Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

PAPER

Check for updates

Cite this: J. Mater. Chem. A, 2021, 9, 4984

Dihydrophenazine linked porous organic polymers for high capacitance and energy density pseudocapacitive electrodes and devices[†]

Huanhuan Zhang, 🕩 a Xiaohui Tanga and Cheng Gu 🕩 *ab

Received 18th November 2020 Accepted 16th January 2021

DOI: 10.1039/d0ta11266f

rsc.li/materials-a

Redox porous organic polymers are promising pseudocapacitive materials. However, their specific capacitance still needs further elevation. Herein, we report a novel dihydrophenazine derived porous organic polymer, GT-POP-1. The GT-POP-1 based electrode and asymmetric device show high specific capacitance and energy density metrics of 97.1 mF cm⁻² and 7.3 μ W h cm⁻².

The demand for powering a great variety of electric vehicles, portable electronics and, in the near future, wearable health products, keeps growing in our daily lives. Scientific and technological improvements relevant to all performance metrics are highly desirable. Electrochemical energy systems that can provide simultaneous high power and energy density are an urgent global need.1 Pseudocapacitors, which exploit the fast faradaic reactions at the surface of electrodes, are a promising candidate as they are capable of overcoming the capacity and mass-transfer limitations of electric double-layer capacitors (EDLCs) and batteries, respectively. Regarding the choice of material for pseudocapacitors, novel redox polymers with electroactive moieties incorporated into the polymer backbone or sidechain have drawn great attention due to their abundant active sites and structural diversity.2-7 They are gradually becoming an important supplement for the conventional transition metal oxides and conducting polymers. Yet, the energy density values for most reported redox polymer materials are still not high enough when compared with those for batteries.⁸⁻¹⁰ According to equation $E = 1/2CV^2$, energy density is proportional to the capacitance and square of the voltage. While voltage can be universally extended by using wide potential window electrolytes like organic or ionic electrolytes, together with asymmetric device architectures, the elevation in capacitance is specific and customized. To sum up, increasing the accessibility of redox sites so as to release the capacitance to the maximum is the guideline. This strategy is mainly carried out *via* the aid of conductivity enhancement,¹¹ two dimensionality or porosity engineering.⁵ Although much literature reports a capacitance higher than 500 F g⁻¹,^{5,12} most redox polymer materials show values much lower.^{8,10,13–16} In the continuous pursuit of new compounds that meet the requirement of competitive high energy density, more novel material designs are desirable.

Apart from the redox active moiety, atoms from other components should contribute as less as possible to the molar mass, only if they undertake the functions of suppressing dissolution, distributing charges or building porous structures. Guided by this principle, we designed a dihydrophenazine (DHPAZ) derived covalent triazine polymer which is synthesized by simple cyclo-trimerization of 4,4'-(phenazine-5,10-divl) dibenzonitrile (DHPAZ-2CN) (Fig. 1a). The redox active 5,10diphenyl-5,10-dihydrophenazine core can undergo two stepwise redox processes.17-19 The covalent triazine linkage minimizes the molecular weight of inactive groups and helps to build a rigid and porous structure.^{20,21} The obtained GT-POP-1 electrode exhibits a high specific capacitance of 97.1 mF cm⁻² (324 F g^{-1}) at a current density of 0.1 mA cm⁻². To fabricate supercapacitor devices with high energy density, an asymmetric supercapacitor with GT-POP-1 as the cathode and activated carbon as the anode (GT-POP-1//AC) is assembled. The GT-POP-1//AC device delivers a capacitance of 7.51 mF cm⁻² at a current density of 0.1 mA cm⁻². The energy density of the GT-POP-1//AC device is 7.3 μ W h cm⁻² (24.5 W h kg⁻¹) at a power density of 59.7 μ W cm⁻² (193 W kg⁻¹) and remains almost unchanged at a high power density of 2987 μ W cm⁻² (9642 W kg⁻¹). Moreover, stable cycling performance is achieved with 84% capacitance retention after 2000 charge–discharge cycles at 0.2 mA cm^{-2} .

