PCCP

PAPER

Check for updates

Cite this: Phys. Chem. Chem. Phys., 2017, 19, 13696

Received 14th February 2017, Accepted 16th March 2017

DOI: 10.1039/c7cp00990a

rsc.li/pccp

Introduction

Over the past few decades, lithium ion batteries (LIBs) have been applied in portable electronic devices and electric vehicles due to their high energy density and long cycle life.^{1–4} However, the limited resources of lithium have led to a drastic increase in cost. Thus, a substitute for lithium is highly needed. Sodium, with similar physicochemical properties to lithium, is an abundant and cheap element. Therefore, sodium ion batteries (SIBs) represent potential alternatives for developing low-cost and large-scale energy storage devices.^{5–9} However, the ionic radius of sodium is larger than that of lithium (98 *vs.* 69 pm), resulting in sluggish kinetics, dramatic volume variation, and fast capacity fading. Electrode materials with fast kinetics and small volume change during Na⁺ intercalation/de-intercalation

E-mail: mlq518@whut.edu.cn, liangzhou@whut.edu.cn

Methyl-functionalized MoS₂ nanosheets with reduced lattice breathing for enhanced pseudocapacitive sodium storage[†]

Lei Huang,^a Qiulong Wei,^a Xiaoming Xu,^a Changwei Shi,^a Xue Liu,^a Liang Zhou*^a and Liqiang Mai ^b*^{ab}

Sodium ion batteries (SIBs) possess the potential to realize low-cost and large-scale energy storage due to the abundance of sodium. However, the large ionic radius of sodium often leads to sluggish kinetics and large volume change, limiting the further development of SIBs. Layered MoS_2 , with a large interlayer distance, is a promising intercalation anode material for SIBs. In this work, we report the synthesis of methyl-functionalized MoS_2 (M-MoS₂) nanosheets through a facile second solvothermal method. During the second solvothermal treatment, the pristine MoS_2 is mostly converted from the 2H to 1T phase and the interlayer distance is expanded from 0.65 to 0.80 nm. When evaluated as the anode for SIBs, the M-MoS₂ exhibits superior cycling stability and rate capability. Kinetic analysis shows that the capacity is mainly contributed from a pseudocapacitive process. *Ex situ* XRD shows that the M-MoS₂ exhibits inhibited lattice breathing and thus reduced volume change during cycling. This work demonstrates that the M-MoS₂ is a promising candidate for pseudocapacitive sodium storage.

are highly desired. Pseudocapacitance generated from redox reactions often shows high power density and long cycle life, because the process is non-diffusion-controlled and does not cause large volume change.^{10–12} Therefore, it is expected that SIBs with longer cycle life and better rate capability can be achieved by taking advantage of pseudocapacitive sodium storage. To realize intercalation pseudocapacitive charge storage, the electrode material should possess the following characteristics:^{13–16} (1) nanosized structure to reduce the ion diffusion length; (2) high conductivity and rapid ion diffusion; (3) no phase transition during electrochemical reactions. Hence, to realize reversible and rapid sodium storage, materials with small size, large diffusion channels, high conductivity and no phase transition during electrochemical reactions are required.

Two-dimensional (2D) 2H MoS₂, which consists of trigonal prismatic coordination of sulfur around the molybdenum and stacks along the *c*-axis through van der Waals forces, possesses an interlayer distance of 0.62 nm.^{17,18} The 2D structure can facilitate the insertion/extraction of Na⁺. However, MoS₂ suffers from large lattice breathing along the *c*-axis and dramatic volume change, leading to the collapse of the 2D structure and fast capacity fading.¹⁹ Besides, during ion intercalation process, MoS₂ also suffers from a phase transition from the semiconducting 2H to the metallic 1T phase and the coordination environment of Mo atoms changes from trigonal prismatic to octahedral.^{20–22} Several studies have focused on expanding the interlayer spacing to reduce the structural change and facilitate

View Article Online

CHEMISTRY

^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, Hubei, China.

