous metal oxides. [177,178] It promotes TMOs nanoscale building blocks to construct hierarchically porous bulks.
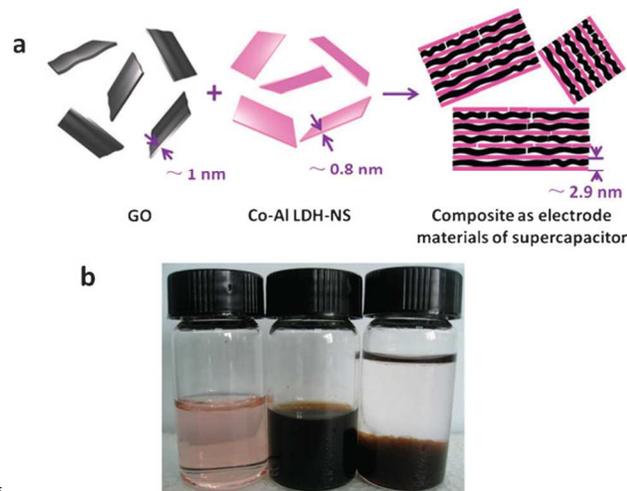
5.2 Weak interactions

Fig. 12 (a) Schematic of the formation and structure of Co-Al LDH nanosheets/graphene oxide composite. (b) Digital photographs of (left) an aqueous dispersion of LDH nanosheets, (middle) an aqueous dispersion of graphene oxide, and (right) a mixture of LDH nanosheets and graphene oxide. [179]

Nanoelectrodes have higher electrode/electrolyte contact areas and short path lengths for electronic and ionic transport.[92] Various flexible techniques are developed for nanomaterials, however, most of these rely on slurry-pasting. Slurry-pasting is more suitable for nanomaterials than nanoelectrodes, inferior packing of particles leading to lower volumetric energy densities.[92] Robust contacts between working materials and substrates are pivotal. Step-by-step growing promotes a additive-free robust adhesion with current collectors with a small mass loading.

Co-Al LDH nanosheets/GO composite could be produced by simply mixing dispersions of each component to maximize the contact area of graphene and nanosheets and to optimize the utilization rate of the nanosheets as active materials (1031 F/g 1 mg/cm^2, at 1 A/g; nearly 100% after 6000 cycles, at 20 A/g), (Fig. 12) these conductive additive-free assembled materials still needs binders to contact with current collectors.[179,180] It could be achieved by electrophoretic deposition or self-assembly thin film.[137,181] It implies interfacial assembly with current collectors is operable. Robust adhesion with substrates and smart hybrid can be achieved by layer-by-layer assembly, however, to have a large mass loading is time-consuming, co-assembly of mixed nano-objects with different sizes and/or shapes represents a fundamentally interesting topic, co-assembly of nanowires and GO nanosheets directs unidirectional self-alignment of nanowires at the air-water interface,[182] co-assemblies of multicomponent colloids remain to be attractive for applications in electronics and electrodes.[183]

Textiles could absorb polar solvents, the interactions of functional groups with solutes, the weak interactions combine textiles with solutes when the solvents are evaporated.[145] Various interfacial assemblies of nanomaterials have been improved, it has been widely accepted interfacial assembly is solvent-assisted and substrate-dependent.[184-186] Integrated system could be built up with dispersion of nanomaterials in suitable solvents and substrate surface modification. Filtration contains structure-induced interfacial assembly; transition metal oxide nanowire/CNT intertwined mesh could be prepared by a filtration method with the nanowires trapped on the CNT films.[187]

As another point of view, instead of building robust interfaces with substrates, dispersing active materials in a liquid electrolyte may meet the demand for batteries of higher energy and power. Flow architecture is named as semi-solid flow battery, Duduta et al. designed diffusion-limited cluster aggregation of conductive nanoparticles as percolating conductor networks and "hit and stick" behavior that forms fractal particle stabilizing the larger particles from settling out of suspension, the semi-solid flow battery shows an increasing energy density.[188-190] It can be inferred that the stability of suspensions and conductor networks plays a pivotal role, during the electrochemical process actives materials adhering to electrodes are undesirable. Molecules and ions in solutions are stable and homogenous dispersed, active materials homogenous dispersed will be better for electrochemical devices. Yang et al. proposed a new room-temperature lithium/polysulde semi-liquid battery, no insoluble phases exist in the proof-of-concept battery with high energy density.[191]

