View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Yang, M. Shi, X. Song, X. Zhao, L. Zhao, J. Liu, P. Zhang and L. Gao, *J. Mater. Chem. A*, 2018, DOI: 10.1039/C8TA00255J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

ARTICLE



A Robust Hierarchical Microcapsule for Efficient Supercapacitors Bearing Ultrahigh Current Density of 300 A/g

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Cheng Yang, Minjie Shi, Xuefeng Song*, Xiaofeng Zhao, Liping Zhao, Jing Liu, Peng Zhang, Lian Gao*

A unique three dimensional (3D) hierarchical microcapsule structure (NiS_x@NCV) has been put forward , which is realized by the ensemble of N-doped carbon vesicles encapsulating dual-NiS_x (α -NiS/NiS₂) nanoparticles via an in situ nanospaceconfined pyrolysis strategy. The NiS_x@NCV shows a high pseudocapacitance of 1600 F/g at 1 A/g and impressive rate performance (capacitance retention ratio of 84.5%, from 1 to 25 A/g). Benefiting from the intriguing configuration, a kind of high performance asymmetric supercapacitors (ASCs) has been fabricated, using 3D NiS_x@NCV microcapsules and nanoporous carbon (NPC) as positive and negative electrodes, respectively. Remarkably, the fabricated ASCs achieve a capability of 135.06 F/g at 1 A/g and exhibit outstanding rate capability at 32 A/g. More importantly, a high capacitance retention ratio of 87% is still achieved even at current density from 32 to 300 A/g, which well displays the ultrahigh rate performance of NiS_x@NCV//NPC ASCs. In addition, NiS_x@NCV//NPC ASCs deliver an attractive energy density of 48.02 Wh/kg at a power density of 800 W/kg, and still maintain 30 Wh/kg even at an ultrahigh power density of 240 kW/kg. This is contributed to rich redox reaction and interface effect of dual-NiS_x nanoparticles, abundant active sites and high electrical conductivity from N-doped carbon vesicles.

Introduction

Published on 23 February 2018. Downloaded by RMIT University Library on 25/02/2018 16:10:53

Supercapacitors (SCs) have been considered as a promising power source for applications in portable electronic devices, electrical vehicles and stand-by power systems, owing to their fast charging/discharging process, long cycle life, security and reliability. Nickel sulfides, such as NiS¹⁻⁷, NiS₂⁸⁻¹⁰, Ni₃S₂¹¹⁻¹⁴, Ni₇S₆¹⁵ and Ni₃S₄¹⁶, have attracted increasing interest as electrodes for SCs because of their high redox activity and theoretical capacitance. Unfortunately, nickel sulfides based electrode material mostly suffers from mediocre rate capability, especially, while the current density is more than 10 A/g^{4, 5, 8, 9, 17}. For instance, NiS₂ nanocubes delivered a specific capacitance of 695 F/g at 1.25 A/g, whereas the capacitance only maintained 22.7% at 12.5 A/g⁹. It is ascribed to the insufficient electron transfer and ion diffusion rates between electrolyte and electrodes, as well as the lack of structural stability of those electrodes.

To address these problems, combining nickel sulfides with carbonaceous materials is regarded as a promising strategy, owing to their high conductivity, which delivers high electronic/ionic conductivities to reduce capacitance degradation, especially at high current densities^{11, 18-20}. In general, nitrogen-doped (N-doped) carbonaceous materials can increase the electrical conductivity of the electrode, and provide abundant active sites, which allow for

State Key Laboratory for Metallic Matrix Composite Materials,

School of Materials Science and Engineering,

*E-mail: songxfeng@sjtu.edu.cn (X. F. Song); liangao@mail.sic.ac.cn (L. Gao).

high charge transfer and ion diffusion rates between electrolyte and electrodes, leading to excellent rate capability²¹⁻²⁷. Despite these kinetics advances mentioned above, nickel sulfides inevitably tend to detach from the carbonaceous scaffold, such as graphene², carbon fibers and carbon nanotubes^{6, 13, 20}, especially at high current densities, due to the unfirm contact between nickel sulfides and carbonaceous species. For example, according to Zhang's report, NiS nanoparticles immobilized on N-doped carbon fiber aerogels (NiS/N-CFA) shows enhanced rate performance compared with pure NiS nanoparticles arising from higher conductivity⁶. However, only 60% of the specific capacitance at 1 A/g of NiS/N-CFA is retained when current density increases to 20 A/g. Consequently, it is desirable to develop a kind of nickel sulfides based electrode material that not only has kinetic virtue, including high conductivity, high surface area, plentiful active sites and porous structure, but also possesses sturdy stability of integral structure.

From the material configurations aspect, it is anticipated that control over the morphology and assembly of the original building blocks to 3D hierarchical hollow microspheres with high surface area as well as abundant accessible reaction sites could result in unifying structural stability with long cycle life and high electronic/ionic conductivities. More recently, extensive attention has been paid to the design of 3D hierarchical hollow architectures composed of subunits (e.g. nanoparticles, nanorods or nanosheets) in the applications of energy storage²⁸⁻⁴⁰. These progresses include the synthesis of self-assembled V_2O_5 hollow microspheres from nanorods²⁸, the preparation of hydrangea-like multi-scale carbon hollow submicron spheres³⁰, and the design of 3D CoS₂ hollow

Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ARTICLE

Published on 23 February 2018. Downloaded by RMIT University Library on 25/02/2018 16:10:53

microspheres constructed by nanosheets³³. Even though enhanced electrochemical performance in some cases, these 3D architectures still can hardly meet the demand for practical applications especially at high current densities, since the integrating force associating with van der Walls' interactions or chemical bonding between the contacting subunits in these 3D architectures is not enough to well maintain the integrity of structure³⁴. For instance, only 34.6% of the specific capacitance of the 3D CoS₂ hollow microspheres constructed by nanosheets is retained as the current density increases from 1 to 20 A/g. Hence, it is highly desirable but challenging to develop a kind of electrode material with ultrahigh rate performance for SCs.