The synthesis of GT-POP-1 was conducted by cyclotrimerization of DHPAZ-2CN with triflic acid (TfOH) as the catalyst (Fig. 1a, ESI[†]).^{22,23} To confirm the formation of GT-POP-1, Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted (Fig. 1b). The emergence of two vibration peaks at

[&]quot;State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, No. 381 Wushan Road, Tianhe Distinct, Guangzhou, 510640, P. R. China. E-mail: gucheng@scut.edu.cn

^bGuangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology, No. 381 Wushan Road, Tianhe Distinct, Guangzhou, 510640, P. R. China

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ta11266f



Fig. 1 (a) Synthesis route for GT-POP-1 and schematic demonstration of its reversible redox processes in an Et_4NBF_4 electrolyte; (b) FTIR spectra of GT-POP-1 and its precursor DHPAZ-2CN; (c) N₂ and CO₂ adsorption/desorption isothermal curves of GT-POP-1 at 77 and 195 K, respectively; (d) PXRD pattern and (e) SEM image of the as-prepared GT-POP-1 powder.

1674 and 1321 cm⁻¹ indicated the formation of triazine rings, while the disappearance of the characteristic nitrile stretching band at 2230 cm⁻¹ verified the complete cyclization of 1,4dicvanobenzene.²⁴⁻²⁶ The new peak at 1254 cm⁻¹ together with those at 1112 cm⁻¹ and 1082 cm⁻¹ may be ascribed to the characteristic vibration of S=O and C-F from residual TfOH, respectively.27 The ¹³C NMR spectra further confirmed the presence of carbon from the C=N linkage in the triazine unit by showing a new peak at 178 ppm (Fig. S1[†]). The chemical environments of typical elements including C, N, F and S, embedded in GT-POP-1 or from residual TfOH, were also investigated by X-ray photoelectron spectroscopy (XPS) (Fig. S2[†]). The C 1s spectrum could be deconvoluted into four peaks with binding energies of 284.6, 285.6, 288.2 and 291.8 eV, ascribed to C=C in the benzene ring, C-N in the DHPAZ ring, C=N in the triazine ring, and quaternary carbon in residual TfOH, respectively. The deconvoluted peaks in the N 1s spectrum at 399.6, 400.2 and 400.8 eV are attributed to N=C in the triazine ring, tertiary amine and protonated tertiary amine in DHPAZ due to TfOH, respectively. The appearance of S 2p and F 1s in the sample was arbitrarily attributed to TfOH. By quantitatively comparing the amount of introduced S (or F) with that of inherent N, about 0.40 M (or 0.46 M) TfOH per mole of DHPAZ was trapped in the polymer. The porosity was detected by gas sorption measurements. As shown in Fig. 1c, N2 uptake at 77 K was neglectable. However, a substantial amount of CO₂ (121 mg g^{-1}) uptake was observed at 195 K, implying the polar properties of the GT-POP-1 surface which selectively adsorbs polar CO2 and excludes nonpolar N2.28 The Brunauer-Emmett-Teller (BET) surface area was calculated to be 320 m² g⁻¹. Evaluation of the pore size distribution was performed according to the slit-pore non-local-density functional theory (NLDFT) model, verifying that GT-POP-1 has a micropore-dominated

structure with pore sizes of 0.34 and 0.38 nm under CO₂ and N₂, respectively (Fig. S3[†]). The powder X-ray diffraction (PXRD) pattern indicated the amorphous nature of GT-POP-1. The broad band at $2\theta = 22^{\circ}$ can be attributed to π - π stacking (Fig. 1d). Scanning electron microscopy (SEM) images also showed the porous and amorphous morphology of GT-POP-1 (Fig. 1e). High-resolution transmission electron microscopy (HR-TEM) revealed the highly porous textiles (Fig. S4[†]). Thermogravimetric (TG) analysis showed that GT-POP-1 remains stable before decomposition above 300 °C (Fig. S5[†]).