^b Department of Chemistry, University of California, Berkeley, California 94720, USA

[†] Electronic supplementary information (ESI) available: SEM, TEM and HRTEM images and SAED pattern of the pristine MoS₂; FTIR results of M-MoS₂, MoS₂ and methanol; Raman spectra of M-MoS₂ and MoS₂; the discharge/charge curves of M-MoS₂ and MoS₂ at a current density of 1 A g⁻¹; the rate performances of M-MoS₂ and MoS₂; log(*i*) vs. log(v) plots and the capacitive contributions analysis results of M-MoS₂ and MoS₂, and the morphology of M-MoS₂ after cycling. See DOI: 10.1039/c7cp00990a

Paper

Na⁺ diffusion.^{23,24} For example, Hu et al. expanded the interlayer spacing of MoS₂ to 0.67 nm through a hydrothermal method and its electrochemical performance was enhanced; further kinetic analysis showed that the insertion/extraction of Na⁺ were pseudocapacitive processes.²³ In order to inhibit the phase transition during the electrochemical reaction, stabilized 1T MoS₂ has to be prepared. Several methods have been proposed to stabilize 1T MoS₂, such as pre-intercalation,^{25,26} doping,²⁷ and covalentfunctionalization.²⁸ Recently, 1T@2H MoS₂ was synthesized through solvothermal treatment of MoS₂ in ethanol.^{29,30} This approach incorporates 1T MoS₂ into the 2H MoS₂ matrix and introduces ferromagnetism into the MoS₂ nanosheets. However, this method does not change the interlayer distance of MoS₂ and the phase composition is still dominated by 2H MoS₂. Thus, the simultaneous realization of stabilized 1T-phase MoS₂ for phase transition inhibition and expanded interlayer spacing through a facile method for lattice breathing inhibition is needed to boost the pseudocapacitive sodium storage in MoS₂.

Herein, methyl-functionalized MoS₂ (M-MoS₂) nanosheets were synthesized through a facile second solvothermal method using methanol as the solvent. The M-MoS₂ shows a dominated 1T phase and an expanded interlayer spacing of 0.80 nm. The expanded interlayer spacing not only facilitates the diffusion of Na⁺ in the 2D channels but also reduces the volume change of MoS₂ during discharge/charge; meanwhile, the 1T-phase can inhibit the phase transition during Na⁺ intercalation/de-intercalation. When evaluated as the anode material for SIBs, the obtained M-MoS₂ exhibits better cycling stability and rate capability than pristine MoS₂. The improved sodium storage performances are ascribed to the enhanced capacitive contribution and reduced lattice breathing.

Experimental section

Materials synthesis

Analytical grade $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $CS(NH_2)_2$, methanol, and hydrochloric acid were used as received without further treatment.

Preparation of pristine MoS₂. The preparation of pristine MoS₂ was modified from a previously reported method.³¹ First, 1.366 g (NH₄)₆Mo₇O₂₄·4H₂O, 2.534 g CS(NH₂)₂ and 100 μ L HCl were dissolved in 39 mL distilled water. The solution was stirred for 1 h to form a homogeneous and clear solution. Then, the solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. The obtained products were washed with water and ethanol several times.

Preparation of M-MoS₂. The M-MoS₂ was obtained through a second solvothermal method. 0.16 g as-prepared MoS₂ was dispersed into 35 mL methanol under stirring for 30 min, followed by sonication for 1 h. The suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 180 $^{\circ}$ C for 24 h. The obtained products were washed with ethanol several times.

Materials characterization

The morphology of the as-prepared samples was studied by field emission scanning electron microscopy (FESEM, JEOL 7100F), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEM-2100F). The crystallographic information was obtained through a Bruker D8 DISCOVER X-ray diffractometer (XRD). The phase composition was obtained through X-ray photoelectron spectroscopy (XPS) measurements (VG MultiLab 2000). Raman spectroscopy was done on a micro-Raman spectrometer (Renishaw in Via plus at 514.5 nm laser). A 60-SXB IR spectrometer was used to collect the Fourier transformed infrared (FTIR) transmittance spectra. The carbon content was determined using a Vario EL cube CHNS/O elemental analyzer.