In this work, we develop an in situ nanospace-confined pyrolysis strategy for 3D hierarchical microcapsule structure (NiS_x@NCV), in which dual-NiS_x (α -NiS/NiS₂) nanoparticle is well confined in the compartment of N-doped carbon vesicles. The ultrathin α -NiS layer was obtained in the control of the space-confinement by the Ndoped carbon vesicle. Moreover, the interface effect of α -NiS/NiS₂ encapsulated in N-doped carbon vesicles effectively enhances the rate performance. Such a design has multiple advantages: (1) the ultrathin α -NiS layer obtained through a space-confined reaction can be conductive to charge transport and Faradic reactions during the charge-discharge process, because of the higher conductivity and more Ni atoms exposed on the surface; (2) the rate performance is effectively enhanced owing to the interface effect of α -NiS/NiS₂ encapsulated in N-doped carbon vesicles, which provides abundant Faradic reactive sites for pseudocapacitance reaction; (3) the porous N-doped carbon vesicles derived from PDA can be utilized to improve the electrochemical performance, which not only provide plenty of active sites and rich access channels beneficial for charge storage, but also function as electrical highway to ensure all nanoparticles are electrochemically active, allowing for efficient charge transfer between the electrode and electrolyte; (4) the unique 3D hierarchical hollow structure can provide high surface area and effectively enhance the structural integrity of the whole microcapsule, since all nanoparticles are interconnected and linked up by N-doped carbon.

Benefiting from the intriguing architecture, NiS_x@NCV shows a high pseudocapacitance of 1600 F/g at 1 A/g, impressive rate performance (capacitance retention ratio of 84.5%, from 1 to 25 A/g) and strong durability (94.4% retention after 5000 cycles). Further, the high-performance asymmetric supercapacitors (ASCs) were fabricated, using 3D NiS_x@NCV microcapsules and nanoporous carbon (NPC) as positive and negative electrodes, respectively. Remarkably, the fabricated ASCs achieve a capability of 135.06 F/g at 1 A/g and exhibit outstanding rate capability at 32 A/g. More importantly, an ultrahigh specific capacitance is still maintained even at a high current density of 300 A/g (capacitance retention ratio of 87%, from 32 to 300 A/g), which well displays the ultrahigh rate performance of NiS_x@NCV//NPC ASCs. Moreover, the whole devices deliver a maximum energy density of 48.02 Wh/kg (based on the mass of active materials) at a power density of 800 W/kg and still remain an energy density of 30 Wh/kg even at an ultrahigh power density of 240 kW/kg, superior to those of previous nickel sulfides based ASCs.41, 42 Thereby, the fabricated NiS_x@NCV//NPC ASCs pave a novel and efficient way to fabricate high-power energy storage systems.

Experimental Synthesis of NiS₂

NiS₂ hollow spheres (pristine NiS₂) were generated through an exchanging reaction between rod-like supermolecular precursor and L-cysteine according to our previous work with some improvement⁴³. Firstly,1.5 g NiCl₂·6H₂O and 2.4 g sodium acetate were dissolved in 40 ml of ethylene glycol in a warm-water bath at 60 °C with constant agitation. Then, 0.8 g of polyethylene glycol and 2 g of deionized water were added into the mixture under vigorous agitation dropwise. The as-prepared green transparent solution was introduced into a 50 ml Teflon-lined autoclave. The reaction was kept at 160 °C for 1 h. After cooling to room temperature, the products were collected by centrifugation, washed with ethanol and deionized water for several times and finally dried in a vacuum oven at 60 °C overnight. 0.1 g nickel precursor synthesized above and 0.4 g L-cysteine were dissolved in 15 ml of deionized water with constantly stirring at room temperature. The as-formed brown solution was introduced into a Teflon-lined autoclave (25 ml) and maintained at 200 °C for 4 h. After cooling to room temperature, the products were collected by centrifugation and washed with deionized water several times. Eventually, the obtained products were dried in an oven at 60 °C overnight.

Synthesis of NiS_x@NCV microcapsules

The preparation of NiS_x@NCV microcapsules was carried out in two steps. Firstly, 0.2 g NiS₂ hollow spheres was incubated in 100 ml of the freshly prepared dopamine (DPA) solution (2 mg/mL) in Tris buffer (10 mM, pH 8.5) for 24 h at room temperature. Polymerization of DPA occurred in this incubation and resulted in crosslinking of NiS₂@PDA (polydopamine) composites after carefully cleaning. Secondly, followed by thermal treatment at 500 °C for 20 min under nitrogen atmosphere, the NiS₂@PDA composites were turned into NiS_x@NCV microcapsules. For comparison, the resultant black powder was collected and stirred in a 1 M HCl aqueous solution for 8 h to remove NiS, receiving NiS₂@PDA. MiS₂@PDA at 500 °C for 3 h under nitrogen atmosphere.

Characterization methods

Field emission scanning electron microscope (FESEM, FEI Sirion 200) and Transmission electron microscopy (TEM, JEM-2010F) were carried out to characterize the morphology of the samples. X-ray diffraction (XRD) patterns were characterized on a powder XRD system with Cu Ka radiation. Nitrogen absorption and desorption measurements were performed with an Autosorb IQ instrument at 77 K. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were determined from the adsorption branch of the isotherms based on the density functional theory (DFT).

Ex-situ X-ray diffraction

Before starting the ex-situ XRD test, cyclic voltammetry (CV) scanning with a rate of 50 mV/s has been conducted for 50 cycles to stabilize the electrochemical signature of the electrodes. For ex-situ XRD experiment, electrodes were charged and discharged at current density of 25 A/g, and the stop positions of the GCD test are

Journal Name

View Article Online DOI: 10.1039/C8TA00255J

shown in Fig. 4. Once the electrodes were charged and discharged to a desired voltage point, the GCD test paused and the electrodes were lifted out of the KOH solution to be washed clean and then tested by XRD analysis. After XRD analysis, the electrodes continued the unfinished GCD test until the next desired voltage point, and were lifted out of the KOH solution to be washed clean and then tested by XRD analysis. Above steps were repeated until getting all the XRD patterns of pristine NiS₂ and NiS_x@NCV electrodes at various constant potentials.