We systematically investigated the electrochemical properties of the GT-POP-1 electrode. First of all, cyclic voltammetry (CV) measurements were conducted to characterize the voltammetry response in a three-electrode configuration, with the active material as the working electrode, Pt wire as the auxiliary electrode and Ag⁺/Ag as the reference electrode. At a slow scan rate of 10 mV s⁻¹, the GT-POP-1 exhibited two pairs of reversible redox bands in succession at about -0.5-0.5 V and 0.5-1.25 V during the anodic scan and -0.5-0.25 V and 0.25-1.0 V during the cathodic scan, which were ascribed to the 5,10-diphenyl-5,10-dihydrophenazine moiety losing or regaining its first and second electrons, respectively (Fig. 2a).29 Each band had fine peak structures, probably because of the various environments of the dihydrophenazine moiety in the polymer; for example, the protonated DHPAZ by TfOH. To verify the effect of the residual TfOH on the electrode performance, I-V conductivity tests were conducted (Fig. S6[†]). The calculated electronic conductivity of GT-POP-1 is only 1.8×10^{-8} S cm⁻¹, which can hardly have any enhancement effect on the performance. The reduction properties of GT-POP-1 were also investigated. During the potential scan of 0--2 V, an irreversible reduction peak appeared at -1.55 V, ascribed to the reduction of the triazine moiety. The shoulder peak at ca. -0.75 V was probably caused



Fig. 2 (a) Anodic and cathodic scans of the GT-POP-1 electrode at a scan rate of 10 mV s⁻¹; (b) cyclic voltammetry responses at different scan rates. The scan rates were (from in to out) 10, 20, 50, 100, 200 and 400 mV s⁻¹; (c) currents of redox peaks as a function of scan rate, the slope of the fitting line gives the *b* value; (d) k_1 , k_2 analysis eqn (2) at a scan rate of 10 mV s⁻¹. These shaded regions show the contribution of pseudocapacitance as a function of potential; (e) galvanostatic charge/discharge curves and (f) capacitance retention and coulombic efficiency at current densities of 0.2, 0.5, 1.0, and 2.0 mA cm⁻². The electrolyte was 1.0 M Et₄NBF₄ in propylene carbonate.

by the reduction of the trace H_2O/O_2 complex in GT-POP-1. The anodic CV curves at difference scan rates are shown in Fig. 2b. As the scan rate increased, the current accordingly increased. The fine redox peaks merged into a broad band. The log(i) versus log(v) plot of the forward anodic (ox1, ox2) and backward cathodic (red1, red2) peak current response is plotted in Fig. 2c, to investigate the charge storage kinetics. According to eqn (1),

$$i = a\nu^b \tag{1}$$

where *a* and *b* are dimensionless coefficients, *i* is the peak current density (mA cm⁻²) and ν is the scan rate (mV s⁻¹). Typically, when b = 0.5, the redox process is controlled by semiinfinite diffusion, while b = 1 indicates capacitive behaviour.^{30,31} The *b* values of four redox peaks lie in the range of 0.7–0.75, indicating a mixed-control process. The current response is a combination of capacitor-like and diffusion-controlled behaviours; consequently, the capacitance is contributed by the EDLC and pseudo-capacitance. The fraction of each component was calculated according to eqn (2),

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

where k_1 and k_2 are constants at a certain voltage. At a scan rate of 10 mV s⁻¹, pseudocapacitance contributes 71% of the total capacitance. As the scan rate increases, the pseudo fraction gradually decreases, along with the EDLC component gradually increasing. At a scan rate of 400 mV s⁻¹, the pseudo contribution was only 28%; the EDLC capacitance became predominant (Fig. S7†). To calculate the specific capacitance, galvanostatic charge/discharge tests were performed, as shown in Fig. 2d. The GT-POP-1 electrode exhibited a high specific areal capacitance of 97.1 mF cm⁻² (324 F g⁻¹) at a current density of 0.2 mA cm⁻², which is among the top values reported for various porous organic polymer electrodes (Table 1). As the current density increased, obvious capacitance loss was observed. When the current density increased tenfold at 2.0 mA cm⁻², 41.5% of the maximum capacitance remained, probably due to the rapid loss of the pseudocapacitance component as discussed in the kinetic analysis.