Electrochemical measurements

The electrochemical performances were evaluated by assembling 2016 coin cells in an argon-filled glove box. The working electrode was prepared by mixing the active material (75 wt%), carbon black (20 wt%), and carboxylmethyl cellulose (CMC) (5 wt%) in an appropriate amount of water and then coating the slurry onto Cu foil. For assembling SIBs, sodium metal was used as the anode; 1 M NaClO₄ in ethylene carbon (EC)/dimethyl carbonate (DEC) (1:1 v/v) with 5 wt% fluoroethylene carbonate (FEC) was used as the electrolyte; Whatman Glass Micro-fibre Filter (Grade GF/F) was used as the separator. Galvanostatic discharge/charge cycling behaviors were investigated at a potential window ranging from 0.6 to 3 V (vs. Na⁺/Na) using a multi-channel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) was tested with an electrochemical workstation (CHI 605E). All the measurements were performed at room temperature.

Results and discussion

The synthesis of M-MoS₂ nanosheets is illustrated in Fig. 1. Pristine MoS₂ nanosheets are synthesized through a simple hydrothermal method. The as-prepared MoS₂ nanosheets are then used as the precursor for preparing interlayer-expanded M-MoS₂ nanosheets through a second solvothermal method. XRD was used to characterize the crystal structure of pristine MoS₂ and M-MoS₂. The (002) diffraction of MoS₂ is located at 13.7°, revealing an interlayer distance of 0.65 nm (Fig. 2a). After the solvothermal treatment, the (002) diffraction shifts to a lower angle of 11.0° , reflecting the expansion of the interlayer distance to 0.80 nm. The enlarged interlayer distance of M-MoS₂ could be attributed to the intercalation of organic compounds. The (102) diffraction of M-MoS₂ also shows a shift towards a lower angle, which is consistent with the enlarged interlayer distance along the *c*-axis. The morphology of M-MoS₂ was characterized by SEM and TEM (Fig. 2b-d). The M-MoS₂ consists of nanosheets with a size between 100-200 nm, and a thickness below 10 nm, which is similar to the pristine MoS₂ (Fig. S1a-c, ESI⁺). This indicates the nanosheet structure is well maintained during the second solvothermal treatment. The HRTEM image of M-MoS₂ shows a 2D laminar structure (Fig. 2e) and the interlayer distance can be clearly observed from the curled edges. The lattice fringes are determined to be 0.80 nm, corresponding to the (002) facet of $M-MoS_2$, larger than that of pristine MoS₂ (0.65 nm, Fig. S1d, ESI[†]). The SAED

Paper



 $\label{eq:Fig.1} Fig. 1 \quad Schematic illustration for the synthesis of pristine MoS_2 and interlayer-expanded M-MoS_2 nanosheets.$



Fig. 2 (a) XRD patterns of MoS_2 and $M-MoS_2$. (b and c) SEM images of $M-MoS_2$. (d and e) TEM and HRTEM images of $M-MoS_2$. (f) SAED pattern of $M-MoS_2$. (g) EDS mapping of $M-MoS_2$.

pattern of M-MoS₂ shows two separated diffraction rings, which correspond to the (100) and (110) planes; the same two diffraction rings were also observed in the pristine MoS_2 (Fig. S1e,

ESI†). The EDS mapping of M-MoS₂ is shown in Fig. 2g; the C element is uniformly distributed with Mo and S, indicating the homogenous intercalation of organic compounds.