Electrochemical Measurements

All the electrochemical measurements were carried out using a VMP3 multi-functional electrochemical analysis instrument (Bio-Logic, France). Electrochemical behaviors were investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance (EIS) methods. The CV and GCD tests were measured at various scan rates and current densities. The EIS plots were performed in the frequency ranging from 0.05 Hz to 100 kHz with 5 mV AC amplitude. The working electrode was prepared by mixing our samples (NiS_x@NCV microcapsules, pristine NiS₂, NiS₂@NCV, NiS_x@NCV-2 or NPC) with acetylene black and polyvinylidenefluoride (PVDF) as the binder dissolved in N-methyl-2-pyrrolidone (NMP) in a weight ratio of 8:1:1. The resulting slurry was pressed onto the Ni foam current collector as the working electrodes. The platinum (Pt) foil and Hg/HgO electrodes were used as the counter and reference electrodes, respectively. All tests were conducted in a 6 M KOH electrolyte. The asymmetric supercapacitors were constructed in a coin cell by using a nanoporous carbon(denoted as NPC) electrode as the negative electrode, the NiS_x@NCV microcapsules electrode as the positive electrode and one piece of cellulose paper as the separator in 6 M KOH.

Results and discussion

A schematic illustration for the detailed evolution process of the 3D hierarchical NiS_x@NCV microcapsules assembled by N-doped carbon vesicles encapsulating dual-NiS_x nanoparticles is presented in Fig. 1a. Initially, based on the modified previous method⁴³, the hollow NiS₂ spheres (Fig. 1b) were prepared through a hydrothermal reaction. Sequentially, the dopamine was used as a bio-adhesive cross-linker to accomplish the uniform coating of Ndoped carbon precursor via an aqueous self-polymerization⁴⁵. Finally, the NiS₂/PDA was subjected to a carbonization of PDA layer and part-decomposition of inner encapsulated NiS₂, during which abundant pores/voids were generated in the α -NiS layer (converted from the incomplete reaction of NiS₂ to α -NiS)⁴⁵. Meanwhile, the outer PDA-coating layer was converted into amorphous carbon, making for uniform N-doped carbon-encapsulation of the microcapsules^{46, 47}. It has been reported that crystal structures may be determined by size constraint through crystallization of materials⁴⁸. Clearly, the space-confinement by the N-doped carbon vesicle is crucial to the formation of α -NiS and prevents its possible transformation to β-NiS.

As shown in the FESEM images (Fig. 1c and d), it is revealed that the $NiS_x@NCV$ microcapsules are highly uniform spheres with an



Fig. 1 (a) Schematic illustrations of the preparation process of NiS_x@NCV microcapsules. Typical FESEM images of (b) pristine NiS₂, (c) NiS_x@NCV microcapsules and (d) partially broken NiS_x@NCV microcapsules, respectively. TEM images (e-f) and high-resolution TEM (HRTEM) image (g) of NiS_x@NCV microcapsules.

average size of about 1.2 µm. The microcapsules show rough surface, and are composed of sphere-like subunits. Some of the microcapsules are partially broken (Fig. 1d and Fig. S1), clearly demonstrating the hollow nature of the as-prepared microcapsules, which is further confirmed by the transmission electron microscopy (TEM) images in Fig. 1e and f. It is worth mentioning that each microcapsule is coated with uniform carbon layer, wherein N-doped carbon serves as bridges for electrons transportation and ensures that all nanoparticles are electro-active, interconnected and linked up, thus preserving enhanced structural integrity compared to previous 3D hierarchical hollow architectures composed of nanoparticles^{35,36}, nanorods^{28,32} or nanosheets^{31,33}. The HRTEM image (Fig. 1g) displays amorphous carbon and the lattice interplanar spacings of around 0.27 and 0.296 nm corresponding to the distances of (200) plane of NiS₂⁸ and (100) plane of α -NiS¹⁷, respectively, indicating the successfully obtained carbon vesicles encapsulating α -NiS/NiS₂ in the NiS_x@NCV microcapsules. Meanwhile, the X-ray diffraction (XRD) pattern is consistent with the result of HRTEM, exhibiting both the typical peaks indexed to NiS₂ (JCPDF11-0099) and α -NiS (JCPDF02-1280) (Fig. 2a). Moreover, the NiS_x@NCV microcapsules possess higher specific surface area as high as 64.28 m²/g, pore volume of 0.208 cm³/g and abundant mesopores ranging from 3 to 12 nm (Fig. 2b), which is favorable for the electrolyte diffusion in and out of the electro-active materials^{49,} ⁵⁰. More characterization of NiS_x@NCV microcapsules are performed to further confirm the fine structure as shown in Fig. S1-5. From characterization for the NiS_x@NCV, the C coating content, N doping content are 14.82% and 7.72%, respectively. Additionally, the thickness of the carbon vesicles is about 10 nm. Profiting from this optimized architecture, it is expected that the robust NiS_x@NCV microcapsules with high specific surface area and abundant pores exhibit excellent rate capability and satisfactory cycling stability for SCs.



corresponding pore size distribution curve.

electrochemical performance of NiS_x@NCV The the microcapsules was evaluated by cyclic voltammograms (CV) and galvanostatic charge-discharge (GCD) measurements in a threeelectrode beaker cell with a 6 M KOH aqueous electrolyte. For comparison, pristine NiS₂, NiS₂@NCV and NiS_x@NCV-2 were also carried out at the same test conditions using the identical assembled configuration. As the annealing time prolonged, the amount of α -NiS increased while the amount of NiS₂ decreased within obtained product (denoted as NiS_x@NCV-2). More information about pristine NiS₂, NiS₂@NCV and NiS_x@NCV-2 are provided in the Fig. S6-8. The typical CV curves of NiS_x@NCV, pristine NiS₂, NiS₂@NCV and NiS_x@NCV-2 obtained with a scan rate of 5 mV/s display two peaks in the potential ranging from -0.1 to 0.38 V, which demonstrate the pseudocapacitive characteristics of the samples. The reaction mechanism is similar to those of previous literatures^{1, 8}, associated with the following reversible reaction: NiS-(1)