By taking advantage of two different electrode materials, asymmetric supercapacitors can extend their operating voltage window, thus providing a solution to the energy storage limitation of symmetric supercapacitors.37 Herein, asymmetric capacitors were assembled with GT-POP-1 as the cathode and active carbon (AC) as the anode. AC showed a nearly rectangular current response in the potential range 0--2.0 V at a scan rate of 10 mV s⁻¹ (Fig. 3a). The asymmetric device of GT-POP-1//AC will have a voltage as high as 3 V in theory. CV scans at different voltage cut-offs were conducted to make sure of the best working voltage. As the voltage increases, the current of the device increases, and broad redox peaks appear indicating that the contribution of pseudocapacitance originated from dihydrophenazine (Fig. 3b). The optimized voltage of GT-POP-1 was 2.8 V. The galvanostatic charge/discharge behaviours at different current densities are shown in Fig. 3c. The specific capacitance of the device at different current densities was calculated from the discharge curve. The capacitance retention or rate stability of the asymmetric device was calculated to be 95% (from 7.51 mF cm $^{-2}$ at 0.1 mA cm $^{-2}$ to 7.13 mF cm $^{-2}$ at 4.4 mA cm^{-2}) (Fig. 3d). Electrochemical impedance spectroscopy

Table 1	Comparison of capacitance	for selected supercapacitor	electrodes based on porous	organic polymers
---------	---------------------------	-----------------------------	----------------------------	------------------

Materials	BET surface area $(m^2 g^{-1})$	Pore size (nm)	Electrolyte	Maximum capacitance	Current density	Ref.
[TEMPO]100%-NiP-COF	5.2	1.4	0.1 M Bu₄NClO₄	167 F g^{-1}	$0.1 \mathrm{A g}^{-1}$	10
Aza-MOFs@COFs	365	0.7	$1 \text{ M Et}_4 \text{NBF}_4$	$20.35 \ \mu F \ cm^{-2}$	0.2 A cm^{-2}	32
Benzil-CMP	149	${\sim}0.7$	1 M H ₂ SO ₄	189 Fg^{-1}	1 A g^{-1}	33
Hex-aza-COF-3	124	_	$1 \text{ M H}_2 \text{SO}_4$	663 F g^{-1}	1 A g^{-1}	5
p(TPA-EDOT)	_	_	0.1 M Bu ₄ NPF ₆	151.2 mF cm^{-2}	1 mA cm^{-2}	34
DAAQ-TFP-COF	_	_	0.1 M Bu ₄ NPF ₆	3.0 mF cm^{-2}	$150 \ \mu A \ cm^{-2}$	9
-	435	0.2	1 M H ₂ SO ₄	$48\pm10~\mathrm{F~g^{-1}}$	10 mV s^{-1}	8
TpPa-(OH) ₂ -COF	369	$0.10{\sim}0.18$	1 M phosphate buffer	416 F g^{-1}	$0.5 \mathrm{A g}^{-1}$	35
TpOMe-DAQ	1734	2.3	$3 \text{ M H}_2 \text{SO}_4$	1600 mF cm^{-2} 169 F g ⁻¹	3.3 mA cm^{-2}	16
Dq ₁ Da ₁ TpCOF	804	2.0-2.3	1 M H ₂ SO ₄	111 Fg^{-1}	1.56 mA cm^{-2}	14
PDI-triptycene	185	~3	$1 \text{ M Na}_2 \text{SO}_4$	352 Fg^{-1}	0.2 Ag^{-1}	36
GT-POP-1	320	0.34	1 M Et ₄ NBF ₄	97.1 mF cm ⁻² 324 F g ⁻¹	0.1 mA cm^{-2} 0.5 A g^{-1}	This work

Published on 18 January 2021. Downloaded by University of New Mexico on 5/15/2021 7:42:48 AM.

(EIS) was also conducted to probe the interface and bulk conditions. The EIS curve exhibits a typical frequency response of supercapacitor devices with a semi-circle in the high frequency region and a straight line in the low frequency region (Fig. 3e). This response behaviour can be fitted into the equivalent circuit of $[LR_s(R_{ct}C)W]$, which consists of internal resistance (R_s) including solution resistance of the bulk electrolyte as well as electrical resistance of the electrodes, charge transfer resistance (R_{ct}) between the electrolyte and the electrode interface in parallel with the capacitor (C) related to the electrode surface capacitance and Warburg diffusion impedance (W) indicating the ion and mass transfer process. An inductor element (L) was also added in the circuit to show the oscillation impedance caused by the coiled wire in the very high frequency