Paper

To identify the intercalated species, FTIR tests were performed using the KBr pellet method. As shown in Fig. S2a (ESI⁺), M-MoS₂ displays two strong signals at 943 and 1292 cm⁻¹, which are attributed to the methyl rocking and deformation modes, respectively.³² The peak at 700 cm⁻¹ is attributed to the S-C stretching.^{32,33} FTIR tests in paraffin oil were performed to determine the presence of hydroxyl groups (Fig. S2b, ESI[†]). The O-H stretch vibration of methanol is located at 3356 cm^{-1} (Fig. S3, ESI[†]). As shown in Fig. S2b (ESI[†]), no signal from hydroxyl groups is detected in both MoS₂ and M-MoS₂. In addition, the three peaks shown in the KBr pellet method are also observed. The FTIR results indicate that the expansion of the interlayer distance in M-MoS₂ is not caused by the intercalation of methanol molecules but the functionalization of methyl groups. The carbon content of M-MoS₂ is determined by the CHNS/O elemental analyzer to be 3.44 wt%, suggesting a methyl group content of 4.3 wt%.

XPS was used for phase composition analysis. Fig. 3a shows the Mo 3d spectrum of pristine MoS₂. The peaks at 232.1 and 228.9 eV are attributed to the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ of 2H MoS₂, respectively.³⁴ And the peak located at 226.1 eV is attributed to S 2s. For M-MoS₂, the main peaks in the Mo 3d spectrum shift towards lower binding energies, indicating the formation of 1T-phase MoS₂ (Fig. 3c).²⁹ The binding energies of the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ peaks for 1T-phase MoS₂ are ~0.5 eV lower than those of 2H-phase MoS₂, and the peaks located at 235.3 and 232.1 eV could be attributed to Mo(vi).³⁵ The Mo 3d XPS spectrum demonstrates that the M-MoS₂ is dominated by the 1T phase. The S 2p spectrum of pristine MoS₂ shows two peaks at 163.2 and 161.8 eV (Fig. 3b).³⁶ Compared to the pristine MoS₂, the M-MoS₂ shows two extra peaks from the 1T-phase MoS₂ (located at 162.7 and 161.3 eV) and two extra peaks from the newly formed S-C (located at 163.9 eV and 162.5 eV).³² The S2p spectrum further confirms the functionalization of MoS₂ by methyl groups. Raman spectroscopic analysis also confirms the phase transition from 2H to 1T (Fig. S4, ESI[†]). For pristine MoS₂, the two peaks located at 380 and 405 cm⁻¹ represent the in-plane



Fig. 3 The (a) Mo 3d and (b) S 2p spectra of MoS_2 ; the (c) Mo 3d and (d) S 2p spectra of M-MoS₂.

opposite vibration of the S atoms based on Mo atoms (E_{2g}^1) and out-of-plane opposite vibration of the S atoms (A_{1g}) (Fig. S4a, ESI†).^{37–39} For the M-MoS₂, the spectrum shows two additional peaks at around 150 and 320 cm⁻¹, which are ascribed to the J1 and J3 vibration modes of 1T-phase MoS₂ (Fig. S4b, ESI†).^{40,41} The XPS and Raman results reveal that the pristine MoS₂ is mostly converted from the 2H to 1T phase after methyl functionalization.

Coin cells (2016-type) were assembled to evaluate the electrochemical performances of M-MoS₂ and MoS₂. Fig. 4a shows the cycling stability of the samples. At a current density of 1 A g^{-1} , the pristine MoS_2 demonstrates a capacity of 174 mA h g⁻¹ at the initial discharge process and fast capacity fading during cycling. After 500 cycles, the capacity fades to 29 mA h g^{-1} (~17%) capacity retention). In contrast, the M-MoS₂ shows an initial discharge capacity of 129 mA h g^{-1} , retaining 64 mA h g^{-1} after 5000 cycles (\sim 50% capacity retention). The results demonstrate that the M-MoS₂ possesses much better cycling stability than the pristine MoS₂ in sodium storage. Representative discharge/ charge curves are shown Fig. S5 (ESI⁺). The specific capacity of pristine MoS₂ decreases dramatically during cycling, while the specific capacity of M-MoS₂ is well maintained. Besides, the discharge/charge curves of M-MoS2 are quasi-linear, revealing a pseudocapacitive sodium storage property. The rate performances are shown in Fig. S6 (ESI[†]). At a low current density of 0.2 A g^{-1} , the pristine MoS₂ shows an initial specific capacity of 262 mA h g^{-1} , higher than that of M-MoS₂ (159 mA h g^{-1}). This is