NIS+OH- NISOH+e-	
NiS ₂ +OH⁻≓NiS ₂ OH+e⁻	

Published on 23 February 2018. Downloaded by RMIT University Library on 25/02/2018 16:10:53

Obviously, NiS_x@NCV microcapsules exhibit larger CV areas than pristine NiS₂, NiS₂@NCV and NiS_x@NCV-2, indicating the greatly enhanced electrochemical performance of NiS_x@NCV microcapsules (Fig. S8). For NiS_x@NCV, the anodic peak shifts towards positive potential while the cathodic peak shifts towards negative potential with the increasing scan rate (Fig. 3a), which rapid electronic/ionic transport indicates and plentiful electrochemical active surface area of the electrode⁶.

(2)

Fig. 3b shows the GCD curves of the NiS_x@NCV electrode, wherein the negligible "IR drop" of discharge curve is observed, strongly evincing the low internal resistance of the electrode. According to Fig. 3c, the calculated discharge capacitance of NiS_x@NCV microcapsules is 1600, 1550, 1498, 1466, 1431 and 1348 F/g at current densities of 1, 5, 10, 15, 20 and 25 A/g, respectively (Fig. 3c). Notably, for the NiSx@NCV microcapsules electrode, the capacitance retention rate as high as 84.25% is much higher than those of pristine NiS₂, NiS₂@NCV, NiS_x@NCV-2 and previously reported nickel sulfides based materials (Table S1), such as NiS2 nanocubes (capacitance retention ratio of 22.7%, from 1.25 to 12.5 A/g)⁹, NiS nanoframes (capacitance retention ratio of 33.6%, from 1 to 20 A/g)⁴ and Ni₃S₂/MWCNT (capacitance retention ratio of 46.8%, from 0.8 to 25 A/g)¹¹. Additionally, 80% of the specific capacitance at 1 A/g of $NiS_x@NCV-2$ is retained as the discharge current density increases to 25 A/g, which is comparable to that observed for NiS_x@NCV. However, the specific capacitance of NiS_x@NCV-2 is much lower than that of NiS_x@NCV at the same current densities, due to the lower theoretical specific capacitance of α -NiS. Moreover, the NiS_x@NCV electrode exhibits a durable cycle life with



Fig. 3 (a) CV curves at various scan rates (2-100 mV/s), and (b) GCD curves at different current densities (1-25 A/g) of NiS_x@NCV electrode. (c) The specific capacitances at various current densities, (d) cycling stabilities at a current density of 1 A/g for 5000 cycles of NiS_x@NCV, NiS₂@NCV, NiS_x@NCV-2 and pristine NiS₂ electrodes. Inset in d shows the EIS plots of NiS_x@NCV, NiS₂@NCV, NiS_x@NCV-2 and pristine NiS₂ electrodes.

only 5.64% capacitance loss after 5000 cycles while the pristine NiS₂ electrode suffers from 30% capacitance loss during the long cycle life (Fig. 3d). Obviously, NiS_x@NCV and NiS_x@NCV-2 exhibit more durable cycling stability and higher rate capability compared with pristine NiS₂ and NiS₂@NCV, attributed to enhanced structural stability and higher electronic/ionic conductivities, which is supported by their FESEM images after 5000 cycles (Fig. S9) and EIS plots (inset in Fig. 3d).

In order to provide insights into the electrochemical reaction of pristine NiS₂ and NiS_x@NCV in 6 M KOH, ex-situ XRD analysis coupled with GCD test has been performed. Before starting the exsitu XRD test, cyclic voltammetry (CV) scanning with a rate of 50 mV/s has been conducted for 50 cycles to stabilize the electrochemical signature. The GCD curves for pristine NiS2 and NiS_x@NCV at high current density of 25 A/g are shown in Fig. 4a and b. The XRD diffraction patterns of pristine NiS₂ and NiS_x@NCV electrodes were recorded at various potentials (A, B, C, D and E) during the galvanostatic charging-discharging cycle (Fig. 4c and d). As for charging section, the XRD patterns recorded in this potential region (A to C) clearly reveal a shift of the reflections to lower 20 values, indicating an increase of the lattice parameters due to the expansion of the NiS₂ and α -NiS host lattice caused by the intercalation of OH⁻ within the electrodes⁵¹⁻⁵³. Then a progressive shift of the NiS₂ (200) and α -NiS (100) peaks to higher 2 θ values is observed when discharged from 0.38 V back to -0.1 V, which evidences a decrease of the lattice spacings, ascribed to the

ARTICLE

Chemistry

Materials



Fig. 4 GCD curves at high current density of 25 A/g of (a) pristine NiS₂ and (b) NiS_x@NCV electrodes. Electrochemical ex-situ X-ray diffraction study of (c) pristine NiS₂ and (d) NiS_x@NCV electrodes at various constant potentials in 6 M KOH electrolyte. The scans referring to the different potentials marked in panel a and b are indicated by different colors: A black, B red, C blue, D green and E magenta.

deintercalation of OH⁻ in the NiS₂ and α -NiS. In the case of pristine NiS₂ electrode, the (200) peak initially observed at 31.580° at -0.1 V shifts to 31.217° when charged to 0.38 V. However, even when discharged to -0.1 V, the (200) peak can not reversibly shift back to the original 20 position, more specifically about a decrease of 0.205°. In contrast, as for NiS_x@NCV electrode, the (100) peak of α -NiS initially occurred at 30.160° and shifts to 29.998°, while the (200) peak of NiS₂ exhibits a decrease of 0.171° from 31.580° when

charged to 0.38 V. Then, the (100) and (200) peaks shift to 30.073° and 31.506° when discharged to -0.1 V, respectively, which are nearly the same as their original 20 positions, demonstrating a relatively reversible transition within NiS_x@NCV electrode during the charging-discharging cycle at high current density⁵¹. It is concluded that the structural stability of NiS_x@NCV microcapsules has been effectively enhanced during the electrochemical reactions especially at high current density, which is contributed to high rate capability and strong durability.