5.3 Interconnected structures

Nanostructured materials with well-defined morphologies have obtained success, while, nanostructured electrodes with efficient electron and ion pathways are difficult to control. Nanostructured electrodes could be prepared by attaching active materials on the 3D networked scaffold with robust interfacial bonding between working materials and substrates. However, ideal 3D nanoarchitectured electrode should be interpenetrating active materials and conductive materials for electron and ion networks.[85,82] Chen et al. applied an H$_2$ gas bubble dynamic template route to design 3D nanoarchitectured metal electrodes, followed by a heat treatment for interpenetrated metal/oxide (721.7 mAh/g, at 1 C rate).[19] (Fig. 13) Wang et al. proposed a strategy construct a free-standing, hierarchically porous carbon

with GO sol-gel dropped into the nickel-foam and carbonized for Li-O_2 batteries.[192] Various 3D interpenetrated nanoarchitectures may be constructed with chemical bath deposition or other solution-based methods.[193-198]
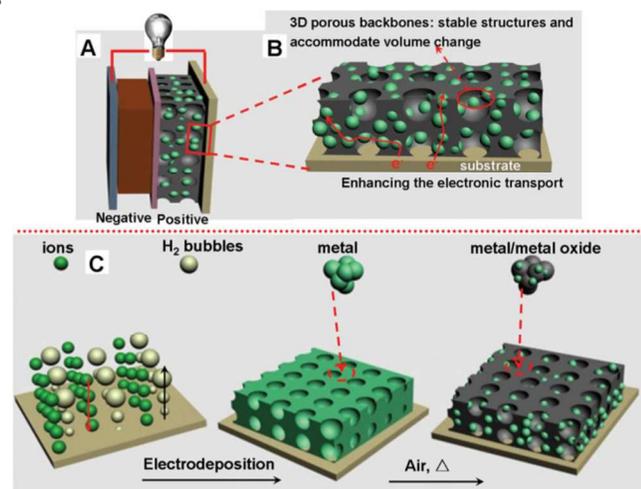

Fig. 13 (A) A schematic of lithium ion batteries, including the porous micro/nanostructured interconnected metal/metal oxide electrode. (B) A structural illustration of a metal/metal oxide electrode. (C) The metal/metal oxide electrode was fabricated via an H_2 gas bubble dynamic template route.[19]

6. Future outlook

Slurry-pasting contains the preparation of the slurry and coating with current collectors, and could be seen as a rough technique to a certain extent. If active materials could be dispersed in the slurry homogenously and steadily, the slurry could be used for semi-solid flow batteries. If the components in the slurry could be controlled with a scrupulous design, interfacial assembly could be achieved with a robust adhere with the matrix. Step-by-step growing provides a robust structure with restricted conditions, while, flexible nanoscale materials need to be integrated with interfacial assembly. Slurry should be studied for flexible step-by-step assembly by combining interfacial self-assembly with nanoscale build blocks.

Acknowledgements

Notes and references

a Key Laboratory of Superlight Material and Surface Technology, Harbin Engineering University,Harbin, 150001, P. R. China.
E -mail: zhqw1888@sohu.com;
Fax: +86 451 8253 3026; Tel: +86 451 8253 3026
bMinistry of Education and Institute of Advanced Marine Materials,
Harbin Engineering University,Harbin, 150001, P. R. China