Fig. 4 (a) Cycling performances of M-MoS₂ and pristine MoS₂ at the specific current of 1 A g⁻¹. (b) CV curves of M-MoS₂. (c) The capacity contributions of M-MoS₂ at different scan rates. (d) CV curves of pristine MoS₂. (e) The capacity contributions of pristine MoS₂ at different scan rates.

because some of the active sites are occupied by the methyl groups. At a high specific current of 5 A g⁻¹, the specific capacity of M-MoS₂ is 69 mA h g⁻¹, showing a capacity retention of 44% against the initial discharge capacity obtained at 0.2 A g⁻¹. At the same current density of 5 A g⁻¹, the specific capacity of MoS₂ is merely 17 mA h g⁻¹ (~6% capacity retention). The enhanced rate capability of M-MoS₂ can be attributed to the enlarged interlayer distance, which facilitates Na⁺ diffusion.

To examine the sodium storage mechanisms and electrochemical kinetic properties in the sodium intercalation/de-intercalation processes, CV tests were performed. For the pristine MoS₂, there are two anodic peaks at 1.04 and 1.36 V at the scan rate of 1 mV s^{-1} (Fig. 4d). These peaks can be attributed to the two-step intercalation of Na⁺.^{24,42} There is only one cathodic peak at 1.94 V (Fig. 4b) in the subsequent cathodic process, revealing the one-step de-intercalation of Na⁺ during charge. For the M-MoS₂, there is only one pair of redox peaks in the CV curves at the scan rate of 1 mV s⁻¹, which are located at 1.3/1.62 V. The CV curves of M-MoS₂ tend to be more like a capacitor with smaller polarization. For both samples, the anodic and cathodic peaks shift slightly with an increase in scan rate, revealing a feature similar to pseudocapacitive materials.43 A related analysis of the current dependence on the scan rate is performed by the following relation:44

$$i = av^b \tag{1}$$

In this equation, *i* is the current, v is the scan rate, *a* is a constant and the value of b indicates the type of charge storage occurring in the material, which is between 0.5 and 1. If b = 0.5, the current is controlled by semi-infinite linear diffusion (diffusion-controlled process); if b = 1, the current is capacitive (surface-controlled process). To solve the *b*-values, the log(i)versus log(v) plot is shown Fig. S7 (ESI^{\dagger}). The anodic and cathodic b-values for M-MoS₂ are 0.93 and 0.98, respectively (Fig. S7a, ESI^{\dagger}), while those for the pristine MoS₂ are 0.80 and 0.87 (calculated from the second anodic peak) (Fig. S7b, ESI†). The results reveal that the electrochemical reactions occurring at the peak current for M-MoS₂ are surface-controlled (capacitive). In contrast, the electrochemical reactions occurring at the peak current for pristine MoS₂ are still largely diffusion-controlled, indicating that the M-MoS₂ shows improved capacitive behaviour over MoS₂. The larger cathodic *b*-values for both M-MoS₂ and MoS₂ are ascribed to the higher conductivity in the full sodiated state, which facilitates electrochemical reactions.

At a particular potential, the current is contributed from both capacitive and diffusion behaviours, thus, the capacitive contributions can be identified by the following equation:⁴⁵

$$i = k_1 \nu + k_2 \nu^{1/2} \tag{2}$$

The capacitive and diffusion contributions to the current are determined by solving k_1 and k_2 . Fig. 4c and e show the results of the analysis applied to M-MoS₂ and pristine MoS₂. The capacitive contribution in M-MoS₂ is higher than that in pristine MoS₂. At a slow rate of 0.1 mV s⁻¹, 68.2% of the capacity of M-MoS₂ comes from capacitive processes, which is 13.8% higher than that of pristine MoS₂. At 1 mV s⁻¹, the diffusion-controlled

contributions are only 20.9% and 14.8% for pristine MoS_2 and M-MoS₂, respectively. The higher capacitive contribution in M-MoS₂ implies that the expanded interlayer can facilitate ion diffusion and thus enhance the rate performance. Moreover, the capacitive contributions to the current at each potential are shown in Fig. S8 (ESI[†]). In the peak regions, the current of M-MoS₂ is mainly contributed from capacitive processes, which is consistent with the *b*-value analysis. The *b*-value and capacity contribution analyses demonstrate that the sodium storage in M-MoS₂ is dominated by capacitive processes, which results from the reduced phase transition and enlarged interlayer spacing.