Nanoporous carbon (NPC) is one of the most promising candidates for constructing ASCs owing to the high specific surface area and appropriate pore structure⁵⁴⁻⁶². Herein, metal-organic frameworks (MOF)-derived NPC obtained via direct carbonization of ZIF-8, a well-studied MOF material with unique polyhedral morphology, is prepared as the negative electrode material. It is worth mentioning that ZIF-8 derived NPC can not only retain the stable porous architecture, but also provide a high specific surface area, which is beneficial to the electrochemical performances of electrodes. As shown in the FESEM image of NPC (Fig. 5a), it is confirmed that the NPC is composed of uniformly sized and dispersed particles with rhombic dodecahedral shape. The average particle size is around 1.5 µm. The magnified FESEM image (inset in Fig. 5a) shows that NPC possesses well-defined polyhedral shape with sharp edges and smooth surface. Moreover, Fig. 5b gives the TEM image of NPC, which reveals that NPC has a uniform texture without large cavity or cracks. The magnified TEM image (inset in Fig. 5b) on the edge of the NPC clearly presents the existence of plentiful micro-/mesopores, which indicates the nanoporous characteristic of NPC. It is worth noting that the BET specific surface



Fig. 5 (a) FESEM image and (b) TEM image of nanoporous carbon particles. Inset in a is the magnified FESEM image of NPC and inset in b is the magnified TEM image on the edge of the NPC. (c) Nitrogen adsorption/desorption isotherm of nanoporous carbon particles. Inset in c is the corresponding pore size distribution curve. (d) CV curves at various scan rates (20-500 mV/s) and (e) the specific capacitances at various current densities (1-25 A/g) of nanoporous carbon particles. Inset in e is the corresponding GCD curves at different current densities (1-25 A/g). (f) Cycling stability of the NPC electrode at a current density of 1 A/g for 5000 cycles, and the inset shows the corresponding EIS spectra.

Published on 23 February 2018. Downloaded by RMIT University Library on 25/02/2018 16:10:53

Page 6 of 9





Fig. 6 (a) Schematic illustration of the asymmetric supercapacitor configuration. (b) CV curves at various scan rates (5-500 mV/s) and (c) the specific capacitances at various current densities (1-300 A/g) of the NiS_x@NCV//NPC asymmetric supercapacitor. Inset in c is the corresponding GCD curves at different current densities. (d) Comparative Ragone plots of the energy density and power density of our NiS_x@NCV//NPC ASCs with various previously reported nickel sulfides based supercapacitors. (e) Cycling stability of the NiS_x@NCV//NPC ASCs at a current density of 1 A/g for 10000 cycles, and the inset shows the corresponding EIS spectra.

area of NPC is up to 1620 m²/g (Fig. 5c). The pore size distribution (inset of Fig. 5c) reveals the abundant mesopores (about 2.6 nm) of the NPC, which is beneficial to the ionic diffusion and charge transport. More characterization of nanoporous carbon particles are described in Fig. S10 and 11.

The CV curves of NPC measured in 6 M KOH solution exhibit the typical rectangular shapes without obvious distortion even at a scan rate of 500 mV/s (Fig. 5d), indicating an ideal capacitance behavior and fast diffusion of electrolyte ions within the electrode. It is also supported by the near-triangle GCD curves of NPC at various current densities (1-25 A/g) within a potential window of -1-0 V (inset of Fig. 5e). The negligible "IR drop" of discharge curve strongly evinces the favorable resistance of the NPC based electrode (inset in Fig. 5e). By calculating, the NPC based electrode delivers large specific capacitance as high as 400 F/g at 1 A/g (Fig. 5e), higher than that of previous advanced carbon based negative electrodes⁶³⁻⁶⁵. Furthermore, the NPC electrode shows a superior cycling stability with high retention of 97.46% of the initial capacity after 5000 cycles at 1 A/g (Fig. 5f), owing to the unique architecture of the polyhedron that may avoid the stacking/aggregation problem (because of multi-face) during the repeated charge/discharge processes (Fig. S12)⁵⁴. Profiting from the excellent electrochemical performances, it is obvious that NPC has a great potential application in the field of high-efficient ASCs.

On the basis of the excellent electrochemical performance of both NiS_x@NCV microcapsules and NPC, the NiS_x@NCV//NPC ASCs

are fabricated in 6 M KOH solution by using NiS_x@NCV and NPC as the positive and negative electrodes (with mass loading of 1.5 mg/cm²), respectively (Fig. 6a). The CV curves of this device exhibit obvious capacitance from both electric double-layer capacitance and pseudocapacitance with a wide working voltage window of 1.6 V (Fig. 6b). As shown in the GCD curves (inset in Fig. 6c and Fig. S13), no obvious "IR" drop is observed, connoting the low internal resistance of the ASCs (0.9 Ω , inset in Fig. 6e). Calculated from the GCD curves, the fabricated ASCs achieve a maximum capability of 135.06 F/g at 1 A/g and exhibit high rate capability at 32 A/g. The specific capacitance was slightly increased with the current density increasing between 32 and 75 A/g. It might be attributed to the activation caused by high-rate discharging/charging. With the progress of charging and discharging, the electrochemical active channel gradually opened and the electrolyte was fully immersed, which was conducive to giving full play to the capacitance characteristics of the electrode material. More interestingly, the NiS_x@NCV//NPC ASCs can achieve ultrahigh capacitance retention ratio of 87% from 32 to 300 A/g (Fig. 6c), which outperform most previously reported nickel sulfides based ASCs (Table S2), such as NiS microflower//AC (capacitance retention ratio of 43.7%, from 1 A/g to 10 A/g)¹⁷, Ni₂S₃@ β -NiS//AC (capacitance retention ratio of 39.8%, from 1 A/g to 30 A/g)¹⁴ and Ni₃S₂/CNF//CNF (capacitance retention ratio of 62.5%, from 1 A/g to 10 A/g) 13 .