1   J. B. Goodenough, *Acc. Chem. Res.*, 2012, **46**, 1053-1061.
2   P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, 7, 845-854.
3   J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan and X. W. Lou, *Adv. Mater.*, 2012, **24**, 5166-5180.
4   S. Xin, Y.G. Guo and L.J. Wan, *Acc. Chem. Res.*, 2012, **45**, 1759-1769.
5   K. Naoi, W. Naoi, S. Aoyagi, J.i. Miyamoto and T. Kamino, *Acc. Chem. Res.*, 2013, **46**, 1075-1083
6   L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C. K. Tee, Y. Shi, Y. Cui and Z. Bao, *P. Natl. Acad. Sci. USA.*, 2012, **109**, 9287-9292.
7   D. R. Rolison, R. W. Long, J. C. Lytle, A. E. Fischer, C. P. Rhodes, T. M. McEvoy, M. E. Bourga and A. M. Lubers, *Chem. Soc. Rev.*, 2009, **38**, 226-252.
8   H. Jiang, J. Ma and C. Li, *Adv. Mater.*, 2012, **24**, 4197-4202.
9   Q. Lu, J. G. Chen and J. Q. Xiao, *Angew. Chem. Int. Edit.*, 2013, **52**, 1882-1889.
10 M. Pumera, *Energ. Environ. Sci.*, 2011, 4, 668-674.
11 H. Jiang, P. S. Lee and C. Li, *Energ. Environ. Sci.*, 2013, **6**, 41-53.
12 S. Yang, R. E. Bachman, X. Feng and K. Müllen, *Acc. Chem. Res.*, 2012, **46**, 116-128.
13 M. Zhou, J. Qian, X. Ai and H. Yang, *Adv. Mater.*, 2011, **23**, 4913-4917.
14 B. Babakhani and D. G. Ivey, *Electrochim. Acta*, 2010, **55**, 4014-4024.
15 H. J. Lin, L. Li, J. Ren, Z. B. Cai, L. B. Qiu, Z. B. Yang and H. S. Peng, *Sci. Rep.*, 2013, **3**, 1353.
16 Q. F. Zhang, E. Uchaker, S. L. Candelaria and G. Z. Cao, *Chem. Soc. Rev.*, 2013, **42**, 3127-3171.
17 W. Wei, X. Cui, W. Chen and D. G. Ivey, *Chem. Soc. Rev.*, 2011, **40**, 1697-1721.
18 W. Deng, X. Ji, Q. Chen and C. E. Banks, *Rsc Adv.*, 2011, **1**, 1171-1178.
19 X. Chen, K. Sun, E. Zhang and N. Zhang, *Rsc Adv.*, 2013, **3**, 432-437.
20 L. Wang, D. Wang, Z. Dong, F. Zhang and J. Jin, *Nano Lett.*, 2013, **13**, 1711-1716.
21 P. Yang and J.M. Tarascon, *Nat. Mater.*, 2012, **11**, 560-563.
22 Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577-3613.
23 F. Y. Cheng, J. Liang, Z. L. Tao and J. Chen, *Adv. Mater.*, 2011, **23**, 1695-1715.
24 M. Pasta, C. D. Wessells, R. A. Huggins and Y. Cui, *Nat. Commun.*, 2012, **3**, 1149-1155.
25 C. Cheng and H. J. Fan, *Nano Today*, 2012, **7**, 327-343.
26 J. Jiang, Y. Li, J. Liu and X. Huang, *Nanoscale*, 2011, **3**, 45-58.
27 Y. Li, Z.Y. Fu and B.L. Su, *Adv. Funct. Mater.*, 2012, **22**, 4634-4667.
28 J. Liu and X.W. Liu, *Adv. Mater.*, 2012, **24**, 4097-4111.
29 J. Lee, J. Kim and T. Hyeon, *Adv. Mater.*, 2006, **18**, 2073-2094.
30 J. Liu, J. Jiang, C. Cheng, H. Li, J. Zhang, H. Gong and H. J. Fan, *Adv. Mater.*, 2011, **23**, 2076-2081.
31 X. Xia, J. Tu, Y. Zhang, X. Wang, C. Gu, X. B. Zhao and H. J. Fan, *Acs Nano*, 2012, **6**, 5531-5538.
32 G.-R. Li, Z.-L. Wang, F.-L. Zheng, Y.-N. Ou and Y.-X. Tong, *J. Mater. Chem.*, 2011, **21**, 4217-4221.
33 J. Liu, J. Jiang, M. Bosman and H. J. Fan, *J. Mater. Chem.*, 2012, **22**, 2419-2426.
34 R. Liu and S. B. Lee, *J. Am. Chem. Soc.*, 2008, **130**, 2942-2943.
35 L. Bao, J. Zang and X. Li, *Nano Lett.*, 2011, **11**, 1215-1220.
36 X. Xiao, T. Ding, L. Yuan, Y. Shen, Q. Zhong, X. Zhang, Y. Cao, B. Hu, T. Zhai, Li. Gong, J. Chen, Y. Tong, J. Zhou and Z. Wang, *Adv. Energ. Mater.*, 2012, **2**, 1328-1332.
37 Z. Tang, C. Tang and H. Gong, *Adv. Funct. Mater.*, 2012, **22**, 1272-1278.
38 L. Huang and M. Liu, *Nano Lett.*, 2013, **13**, 3135–3139.
39 J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen and G. Shen, *ACS Nano*, 2013, **7**, 5453–5462.
40 C. Yuan, L. Yang, L. Hou, J. Li, Y. Sun, X. Zhang, L. Shen, X. Lu, S. Xiong and X. W. Lou, *Adv. Funct. Mater.*, 2012, **22**, 2560-2566.
41 C. Zhou, Y. Zhang, Y. Li and J. Liu, *Nano Lett.*, 2013, **13**, 2078-2085.

42   Y. Wang, Z. Zhong, Y. Chen, C. Ng and J. Lin, *Nano Res.*, 2011, **4**, 695-704.

43   X. C. Dong, H. Xu, X.-W. Wang, Y.X. Huang, M. B. Chan-Park, H. Zhang, L.H. Wang, W. Huang and P. Chen, *Acs Nano*, 2012, **6**, 3206-3213.

44   M. A. Abbasi, Z. H. Ibupoto, M. Hussain, Y. Khan, A. Khan, O. Nur and M. Willander, *Sensors*, 2012, **12**, 15424-15437.

45   W. Dong, T. Zhang, J. Epstein, L. Cooney, H. Wang, Y. Li, Y.B. Jiang, A. Cogbill, V. Varadan and Z. R. Tian, *Chem. Mater.*, 2007, **19**, 4454-4459.