Fig. 3 (a) CV curves of the AC cathode and GT-POP-1 anode, scan rate 50 mV s⁻¹; (b) CV curves at different cut off voltages of 0.5, 1.0, 2.0, and 3.0 V; (c) galvanostatic charge/discharge at different current densities of 0.1, 0.2, 0.5, 1.0, and 2.0 mA cm⁻²; (d) capacitance retention and coulombic efficiency calculated from the discharge curves; (e) Nyquist plots (inset is the enlarged part in the high frequency region); (f) Ragone plots and (g) repeated charge/discharge stability (capacitance retention and coulombic efficiency η) of the GT-POP-1//AC asymmetric supercapacitor.

range of 10 000 to 1 M Hz (Fig. S8[†]). The fitting result had an error less than 10% (Table S1[†]). According to the fitting results, the device has a contact and charge transfer resistance of 6.9 Ω , indicating good contact between all interfaces. In the low frequency region, the straight line of GT-POP-1 is inclined to the imaginary axis, indicating a capacitive behaviour; this is also confirmed in the Bode plot where GT-POP-1 has a phase angle of nearly 90° in the low frequency regions (Fig. S7†).³⁰ Specific energy and power density are crucial parameters for supercapacitor commercialization. The asymmetric device exhibited the highest energy density of 7.3 μ W h cm⁻² (24.5 W h kg⁻¹) at a power density of 59.3 μ W cm⁻² (193 W kg⁻¹) and showed high rate stability with the energy density remaining unchanged even when the power density increased to 2987 μ W cm⁻² (9642 W kg^{-1} (Fig. 3f). The energy density is among the top values reported in many state-of-the-art porous polymer based supercapacitors reported recently, even comparable to some transition metal oxide based pseudocapacitors (Table S2[†]).³⁸⁻⁴² Besides, the asymmetric device also showed good cycling stability with a capacitance retention of 84% (67%) after 2000 (5000) galvanostatic charge/discharge cycles (Fig. 3g).

An analogue polymer CTF-400 was also synthesized by the ionothermal reaction with $ZnCl_2$ as the catalyst and the solvent at 400 °C (Fig. S10–S12†). The supercapacitor CTF-400//AC only provided a maximum capacitance of 3.5 mF cm⁻² at a current density of 0.05 mA cm⁻². This comparison demonstrates that the synthesis method using TfOH as the catalyst maintains the redox-activity of the incorporated DHPAZ moiety and maximizes the pseudocapacitance contribution.

Conclusions

A highly redox active dihydrophenazine derived porous organic polymer, GT-POP-1, was synthesized with triflic acid as the catalyst. Cyclo-trimerization of the DHPAZ-2CN precursor yields polymers with as few inactive groups as possible. The covalent triazine linkages also contribute to building a rigid and porous structure. Kinetic study revealed that the capacitance was mainly contributed by pseudocapacitance. The electrochemical tests revealed that the incorporation of redox-active dihydrophenazine endowed the GT-POP-1 electrode with a high specific capacitance of 97.1 mF cm⁻² (324 F g⁻¹). By virtue of the high capacitance and wide voltage window of the asymmetric supercapacitor, the GT-POP-1//AC device shows a high energy density of 7.3 μ W h cm⁻² (24.5 W h kg⁻¹) at a power density of 59.3 μ W cm⁻² and retains excellent rate stability even when the power density increases to 2987 µW cm⁻². Our work demonstrates that by rational molecular design, porous organic polymers can make the best use of redox sites to achieve high capacitance and consequently high energy density.

Credit authorship contribution statement

Huanhuan Zhang: conceptualization, investigation, writing – original draft, funding acquisition. Xiaohui Tang: investigation,

methodology. Cheng Gu: conceiving and directing the research, funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos, 21975078 and 21905098), the China Postdoctoral Science Foundation Grant (2018M643067), the Natural Science Foundation of Guangdong Province (2019B030301003), the 111 Project, the Fundamental Research Funds for the Central Universities, and the Thousand Youth Talents Plan.