By calculating, the assembled ASCs deliver a maximum energy density up to 48.02 Wh/kg at a power density of 0.8 kW/kg and still maintain 30 Wh/kg even at an ultrahigh power density of 240

kW/kg (Fig. 6d and Fig. S14), higher than those of previously reported nickel sulfides based ASCs (Table S2), such as Ni₃S₂//AC (34.6 Wh/kg at 0.15 kW/kg)¹² and NiS₂/ZnS//AC (28 Wh/kg at 0.75 kW/kg)¹⁰. Thanks to the high energy density and high power density, the assembled ASC can light up a 1 W lamp after fully charged (Fig. S15). As known, the long-term cycling stability is a critical parameter to evaluate the electrochemical performance of SCs for practical applications. Hence, the NiS_x@NCV//NPC ASCs are investigated by repeating the galvanostatic charge-discharge between 0 and 1.6 V at a current density of 1 A/g (Fig. 6e). It can be clearly observed that the assembled ASCs show a capacitance retention ratio of 93.9% after 10000 cycles, demonstrating the excellent cycling stability and superiority to most previously reported nickel sulfides based ASCs, including NiS/NF//AC (90.6% retention after 1000 cycles)¹, rod-like NiS₂//rGO (84.1% retention after 4000 cycles)⁸ and Ni₃S₂//AC (85.7% retention after 1000 cycles)¹². After performing numerous cycles, the NiS_x@NCV still retained almost the original topography structure, showing little as-fabricated ASCs inherit the excellent collapse. The electrochemical performance of both NiS_x@NCV and NPC electrodes, while display low internal resistance (0.96 Ω) and maintain good conductivity after cycling (Fig. S19) as well as fast charge transfer (inset in Fig. 6e).

The excellent electrochemical behaviors of NiS_x@NCV//NPC ASCs can be attributed to the following aspects: (1) compared with NiS₂, the ultrathin α -NiS layer has higher conductivity and more Ni atoms exposed on the surface (as shown in Fig. S16 and 17), which is propitious to charge transport and Faradic reactions during the charge–discharge process; (2) the interface effect of α -NiS/NiS₂ encapsulated in N-doped carbon vesicles provides abundant Faradic reactive sites for pseudocapacitive reaction, which is confirmed by comparison of specific capacitance among pristine NiS₂, NiS₂@NCV and NiS_x@NCV (Fig. 3c); (3) the porous N-doped carbon vesicles provide plenty of active sites and rich access channels favorable for charge storage, and function as electrical highway to make all nanoparticles electrochemically active, which allows for efficient charge transfer between the electrode and electrolyte; (4) in a whole NiS_x@NCV microcapsule, the unique 3D hierarchical hollow structure can provide high surface area and ensure the ions from both outer and inner faces to be charged and transferred, while the structural integrity of the whole microcapsule during the charge/discharge cycles is effectively enhanced since all nanoparticles are interconnected and linked up by N-doped carbon, which conduces to high rate capability and strong durability; (5) NPC with well-defined polyhedral shape possesses high specific surface area and plentiful micro-/mesopores, which are beneficial to the ionic diffusion and charge transport, and may avoid the stacking/aggregation problem (because of multi-face) during the repeat charge/discharge processes. Based on above merits, the fabricated NiS_x@NCV//NPC ASCs exhibit ultrahigh rate performance, while achieve high energy density even at an ultrahigh power density, as well as durable cycling life, representing appealing potential for ultrahigh rate SCs in the vehicles, lifts and the other devices.

Conclusions

In conclusion, 3D hierarchical NiS_x@NCV microcapsules have been successfully prepared via a hydrothermal method combined with pyrolysis of PDA. Owing to the high contact area, porous structure, good electronic conductivity, rich active sites, and the interface effect of α-NiS/NiS₂ as well as superior structure stability of 3D hierarchical microcapsules, the as-obtained NiS_x@NCV microcapsules deliver high specific capacitance up to 1600 F/g at 1 A/g and exhibit ultrahigh rate performance (capacitance retention ratio of 84.5%, from 1 to 25 A/g) as well as durable cycling life, which contributes to the excellent electrochemical performance of the ASCs using NiS_x@NCV and NPC as the positive and negative electrodes, respectively. As a result, the fabricated ASCs exhibit a maximum energy density up to 48.02 Wh/kg, maintain 30 Wh/kg at an ultrahigh power density of 240 kW/kg, and display satisfactory cycling stability (93.9% after 10000 cycles) as well as remarkable rate performance even at an ultrahigh current density of 300 A/g (capacitance retention ratio of 87%, from 32 to 300 A/g). After charging, the assembled ASC can light up a 1 W lamp. The work puts forward hierarchical microcapsules and represents a conceptual leap forward, addressing the moderate rate performance of nickel sulfides. Therefore, this encouraging novel electrode can open up the possibility of nickel sulfides based materials for numerous applications in SCs with ultrahigh rate performance, high energy density and power density, and strong durability to meet the diverse demands of high-power energy storage systems.

Acknowledgements

The authors greatly thank Dr. Zhuang Sun for the valuable discussion. This work was supported by the Shanghai Municipal Natural Science Foundation(17ZR1414900), the Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructure(SKL201604SIC), the Shanghai Jiao Tong University Medical (Science) Cross Fund(YG2017MS02), the Shanghai Aerospace Science and Technology Innovation Foundation Project, the Advanced Energy Material and Technology Center of Shanghai Jiao Tong University, and the National Natural Science Foundation of China (51302169, 51672174).