46   J. B. Wu, Y. Lin, X. H. Xia, J. Y. Xu and Q. Y. Shi, *Electrochim. Acta*, 2011, **56**, 7163-7170.

47   Y. Liu, Y. Chu, Y. Zhuo, M. Li, L. Li and L. Dong, *Cryst. Growth Des.*, 2007, **7**, 467-470.

48   J. Liu, X. Huang, Y. Li, X. Ji, Z. Li, X. He and F. Sun, *J. Phys. Chem. C*, 2007, **111**, 4990-4997.

49   J. Y. Lao, J. G. Wen and Z. F. Ren, *Nano Lett.*, 2002, **2**, 1287-1291.

50   J. Liu, Y. Li, X. Huang, G. Li and Z. Li, *Adv. Funct. Mater.*, 2008, **18**, 1448-1458.

51   R.C. Wang and C.H. Li, *Cryst. Growth Des.*, 2009, **9**, 2229-2234.

52   M. McCune, W. Zhang and Y. Deng, *Nano Lett.*, 2012, **12**, 3656-3662.

53   G. Q. Zhang and X. W. Lou, *Adv. Mater.*, 2013, **25**, 976-979.

54   R. Ma and T. Sasaki, *Adv. Mater.*, 2010, **22**, 5082-5104.

55   X. Y. Dong, L. Wang, D. Wang, C. Li and J. Jin, *Langmuir*, 2012, **28**, 293-298.

56   J. Kim, L. J. Cote and J. X. Huang, *Acc. Chem. Res.*, 2012, **45**, 1356-1364.

57   F. Kim, L. J. Cote and J. Huang, *Adv. Mater.*, 2010, **22**, 1954-1958.

58   H. Wang and H. Dai, *Chem. Soc. Rev.*, 2013, **42**, 3088-3113.

59   D. Wang, R. Kou, D. Choi, Z. Yang, Z. Nie, J. Li, L. V. Saraf, D. Hu, J. Zhang, G. L. Graff, J. Liu, M. A. Pope and I. A. Aksay, *Acs Nano*, 2010, **4**, 1587-1595.

60   Y. Su, S. Li, D. Wu, F. Zhang, H. Liang, P. Gao, C. Cheng and X. Feng, *Acs Nano*, 2012, **6**, 8349-8356.

61   Q. Qu, S. Yang and X. Feng, *Adv. Mater.*, 2011, **23**, 5574-5580.

62   Z.S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li and H.-M. Cheng, *Acs Nano*, 2010, **4**, 3187-3194.

63   S. Chen, J. Zhu, X. Wu, Q. Han and X. Wang, *Acs Nano*, 2010, 4, 2822-2830.

64   J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi and F. Wei, *Adv. Funct. Mater.*, 2012, **22**, 2632-2641.

65   S. Chen, J. Zhu and X. Wang, *Acs Nano*, 2010, **4**, 6212-6218.

66   S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl and J. E. Goldberger, *ACS Nano*, 2013, **7**, 2898-2926.

67   M. Osada and T. Sasaki, *Adv. Mater.*, 2012, **24**, 210-228.

68   R. Ma, Z. Liu, L. Li, N. Iyi and T. Sasaki, *J. Mater. Chem.*, 2006, **16**, 3809-3813.

69   Z. P. Liu, R. Z. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 4872-4880.

70   J. Liang, R. Ma, N. Iyi, Y. Ebina, K. Takada and T. Sasaki, *Chem. Mater.*, 2010, **22**, 371-378.

71   D. S. Kim, T. C. Ozawa, K. Fukuda, S. Ohshima, I. Nakai and T. Sasaki, *Chem. Mater.*, 2011, **23**, 2700-2702.

72   Y. Omomo, T. Sasaki, L. Z. Wang and M. Watanabe, *J. Am. Chem. Soc.*, 2003, **125**, 3568-3575.

73   J. Feng, X. Sun, C. Wu, L. Peng, C. Lin, S. Hu, J. Yang and Y. Xie, *J. Am. Chem. Soc.*, 2011, **133**, 17832-17838.