Ex situ XRD was carried out to investigate the structure change during cycling. For pristine MoS₂, the initial discharge to 0.6 V is accompanied by a phase transition from 2H MoS₂ to sodiated 1T Na_xMoS₂ (Fig. 5a). The (002) diffraction of MoS₂ shifts to 9.6° and becomes the (001) diffraction of 1T Na_xMoS₂. During the initial discharge, the interlayer distance is expanded from 0.65 to 0.92 nm, corresponding to an expansion ratio of 42% along the *c*-axis. During the de-sodiation to 3 V, the (001) diffraction shifts back to the original position (the (002) diffraction of MoS₂) and the interlayer distance shrinks to 0.65 nm, implying reversible intercalation/de-intercalation processes. As the cycle number increases, the intensity of the (002) diffraction decreases continually, while the intensity of the (100) diffraction is well maintained. After 50 cycles, the (002) diffraction almost disappears, revealing a collapsed 2D structure (Fig. 5c). For M-MoS₂, the interlayer distance is expanded to 0.93 nm during the initial discharge to 0.6 V, corresponding to an expansion ratio of 16% along the c-axis (Fig. 5b). This result demonstrates that the structure change in the M-MoS₂ is suppressed and the smaller crystallographic



Fig. 5 *Ex situ* XRD patterns of (a) pristine MoS₂ and (b) M-MoS₂ during cycling at 1 A g⁻¹, (i) 1st discharge to 0.6 V, (ii) 1st charge to 3 V, (iii) after 20 cycles, (iv) after 50 cycles. Schematic illustration of the 2D structure changes of (c) MoS₂ and (d) M-MoS₂ during the pseudocapacitive reaction process.

change is consistent with the pseudocapacitive characteristics. During cycling, the intensity of the (002) diffraction is well maintained, revealing a stabilized 2D structure (Fig. 5d). Moreover, *ex situ* SEM was performed after 500 cycles at the current density of 1 A g^{-1} (Fig. S9, ESI[†]). The SEM image clearly shows that the nanosheet structure of M-MoS₂ can be well maintained after cycling, revealing its stable structure. The enhanced structural stability and cycling stability of M-MoS₂ can be attributed to its dominant 1T phase as well as the expanded interlayer distance. The former inhibits phase transition, while the later inhibits lattice breathing during intercalation/de-intercalation.

Conclusion

Methyl-functionalized MoS₂ (M-MoS₂) nanosheets have been synthesized via a facile second solvothermal method. During the second solvothermal treatment, the MoS₂ is mostly converted from the 2H to 1T phase and the interlayer distance is expanded from 0.65 to 0.80 nm. When applied to sodium storage, the stabilized 1T phase inhibits the phase transition, while the expanded interlayer spacing inhibits lattice breathing during sodium intercalation/de-intercalation. As a result, the M-MoS₂ delivers significantly enhanced cycling stability in sodium storage. After 5000 cycles at 1 A g^{-1} , ~50% of its initial capacity can be retained, while the pristine MoS₂ maintains only $\sim 17\%$ of the initial capacity after 500 cycles. Kinetic analysis reveals that the sodium storage capacity of M-MoS₂ is mainly contributed from pseudocapacitive processes. This study demonstrates that the M-MoS₂ is a promising pseudocapacitive material for sodium storage.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2016YFA0202603), the National Basic Research Program of China (2013CB934103), the Programme of Introducing Talents of Discipline to Universities (B17034), the National Natural Science Foundation of China (51521001, 21673171, 51502226), the National Natural Science Fund for Distinguished Young Scholars (51425204), and the Fundamental Research Funds for the Central Universities (WUT: 2016III001, 2016III002). Prof. Liqiang Mai gratefully acknowledges financial support from the China Scholarship Council (no. 201606955096).