Notes and references

1. L. Yu, B. Yang, Q. Liu, J. Liu, X. Wang, D. Song, J. Wang, X. Jing, J. *Electroanal. Chem.*, 2015, **739**, 156-163.

2. F. Cai, R. Sun, Y. Kang, H. Chen, M. Chen, Q. Li, RSC Adv., 2015, 5, 23073-23079.

3. Y. Li, K. Ye, K. Cheng, J. Yin, D. Cao, G. Wang, *J. Power Sources*, 2015, **274**, 943-950.

4. X. Y. Yu, L. Yu, H. B. Wu, X. W. Lou, Angew. Chem. Int. Ed., 2015, 54, 5331-5335.

ARTICLE

Published on 23 February 2018. Downloaded by RMIT University Library on 25/02/2018 16:10:53

5. Z. Wang, C. Nan, D. Wang, Y. Li, RSC Adv., 2014, 4, 47513-47516.

6. Y. Zhang, L. Zuo, L. Zhang, J. Yan, H. Lu, W. Fan, T. Liu, Nano Res., 2016, 9, 2747-2759.

- 7. J. Yang, X. Duan, Q. Qin, W. Zheng, J. Mater. Chem. A, 2013, 1, 7880-7884.
- 8. Y. Ruan, J. Jiang, H. Wan, X. Ji, L. Miao, L. Peng, B. Zhang, L. Lv, J. Liu, J. Power Sources, 2016, 301, 122-130.

9. H. Pang, C. Wei, X. Li, G. Li, Y. Ma, S. Li, J. Chen, J. Zhang, Sci. Rep., 2014, 4, 3577.

- 10. G. C. Li, M. Liu, M. K. Wu, P. F. Liu, Z. Zhou, S. R. Zhu, R. Liu, L. Han, RSC Adv., 2016, 6, 103517-103522.
- 11. C. S. Dai, P. Y. Chien, J. Y. Lin, S. W. Chou, W. K. Wu, P. H. Li, K. Y. Wu, T. W. Lin, ACS Appl. Mater. Interfaces, 2013, 5,12168-12174.
- 12. H. H. Huo, Y. Q. Zhao, C. L. Xu, J. Mater. Chem. A, 2014, 2, 15111-15117.
- 13. W. D. Yu, W. R. Lin, X. F. Shao, Z. X. Hu, R. C. Li, D. S. Yuan, J. Power Sources, 2014, 272, 137-143.
- 14. W. Li, S. Wang, L. Xin, M. Wu, X. Lou, J. Mater. Chem. A, 2016, 4, 7700-7709.
- 15. Z. Li, J. Han, L. Fan, R. Guo, CrystEngComm, 2015, 17, 1952-1958. 16. Y. Zhang, W. Sun, X. Rui, B. Li, H. T. Tan, G. Guo, S. Madhavi, Y. Zong, Q. Yan, Small, 2015, 11, 3694-3702.
- 17. B. Guan, Y. Li, B. Yin, K. Liu, D. Wang, H. Zhang, C. Cheng, Chem. Eng. J., 2017, 308, 1165-1173.

18. C. Wei, C. Cheng, J. Zhao, Y. Wang, Y. Cheng, Y. Xu, W. Du, H. Pang, Chem. - Asian J., 2015, 10, 679-686.

19. Z. C. Xing, Q. X. Chu, X. B. Ren, J. Q. Tian, A. M. Asiri, K. A. Alamry, L. Liu, C. W. Cheng, S. J. Pennycook, John Wang, Adv. Mater., 2017, A. O. Al-Youbi, X. P. Sun, Electrochem. Commun., 2013, 32, 9-13.

20. T. Zhu, H. B. Wu, Y. Wang, R. Xu, X. W. Lou, Adv. Energy Mater., 2012, 2, 1497-1502.

21. S. H. Yang, X. F. Song, P. Zhang, L. Gao, ACS Appl. Mater. Interfaces, 2013, 5, 3317-3322.

22. X. Cui, X. Chen, S. Chen, F. Jia, S. Yang, Z. Lin, Z. Shi, H. Deng, J. Alloys Compd., 2017, 693, 955-963.

23. Z. Gao, X. Liu, J. Chang, D. Wu, F. Xu, L. Zhang, W. Du, K. Jiang, J. Power Sources, 2017, 337, 25-35.

24. F. Sun, J. Gao, X. Pi, L. Wang, Y. Yang, Z. Qu, S. Wu, J. Power Sources, 2017, 337, 189-196.

25. K. Zhao, K. Lyu, S. Liu, Q. Gan, Z. He, Z. Zhou, J. Mater. Sci., 2017, **52**, 446-457.

26. P. lamprasertkun, A. Krittayavathananon, A. Seubsai, N. Chanlek, P. Kidkhunthod, W. Sangthong, S. Maensiri, R. Yimnirun, S. Nilmoung, P. Pannopard, S. Ittisanronnachai, K. Kongpatpanich, J. Limtrakul, M. DOI: 10.1039/C8TA00255J Sawangphruk, Sci. Rep., 2016, 6, 37560.

27. K. Wang, M. Xu, Y. Gu, Z. Gu, Q. H. Fan, J. Power Sources, 2016, **332**, 180-186.

28. G. Cao, J. S. Hu, H. P. Liang, L. J. Wan, Angew. Chem. Int. Ed., 2005, 44, 4391-4395.

29. D. Wu, F. Zhu, J. Li, H. Dong, Q. Li, K. Jiang, D. Xu, J. Mater. Chem., 2012, 22, 11665-11671.

30. D. Guo, X. A. Chen, Z. Fang, Y. He, C. Zheng, Z. Yang, K. Yang, Y. Chen, S. Huang, Electrochim. Acta, 2015, 176, 207-214.

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

32. W. J. Hao, S. M. Chen, Y. J. Cai, L. Zhang, Z. X. Li, S. J. Zhang, J. Mater. Chem. A, 2014, 2, 13801-13804.

33. S. J. Peng, L. L. Li, H. T. Tan, R. Cai, W. H. Shi, C. C. Li, S. G. Mhaisalkar, M. Srinivasan, S. Ramakrishna, Q. Y. Yan, Adv. Funct. Mater., 2014, 24, 2155-2162.