74   Q. Wang and D. O'Hare, *Chem. Rev.*, 2012, **112**, 4124-4155.

75   S. Ida, D. Shiga, M. Koinuma and Y. Matsumoto, *J. Am. Chem. Soc.*, 2008, **130**, 14038-14039.

76   C. Nethravathi, B. Viswanath, M. Sebastian and M. Rajamathi, *J. Colloid Interf. Sci*, 2010, **345**, 109-115.

77   L. Li, R. Ma, Y. Ebina, K. Fukuda, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2007, **129**, 8000-8007.

78   L. Dai, D. W. Chang, J.-B. Baek and W. Lu, *Small*, 2012, **8**, 1130-1166.

79   Z. Chen, D. Zhang, X. Wang, X. Jia, F. Wei, H. Li and Y. Lu, *Adv. Mater.*, 2012, **24**, 2030-2036.

80   Z. Chen, V. Augustyn, J. Wen, Y. Zhang, M. Shen, B. Dunn and Y. Lu, *Adv. Mater.*, 2011, **23**, 791-795.

81   Z. Chen, V. Augustyn, X. Jia, Q. Xiao, B. Dunn and Y. Lu, *Acs Nano*, 2012, **6**, 4319-4327.

82   H.W. Liang, J.W. Liu, H.S. Qian and S.H. Yu, *Acc. Chem. Res.*, 2013.

83   X. Wang and Y. Li, *J. Am. Chem. Soc.*, 2002, **124**, 2880-2881.

84   S. D. Perera, B. Patel, N. Nijem, K. Roodenko, O. Seitz, J. P. Ferraris, Y. J. Chabal and K. J. Balkus, Jr., *Adv. Energ. Mater.*, 2011, **1**, 936-945.

85   J.W. Liu, H.W. Liang and S.H. Yu, *Chem. Rev.*, 2012, **112**, 4770-4799.

86   P. Chen, J. J. Yang, S. S. Li, Z. Wang, T. Y. Xiao, Y. H. Qian and S. H. Yu, *Nano Energy*, 2013, **2**, 249-256.

87   Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang and X. Duan, *ACS Nano*, 2013, **7**, 4042-4049.

88   J. Chen, K. Sheng, P. Luo, C. Li and G. Shi, *Adv. Mater.*, 2012, **24**, 4569-4573.

89   W. Chen and L. Yan, *Nanoscale*, 2011, **3**, 3132-3137.

90   C. Li and G. Shi, *Nanoscale*, 2012, **4**, 5549-5563.

91   Z.S. Wu, Y. Sun, Y.Z. Tan, S. Yang, X. Feng and K. Muellen, *J. Am. Chem. Soc.*, 2012, **134**, 19532-19535.

92   A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. Van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366-377.

93   M. A. Worsley, P. J. Pauzauskie, T. Y. Olson, J. Biener, J. H. Satcher, Jr. and T. F. Baumann, *J. Am. Chem. Soc.*, 2010, **132**, 14067-14069.

94   S. Nardecchia, D. Carriazo, M. Luisa Ferrer, M. C. Gutierrez and F. del Monte, *Chem. Soc. Rev.*, 2013, **42**, 794-830.

95   W. Chen, S. Li, C. Chen and L. Yan, *Adv. Mater.*, 2011, **23**, 5679-5683.

96   Z. Zhang, F. Xiao, Y. Guo, S. Wang and Y. Liu, *ACS Appl. Mater. Inter.*, 2013, **5**, 2227-2233.

97   X.L. Wu, T. Wen, H.L. Guo, S. Yang, X. Wang and A.W. Xu, *ACS Nano*, 2013.

98   H. Zhu, X. Wang, F. Yang and X. Yang, *Adv. Mater.*, 2011, **23**, 2745-2748.

99   Y. Y. Li, Z. S. Li and P. K. Shen, *Adv. Mater.*, 2013, **25**, 2474-2480.

100 Y.H. Lin, T.Y. Wei, H.C. Chien and S.Y. Lu, *Adv. Energ. Mater.*, 2011, **1**, 901-907.

101 H.C. Chien, W.Y. Cheng, Y.H. Wang and S.Y. Lu, *Adv. Funct. Mater.*, 2012, **22**, 5038-5043.

102 Z. Y. Wang, Z. C. Wang, H. B. Wu and X. W. Lou, *Sci. Rep.*, 2013, **3**.

103 N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. W. Chen, *Sci. Rep.*, 2013, **3**.

104 L. Li, K. H. Seng, Z. X. Chen, Z. P. Guo and H. K. Liu, *Nanoscale*, 2013, **5**, 1922-1928.

105 W. Xiao, D. Wang and X. W. Lou, *J. Phys. Chem. C*, 2009, **114**, 1694-1700.

106 X. M. Yin, C. C. Li, M. Zhang, Q. Y. Hao, S. Liu, L. B. Chen and T. H. Wang, *J. Phys. Chem. C*, 2010, **114**, 8084-8088.

107 Q. Qu, Y. Zhu, X. Gao and Y. Wu, *Adv. Energ. Mater.*, 2012, **2**, 950-955.

108 Z. Dong, X. Lai, J. E. Halpert, N. Yang, L. Yi, J. Zhai, D. Wang, Z. Tang and L. Jiang, *Adv. Mater.*, 2012, **24**, 1046-1049.