Notes and references

- 1 S. Fleischmann, J. B. Mitchell, R. Wang, C. Zhan, D.-e. Jiang, V. Presser and V. Augustyn, *Chem. Rev.*, 2020, **120**, 6738–6782.
- 2 G. Dai, Y. Gao, Z. Niu, P. He, X. Zhang, Y. Zhao and H. Zhou, *ChemSusChem*, 2020, **13**, 2264–2270.
- 3 L. Hao, J. Ning, B. Luo, B. Wang, Y. Zhang, Z. Tang, J. Yang, A. Thomas and L. Zhi, *J. Am. Chem. Soc.*, 2015, 137, 219–225.
- 4 Y. Yusran, Q. Fang and V. Valtchev, *Adv. Mater.*, 2020, 32, e2002038.
- 5 S. Kandambeth, J. Jia, H. Wu, V. S. Kale, P. T. Parvatkar, J. Czaban-Jóźwiak, S. Zhou, X. Xu, Z. O. Ameur,
 - E. Abou-Hamad, A. H. Emwas, O. Shekhah, H. N. Alshareef and M. Eddaoudi, *Adv. Energy Mater.*, 2020, **10**, 2001673.
- 6 H. Zhang, X. Tang, D. Zhao, N. Zheng, L. Huang, T. Sun,
 C. Gu and Y. Ma, *Energy Storage Mater.*, 2020, 29, 281–286.
- 7 H. Zhang, Y. Zhang, C. Gu and Y. Ma, Adv. Energy Mater., 2015, 5, 1402175.
- 8 C. R. DeBlase, K. E. Silberstein, T. T. Truong, H. D. Abruna and W. R. Dichtel, *J. Am. Chem. Soc.*, 2013, **135**, 16821–16824.
- 9 C. R. DeBlase, K. Hernández-Burgos, K. E. Silberstein, G. G. Rodríguez-Calero, R. P. Bisbey, H. D. Abruña and W. R. Dichtel, ACS Nano, 2015, 9, 3178–3183.
- 10 F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu and D. Jiang, Angew. Chem., Int. Ed., 2015, 54, 6814–6818.
- 11 W. Lyu, W. Zhang, H. Liu, Y. Liu, H. Zuo, C. Yan, C. F. J. Faul, A. Thomas, M. Zhu and Y. Liao, *Chem. Mater.*, 2020, **32**(19), 8276–8285.
- 12 Y. Liao, H. Wang, M. Zhu and A. Thomas, *Adv. Mater.*, 2018, **30**, 1705710.
- 13 J. Sun, A. Klechikov, C. Moise, M. Prodana, M. Enachescu and A. V. Talyzin, *Angew. Chem., Int. Ed.*, 2018, 57, 1034– 1038.
- M. A. Khayum, V. Vijayakumar, S. Karak, S. Kandambeth, M. Bhadra, K. Suresh, N. Acharambath, S. Kurungot and R. Banerjee, *ACS Appl. Mater. Interfaces*, 2018, **10**, 28139– 28146.

- 15 H. Peng, J. Raya, F. Richard, W. Baaziz, O. Ersen, A. Ciesielski and P. Samori, *Angew. Chem., Int. Ed.*, 2020, **59**(44), 19602– 19609.
- 16 A. Halder, M. Ghosh, M. A. Khayum, S. Bera, M. Addicoat, H. S. Sasmal, S. Karak, S. Kurungot and R. Banerjee, *J. Am. Chem. Soc.*, 2018, 140, 10941–10945.
- 17 G. Dai, Y. He, Z. Niu, P. He, C. Zhang, Y. Zhao, X. Zhang and H. Zhou, *Angew. Chem., Int. Ed.*, 2019, **58**, 9902–9906.
- 18 W. Liu, M. Ulaganathan, I. Abdelwahab, X. Luo, Z. Chen, S. J. Rong Tan, X. Wang, Y. Liu, D. Geng, Y. Bao, J. Chen and K. P. Loh, ACS Nano, 2018, 12, 852–860.
- 19 C. Wang, X. Li, B. Yu, Y. Wang, Z. Yang, H. Wang, H. Lin, J. Ma, G. Li and Z. Jin, *ACS Energy Lett.*, 2020, 5, 411–417.
- 20 D. G. Wang, H. Wang, Y. Lin, G. Yu, M. Song, W. Zhong and G. C. Kuang, *ChemSusChem*, 2018, **11**, 3932–3940.
- 21 L. Hao, B. Luo, X. Li, M. Jin, Y. Fang, Z. Tang, Y. Jia, M. Liang, A. Thomas, J. Yang and L. Zhi, *Energy Environ. Sci.*, 2012, 5, 9747–9751.
- 22 X. Zhu, C. Tian, S. M. Mahurin, S.-H. Chai, C. Wang,
 S. Brown, G. M. Veith, H. Luo, H. Liu and S. Dai, *J. Am. Chem. Soc.*, 2012, 134, 10478–10484.
- 23 S. Ren, M. J. Bojdys, R. Dawson, A. Laybourn, Y. Z. Khimyak,
 D. J. Adams and A. I. Cooper, *Adv. Mater.*, 2012, 24, 2357–2361.
- 24 J. J. Liu, W. Zan, K. Li, Y. Yang, F. X. Bu and Y. X. Xu, *J. Am. Chem. Soc.*, 2017, **139**, 11666–11669.
- 25 H. Zhang, W. Sun, X. Chen and Y. Wang, *ACS Nano*, 2019, **13**, 14252–14261.
- 26 M. Liu, K. Jiang, X. Ding, S. Wang, C. Zhang, J. Liu, Z. Zhan, G. Cheng, B. Li, H. Chen, S. Jin and B. Tan, *Adv. Mater.*, 2019, 31, e1807865.
- 27 L. R. Pizzio, Mater. Lett., 2006, 60, 3931-3935.