34. M. Mo, J. C. Yu, L. Z. Zhang, S. K. A. Li, Adv. Mater., 2005, 17, 756-760.

35. H. Li, L. Shen, G. Pang, S. Fang, H. Luo, K. Yang, X. Zhang, Nanoscale, 2015, 7, 619-624.

36. T. Li, X. Li, Z. Wang, H. Guo, Q. Hu, W. Peng, Electrochim. Acta, 2016, 209, 456-463.

37. C. Guan, X. M. Liu, W. N. Ren, X. Li, C. W. Cheng, John Wang, Adv. Energy Mater., 2017, 7, 1602391.

38. C. Guan, A. Sumboja, H. J. Wu, W. N. Ren, X. M. Liu, H. Zhang, Z. **29**, 1704117.

39. C. Guan, W. Zhao, Y. T. Hu, Z. C. Lai, X. Li, S. J. Sun, H. Zhang, A. K. Cheetham, John Wang, Nanoscale Horiz., 2017, 299, 99-105.

40. C. Guan, Y. D. Wang, Y. T. Hu, J. L. Liu, K. H. Ho, W. Zhao, Z. X. Fan, Z. X. Shen, H. Zhang, John Wang, J. Mater. Chem. A, 2015, 3, 23283-23288.

41. J. Wang, K. Y. Ma, J. Zhang, F. Liu, J. P. Cheng, J. Colloid Interface Sci., 2017, 507, 290-299.

42. J. Balamurugan, C. Li, T. D. Thanh, O. K. Park, N. H. Kim, J. H. Lee, J. Mater. Chem. A, 2017, 5, 19760-19772.

43. X. F. Song, W. H. Shen, Z. Sun, C. Yang, P. Zhang, L. Gao, Chem. Eng. J., 2016, 290, 74-81.

45. J. Liu, Y. R. Wen, Y. Wang, P. A. Van Aken, J. Maier, Y. Yu, Adv.

This journal is C The Royal Society of Chemistry 20xx

^{44.} B. Li, Y. Chen, X. Ge, J. Chai, X. Zhang, T. S. A. Hor, G. Du, Z. Liu, H. Zhang, Y. Zong, Nanoscale, 2016, 8, 5067-5075.

- Mater., 2014, 26,6025-6030.
- 46. K. Tang, L. J. Fu, R. J. White, L. H. Yu, M. M. Titirici, M. Antonietti,
- J. Maier, Adv. Energy Mater., 2012, 2, 873-877.
- 47. J. Liu, Y. Wan, C. Liu, W. Liu, S. Ji, Y. Zhou, J. Wang, *J. Inorg. Chem.*, 2012, **24**, 3825-3829.
- 48. C. Sun, M. Ma, J. Yang, Y. Zhang, P. Chen, W. Huang, X. Dong, *Sci. Rep.*, 2014, **4**, 7054.
- 49. S. H. Yang, X. F. Song, P. Zhang, L. Gao, ACS Appl. Mater. Interfaces, 2015, **7**, 75-79.
- 50. M. J. Shi, T. H. Wu, X. F. Song, J. Liu, L. P. Zhao, P. Zhang, L. Gao, J.
- Mater. Chem. A, 2016, 4, 10666-10672.
- 51. Z. Lin, P. Rozier, B. Duployer, P. L. Taberna, B. Anasori, Y. Gogotsi,
- P. Simon, *Electrochem. Commun.*, 2016, **72**, 50-53.
- 52. G. Minoli, Science, 2013, 341, 1502-1505.
- 53. D. Bresser, E. Paillard, R. Kloepsch, S. Krueger, M. Fiedler, R. Schmitz, D. Baither, M. Winter, S. Passerini, *Adv. Energy Mater.*, 2013, **3**, 513–523.
- 54. R. R. Salunkhe, C. Young, J. Tang, T. Takei, Y. Ide, N. Kobayashi, Y. Yamauchi, *Chem. Commun.*, 2016, **52**, 4764-4767.
- 55. W. Chaikittisilp, M. Hu, H. Wang, H. S. Huang, T. Fujita, K. C. W. Wu, L. C. Chen, Y. Yamauchi, K. Ariga, *Chem. Commun*, 2012, **48**, 7259-7261.
- 56. Y. L. Gao, J. X. Wu, W. Zhang, Y. Y. Tan, J. Gao, J. C. Zhao, T. Bohejin, *J. Solid State Electrochem.*, 2014, **18**, 3203-3207.
- 57. C. Young, R. R. Salunkhe, J. Tang, C. C. Hu, M. Shahabuddin, E. Yanmaz, M. S. A. Hossain, J. H. Kim, Y. Yamauchi, *Phys. Chem. Chem. Phys.*, 2016, **18**, 29308-29315.
- 58. Y. Wang, B. Chen, Y. Zhang, L. Fu, Y. Zhu, L. Zhang, Y. Wu, *Electrochim. Acta*, 2016, **213**, 260-269.
- 59. S. Liu, J. Zhou, Z. Cai, G. Fang, Y. Cai, A. Pan, S. Liang, *J. Mater. Chem. A*, 2016, **4**, 17838-17847.
- 60. D. Yu, B. Wu, J. Ran, L. Ge, L. Wu, H. Wang, T. Xu, *J. Mater. Chem. A*, 2016, **4**, 16953-16960.
- 61. Y. Zhang, B. Lin, J. Wang, J. Tian, Y. Sun, X. Zhang, H. Yang, *J. Mater. Chem. A*, 2016, **4**, 10282-10293.
- 62. M. Jiang, X. Cao, D. Zhu, Y. Duan, J. Zhang, *Electrochim. Acta*, 2016, **196**, 699-707.
- 63. K. Wang, Y. Song, R. Yan, N. Zhao, X. Tian, X. Li, Q. Guo, Z. Liu, *Appl. Surf. Sci.*, 2017, **394**, 569-577.
- 64. D. Lei, K. H. Song, X. D. Li, H. Y. Kim, B. S. Kim, *J. Mater. Sci.*, 2017, **52**, 2158-2168.
- 65. C. Wang, D. Liu, S. Chen, Y. Sang, Y. A. Haleem, C. Wu, W. Xu, Q.

Fang, M. Habib, J. Cao, Z. Niu, P. M. Ajayan, L. Song, *Small* 2016, 12, 5684-5691.

ARTICLE

This journal is © The Royal Society of Chemistry 20xx