109 X. Wang, X.L. Wu, Y.G. Guo, Y. Zhong, X. Cao, Y. Ma and J. Yao, *Adv. Funct. Mater.*, 2010, **20**, 1680-1686.

110 Z. P. Liu, R. Z. Ma, M. Osada, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2005, **127**, 13869-13874.

111 M.Q. Zhao, Q. Zhang, J.Q. Huang and F. Wei, *Adv. Funct. Mater.*, 2012, **22**, 675-694.

112 X. H. Liu, R. Z. Ma, Y. Bando and T. Sasaki, *Angew. Chem. Int. Edit.*, 2010, **49**, 8253-8256.

113 L. Wang, Z. H. Dong, Z. G. Wang, F. X. Zhang and J. Jin, *Adv. Funct. Mater.*, 2012, **23**, 2758-2764.

114 N. Li, G. Zhou, F. Li, L. Wen and H. Cheng, *Adv. Funct. Mater.* 2013, **23**, 5429-5435

115 K. Park, A. Benayad, D. Kang and S. Doo, *J. Am. Chem. Soc.* 2008, **130**, 14930-14931

116 Y. Liu, D. Liu, Q. Zhang, D. Yu, J. Liu and G. Cao, *Electrochim.*

Acta, 2011, **56**, 2559-2565.

117 S. Amaresh, K. Karthikeyan, K. Kim, J. An, S. Cho, K. Chung, B. Cho, K. Nam and Y. Lee, *J. Nanosci. Nanotech.,* 2014, **14**, 7545-7552.

5 118 Y. Liu, Y. Gao, Q. Wang and A. Dou, *J. Alloys and Compounds,* 2014, **605**, 1-6.

119 C. Zhou, Y. Zhang, Y. Li and J. Liu, *Nano Lett.* 2013, **13**, 2078-2085.

120 L. Hu, F. La Mantia, H. Wu, X. Xie, J. McDonough, M. Pasta and 10 Y. Cui, *Adv. Energ. Mater.*, 2011, **1**, 1012-1017.

121 B. Liu, J. Zhang, X. Wang, G. Chen, D. Chen, C. Zhou and G. Shen, *Nano Lett.*, 2012, **12**, 3005-3011.

122 C.T. Hsieh, W.Y. Chen and Y.S. Cheng, *Electrochim. Acta*, 2010, **55**, 5294-5300.

15 123 X. Zhang, X. Lu, Y. Shen, J. Han, L. Yuan, L. Gong, Z. Xu, X. Bai, M. Wei, Y. Tong, Y. Gao, J. Chen, J. Zhou and Z. L. Wang, *Chem. Commun.*, 2011, **47**, 5804-5806.

124 C.T. Hsieh, H. Teng, W.Y. Chen and Y.S. Cheng, *Carbon*, 2010, **48**, 4219-4229.

20 125 J. W. Long, B. Dunn, D. R. Rolison and H. S. White, *Chem. Rev.*, 2004, **104**, 4463-4492.

126 H. Zhang, X. Yu and P. V. Braun, *Nat. Nanotechnolo.*, 2011, **6**, 277-281.

127 S. R. Gowda, A. L. M. Reddy, X. Zhan, H. R. Jafry and P. M. 25 Ajayan, *Nano Lett.*, 2012, **12**, 1198-1202.

128 F. Meng and Y. Ding, *Adv. Mater.*, 2011, **23**, 4098-4102.

129 L. Xingyou, A. Hirata, T. Fujita and C. Mingwei, *Nat. Nanotechnolo.*, 2011, **6**, 232-236.

130 D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, 30 P.L. Taberna and P. Simon, *Nat Nano*, 2010, **5**, 651-654.

131 L. Hu, M. Pasta, F. La Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han and Y. Cui, *Nano Lett.*, 2010, **10**, 708-714.

132 L. Hu, W. Chen, X. Xie, N. Liu, Y. Yang, H. Wu, Y. Yao, M. Pasta, H. N. Alshareef and Y. Cui, *Acs Nano*, 2011, **5**, 8904-8913.

35 133 X. Xie, L. Hu, M. Pasta, G. F. Wells, D. Kong, C. S. Criddle and Y. Cui, *Nano Lett.*, 2011, **11**, 291-296.

134 G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J. R.McDonough, X. Cui, Y. Cui and Z. Bao, *Nano Lett.*, 2011, **11**, 2905-2911.

40 135 L. Bao and X. Li, *Adv. Mater.*, 2012, **24**, 3246-3252.

136 X. Xie, M. Ye, L. B. Hu, N. Liu, J. R. McDonough, W. Chen, H. N. Alshareef, C. S. Criddle and Y. Cui, *Energ. Environ. Sci.*, 2012, **5**, 5265-5270.

137 W. Chen, R. B. Rakhi, L. Hu, X. Xie, Y. Cui and H. N. Alshareef, 45 in *Nano Lett.*, 2011, 11, 5165-5172.

138 J. Ge, H.B. Yao, W. Hu, X.F. Yu, Y.X. Yan, L.B. Mao, H.H. Li, S.S. Li and S.-H. Yu, *Nano Energy*, 2013, **2**, 505-513.

139 L. Hu and Y. Cui, *Energ. Environ. Sci.*, 2012, **5**, 6423-6435.

140 L. Y. Yuan, B. Yao, B. Hu, K. F. Huo, W. Chen and J. Zhou, 50 *Energ. Environ. Sci.*, 2013, **6**, 470-476.

141 L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. La Mantia, L. F. Cui and Y. Cui, *P. Natl. Acad. Sci. USA.*, 2009, **106**, 21490-21494.