Notes and references

- 1 R. Van Noorden, Nature, 2014, 507, 26-28.
- 2 J. B. Goodenough and K.-S. Park, *J. Am. Chem. Soc.*, 2013, 135, 1167–1176.
- 3 B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, 334, 928–935.
- 4 L. Mai, X. Tian, X. Xu, L. Chang and L. Xu, *Chem. Rev.*, 2014, 114, 11828–11862.
- 5 S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder and K. Kang, *Adv. Energy Mater.*, 2012, **2**, 710–721.

- 6 V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzalez and T. Rojo, *Energy Environ. Sci.*, 2012, 5, 5884–5901.
- 7 N. Yabuuchi, K. Kubota, M. Dahbi and S. Komaba, *Chem. Rev.*, 2014, **114**, 11636–11682.
- 8 Y. Liu, H. Wang, L. Cheng, N. Han, F. Zhao, P. Li, C. Jin and Y. Li, *Nano Energy*, 2016, **20**, 168–175.
- 9 W. Ren, W. Zhou, H. Zhang and C. Cheng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 487–495.
- 10 Y. Zhu, L. Peng, D. Chen and G. Yu, *Nano Lett.*, 2016, 16, 742–747.
- 11 P. Simon, Y. Gogotsi and B. Dunn, Science, 2014, 343, 1210-1211.
- 12 D. Chao, C. Zhu, P. Yang, X. Xia, J. Liu, J. Wang, X. Fan, S. V. Savilov, J. Lin, H. J. Fan and Z. X. Shen, *Nat. Commun.*, 2016, 7, 12122.
- 13 V. Augustyn, P. Simon and B. Dunn, *Energy Environ. Sci.*, 2014, 7, 1597–1614.
- 14 G. A. Muller, J. B. Cook, H.-S. Kim, S. H. Tolbert and B. Dunn, *Nano Lett.*, 2015, 15, 1911–1917.
- 15 J. B. Cook, H.-S. Kim, Y. Yan, J. S. Ko, S. Robbennolt,
 B. Dunn and S. H. Tolbert, *Adv. Energy Mater.*, 2016, 6, 1501937.
- 16 V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon and B. Dunn, *Nat. Mater.*, 2013, **12**, 518–522.
- 17 Y. Liang, R. Feng, S. Yang, H. Ma, J. Liang and J. Chen, *Adv. Mater.*, 2011, 23, 640–643.
- 18 E. Benavente, M. A. Santa Ana, F. Mendizábal and G. González, Coord. Chem. Rev., 2002, 224, 87–109.
- 19 J. Park, J.-S. Kim, J.-W. Park, T.-H. Nam, K.-W. Kim, J.-H. Ahn, G. Wang and H.-J. Ahn, *Electrochim. Acta*, 2013, 92, 427–432.
- 20 H. Wang, Z. Lu, S. Xu, D. Kong, J. J. Cha, G. Zheng, P.-C. Hsu, K. Yan, D. Bradshaw, F. B. Prinz and Y. Cui, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 19701–19706.
- 21 X. Wang, X. Shen, Z. Wang, R. Yu and L. Chen, *ACS Nano*, 2014, **8**, 11394–11400.
- 22 L. Wang, Z. Xu, W. Wang and X. Bai, J. Am. Chem. Soc., 2014, 136, 6693–6697.
- 23 Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao and J. Chen, Angew. Chem., Int. Ed., 2014, 53, 12794–12798.
- 24 Y. Li, Y. Liang, F. C. Robles Hernandez, H. Deog Yoo, Q. An and Y. Yao, *Nano Energy*, 2015, **15**, 453–461.
- 25 A. S. Goloveshkin, I. S. Bushmarinov, A. A. Korlyukov, M. I. Buzin, V. I. Zaikovskii, N. D. Lenenko and A. S. Golub, *Langmuir*, 2015, **31**, 8953–8960.
- 26 D. Wang, X. Zhang, S. Bao, Z. Zhang, H. Fei and Z. Wu, J. Mater. Chem. A, 2017, 5, 2681–2688.
- 27 A. N. Enyashin, L. Yadgarov, L. Houben, I. Popov, M. Weidenbach, R. Tenne, M. Bar-Sadan and G. Seifert, J. Phys. Chem. C, 2011, 115, 24586–24591.
- 28 Q. Tang and D.-E. Jiang, Chem. Mater., 2015, 27, 3743-3748.
- 29 L. Cai, J. He, Q. Liu, T. Yao, L. Chen, W. Yan, F. Hu, Y. Jiang,
 Y. Zhao, T. Hu, Z. Sun and S. Wei, *J. Am. Chem. Soc.*, 2015,
 137, 2622–2627.
- 30 P. Zhang, C. Gao, B. Xu, L. Qi, C. Jiang, M. Gao and D. Xue, Small, 2016, 12, 2077–2084.