142 R. B. Rakhi, W. Chen, D. Cha and H. N. Alshareef, *Nano Lett.*, 2012, **12**, 2559-2567.

55 143 D. Wei, B. Wu, Y. Guo, G. Yu and Y. Liu, *Acc. Chem. Res.*, 2012, **46**, 106-115.

144 Y. Ding, M. A. Invernale and G. A. Sotzing, *ACS Appl. Mater. Inter.*, 2010, **2**, 1588-1593.

145 J. Jiang, J. Liu, R. Ding, J. Zhu, Y. Li, A. Hu, X. Li and X. Huang, 60 *ACS Appl. Mater. Inter.*, 2011, **3**, 99-103.

146 G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Lett.*, 2011, **11**, 4438-4442.

147 K. Yu Jin, C. Haegeun, H. Chi-Hwan and K. Woong, *Nanotechnology*, 2012, **23**, 65401-65401.

65 148 Y. J. Kang, S.J. Chun, S.S. Lee, B.Y. Kim, J. H. Kim, H. Chung, S.Y. Lee and W. Kim, *Acs Nano*, 2012, **6**, 6400-6406.

149 Z. Weng, Y. Su, D.-W. Wang, F. Li, J. Du and H.-M. Cheng, *Adv. Energ. Mater.*, 2011, **1**, 917-922.

150 C. Meng, C. Liu, L. Chen, C. Hu and S. Fan, *Nano Lett.*, 2010, **10**, 70 4025-4031.

151 B. G. Choi, J. Hong, W. H. Hong, P. T. Hammond and H. Park, *Acs Nano*, 2011, **5**, 7205-7213.

152 A. Sumboja, C. Y. Foo, X. Wang and P. S. Lee, *Adv. Mater.*, 2013,

75 153 H. C. Gao, F. Xiao, C. B. Ching and H. W. Duan, *ACS Appl. Mater. Inter.*, 2012, **4**, 7020-7026.

154 C. Chen, Q.H. Yang, Y. Yang, W. Lv, Y. Wen, P.X. Hou, M. Wang and H.M. Cheng, *Adv. Mater.*, 2009, **21**, 3007-3011.

155 H. Huang, P. W. Chen, X. T. Zhang, Y. Lu and W. C. Zhan, *Small*, 80 2013, **9**, 1397-1404.

156 J. Zou, J. Liu, A. S. Karakoti, A. Kumar, D. Joung, Q. Li, S. I. Khondaker, S. Seal and L. Zhai, *Acs Nano*, 2010, **4**, 7293-7302.

157 Y. Zhao, J. Liu, Y. Hu, H. H. Cheng, C. G. Hu, C. C. Jiang, L. Jiang, A. Y. Cao and L. T. Qu, *Adv. Mater.*, 2013, **25**, 591-595.

85 158 Z.S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng and K. Muellen, *J. Am. Chem. Soc.*, 2012, **134**, 9082-9085.

159 X. Chen, H. Zhu, Y.-C. Chen, Y. Shang, A. Cao, L. Hu and G. W. Rubloff, *Acs Nano*, 2012, **6**, 7948-7955.

160 F. Liu, S. Song, D. Xue and H. Zhang, *Adv. mater.*, 2012, **24**, 90 1089-1094.

161 K. Wang, Q. H. Meng, Y. J. Zhang, Z. X. Wei and M. H. Miao, *Adv. Mater.*, 2013, **25**, 1494-1498.

162 Z. Xu, Y. Zhang, P. G. Li and C. Gao, *Acs Nano*, 2012, **6**, 7103-7113.

95 163 H.P. Cong, X.C. Ren, P. Wang and S.H. Yu, *Sci. Rep.*, 2012, **2**, 613-613.

167 Z. L. Dong, C. C. Jiang, H. H. Cheng, Y. Zhao, G. Q. Shi, L. Jiang and L. T. Qu, *Adv. Mater.*, 2012, **24**, 1856-1861.

165 P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. 100 Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhou, C. P. Wong and Z. L. Wang, *ACS Nano*, 2013, **7**, 2617-2626.

166 J. Bae, Y. J. Park, M. Lee, S. N. Cha, Y. J. Choi, C. S. Lee, J. M. Kim and Z. L. Wang, *Adv. Mater.*, 2011, **23**, 3446-3449.

167 D. Choi, M.Y. Choi, W. M. Choi, H.J. Shin, H.K. Park, J.S. Seo, J. 105 Park, S.M. Yoon, S. J. Chae, Y. H. Lee, S.W. Kim, J.Y. Choi, S. Y. Lee and J. M. Kim, *Adv. Mater.*, 2010, **22**, 2187-2192.