- 31 J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang,
 Y. Lei, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, 135,
 17881–17888.
- 32 D. Voiry, A. Goswami, R. Kappera, e. SilvaCecilia de Carvalho Castro, D. Kaplan, T. Fujita, M. Chen, T. Asefa and M. Chhowalla, *Nat. Chem.*, 2015, 7, 45–49.
- 33 K. C. Knirsch, N. C. Berner, H. C. Nerl, C. S. Cucinotta, Z. Gholamvand, N. McEvoy, Z. Wang, I. Abramovic, P. Vecera, M. Halik, S. Sanvito, G. S. Duesberg, V. Nicolosi, F. Hauke, A. Hirsch, J. N. Coleman and C. Backes, *ACS Nano*, 2015, 9, 6018–6030.
- 34 H. Wang, C. Tsai, D. Kong, K. Chan, F. Abild-Pedersen, J. K. Nørskov and Y. Cui, *Nano Res.*, 2015, **8**, 566–575.
- 35 S. Hu and X. Wang, J. Am. Chem. Soc., 2008, 130, 8126-8127.
- 36 X. Chen, N. C. Berner, C. Backes, G. S. Duesberg and A. R. McDonald, *Angew. Chem., Int. Ed.*, 2016, 55, 5803–5808.
- 37 F. Xiong, Z. Cai, L. Qu, P. Zhang, Z. Yuan, O. K. Asare, W. Xu, C. Lin and L. Mai, *ACS Appl. Mater. Interfaces*, 2015, 7, 12625–12630.

- 38 G. Huang, T. Chen, W. Chen, Z. Wang, K. Chang, L. Ma, F. Huang, D. Chen and J. Y. Lee, *Small*, 2013, 9, 3693–3703.
- 39 Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, J. Am. Chem. Soc., 2011, 133, 7296–7299.
- 40 X. Fan, P. Xu, D. Zhou, Y. Sun, Y. C. Li, M. A. T. Nguyen, M. Terrones and T. E. Mallouk, *Nano Lett.*, 2015, 15, 5956–5960.
- 41 M. Acerce, D. Voiry and M. Chhowalla, *Nat. Nanotechnol.*, 2015, **10**, 313–318.
- 42 Y. Liu, X. He, D. Hanlon, A. Harvey, J. N. Coleman and Y. Li, ACS Nano, 2016, 10, 8821–8828.
- 43 L. Zhang, K. Zhao, Y. Luo, Y. Dong, W. Xu, M. Yan, W. Ren,
 L. Zhou, L. Qu and L. Mai, *ACS Appl. Mater. Interfaces*, 2016,
 8, 7139–7146.
- 44 C. Chen, Y. Wen, X. Hu, X. Ji, M. Yan, L. Mai, P. Hu, B. Shan and Y. Huang, *Nat. Commun.*, 2015, **6**, 6929.
- 45 T. Brezesinski, J. Wang, S. H. Tolbert and B. Dunn, *Nat. Mater.*, 2010, **9**, 146–151.