168 L. Yuan, X. Xiao, T. Ding, J. Zhong, X. Zhang, Y. Shen, B. Hu, Y. Huang, J. Zhou and Z. L. Wang, *Angew. Chem. Int. Edit.*, 2012, **51**, 4934-4938.

110 169 I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov and G. Yushin, *Science*, 2011, **333**, 75-79.

170 S. Sarkar, P. S. Veluri, S. Mitra, *Electrochim. Acta,*, 2014 **132** 448-456

171 J. Liu, Q. Zhang, Z. Wu, J. Wu, J. Li, L. Huang and S. Sun, *Chem.* 115 *Comm.*, 2014, **50**, 6386-6389

172 Y. Hou, Y. W. Cheng, T. Hobson and J. Liu, *Nano Lett.*, 2010, **10**, 2727-2733.

173 G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V. S. Battaglia, L. Wang and W. Yang, *Adv. Mater.*, 2011, 120 **23**, 4679-4683.

174 Y. Li, X. Zhao, Q. Xu, Q. Zhang and D. Chen, *Langmuir*, 2011, **27**, 6458-6463.

175 B. Kang and G. Ceder, *Nature*, 2009, **458**, 190-193.

176 G. Wang, X. Lu, Y. Ling, T. Zhai, H. Wang, Y. Tong and Y. Li, 125 *Acs Nano*, 2012, **6**, 10296-10302.

177 W. Lai, C. K. Erdonmez, T. F. Marinis, C. K. Bjune, N. J. Dudney, F. Xu, R. Wartena and Y. M. Chiang, *Adv. Mater.*, 2010, **22**, E139-E144.

178 C. J. Bae, C. K. Erdonmez, J. W. Halloran and Y. M. Chiang, *Adv.* 130 *Mater.*, 2013, **25**, 1254-1258.

179 L. Wang, D. Wang, X. Y. Dong, Z. J. Zhang, X. F. Pei, X. J. Chen, B. Chen and J. Jin, *Chem. Commun.*, 2011, **47**, 3556-3558.

180 M. Latorre-Sanchez, P. Atienzar, G. Abellan, M. Puche, V. Fornes, A. Ribera and H. Garcia, *Carbon*, 2012, **50**, 518-525.

135 181 Y. R. Lee, I. Y. Kim, T. W. Kim, J. M. Lee and S.-J. Hwang, *Chem Eur. J.*, 2012, **18**, 2263-2271.

182 Y. Li and Y. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 5851-5857.

183 H. Kang, G. Huang, S. Ma, Y. Bai, H. Ma, Y. Li and X. Yang, *J. Phys. Chem. C*, 2009, **113**, 9157-9163.

140 184 T. Sun, T. Qing, B. Su and L. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 2909-2921.

185 Q. Ye, F. Zhou and W. Liu, *Chem. Soc. Rev.*, 2011, **40**, 4244-4258.

186 L. Hu, M. Chen, X. Fang and L. Wu, *Chem. Soc. Rev.*, 2012, **41**, 1350-1362.

145 187 P.C. Chen, G. Shen, Y. Shi, H. Chen and C. Zhou, *Acs Nano*, 2010,

25, 2809-2815.

4, 4403-4411.

188 M. Duduta, B. Ho, V. C. Wood, P. Limthongkul, V. E. Brunini, W. C. Carter and Y. M. Chiang, *Adv. Energ. Mater.*, 2011, **1**, 511-516.

189 Y. R. Wang, P. He and H. S. Zhou, *Adv. Energ. Mater.*, 2012, **2**, 770-779.

190 W. Yarong, H. Ping and Z. Haoshen, *Adv. Energ. Mater.*, 2012, **2**, 770-779.

191 Y. Yang, G. Y. Zheng and Y. Cui, *Energ. Environ. Sci.*, 2013, **6**, 1552-1558.

192 Z. L. Wang, D. Xu, J. J. Xu, L. L. Zhang and X. B. Zhang, *Adv. Funct. Mater.*, 2012, **22**, 3699-3705.

193 M. B. Sassin, C. N. Chervin, D. R. Rolison and J. W. Long, *Acc. Chem. Res.*, 2012, **46**, 1062-1074.

194 H. Jiang, C. Li, T. Sun and J. Ma, *Chem. Commun.*, 2012, **48**, 2606-2608.

195 F. Cao, G. X. Pan, P. S. Tang and H. F. Chen, *J. Power Sources*, 2012, **216**, 395-399.

196 J. Zhu and J. He, *ACS Appl. Mater. Inter.*, 2012, **4**, 1770-1776.

197 H. P. Cong, X. C. Ren, P. Wang and S. H. Yu, *Acs Nano*, 2012, **6**, 2693-2703.

198 L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya and G. Yushin, *Adv. Energ. Mater.*, 2011, **1**, 356-361.

RSC Advances Accepted Manuscript