- 28 L. Wang, C. Zeng, H. Xu, P. Yin, D. Chen, J. Deng, M. Li, N. Zheng, C. Gu and Y. Ma, *Chem. Sci.*, 2019, **10**, 1023–1028.
- 29 C. N. Gannett, B. M. Peterson, L. Shen, J. Seok, B. P. Fors and
 H. D. Abruna, *ChemSusChem*, 2020, 13, 2428–2435.
- 30 V. Augustyn, P. Simon and B. Dunn, *Energy Environ. Sci.*, 2014, 7, 1597–1614.
- 31 T. Brezesinski, J. Wang, R. Senter, K. Brezesinski, B. Dunn and S. H. Tolbert, *ACS Nano*, 2010, 4, 967–977.
- 32 H. Peng, J. Raya, F. Richard, W. Baaziz, O. Ersen, A. Ciesielski and P. Samori, *Angew. Chem.*, *Int. Ed.*, 2020, **59**, 19602–19609.
- 33 S. Y. Park, C. W. Kang, S. M. Lee, H. J. Kim, Y.-J. Ko, J. Choi and S. U. Son, *Chem.-Eur. J.*, 2020, **26**, 12343–12348.
- 34 W. Li, Y. Guo, Y. Wang, X. Xing, X. Chen, J. Ning, H. Yu, Y. Shi, I. Murtaza and H. Meng, *J. Mater. Chem. A*, 2019, 7, 116–123.
- 35 S. Chandra, D. Roy Chowdhury, M. Addicoat, T. Heine, A. Paul and R. Banerjee, *Chem. Mater.*, 2017, **29**, 2074–2080.
- 36 S. R. Peurifoy, J. C. Russell, T. J. Sisto, Y. Yang, X. Roy and C. Nuckolls, *J. Am. Chem. Soc.*, 2018, **140**, 10960–10964.
- 37 Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn and R. B. Kaner, *Chem. Rev.*, 2018, **118**, 9233–9280.
- 38 Y. Zhou, X. Wang, L. Acauan, E. Kalfon-Cohen, X. Ni,
 Y. Stein, K. K. Gleason and B. L. Wardle, *Adv. Mater.*, 2019,
 31, 1901916.
- 39 X. Liu, C. Guan, Y. Hu, L. Zhang, A. M. Elshahawy and J. Wang, Small, 2018, 14, 1702641.
- 40 L. Dong, G. Liang, C. Xu, W. Liu, Z.-Z. Pan, E. Zhou, F. Kang and Q.-H. Yang, *Nano Energy*, 2017, **34**, 242–248.
- 41 L. Dong, C. Xu, Y. Li, C. Wu, B. Jiang, Q. Yang, E. Zhou,
 F. Kang and Q.-H. Yang, *Adv. Mater.*, 2016, 28, 1675–1681.
- 42 D. P. Dubal, N. R. Chodankar, D. H. Kim and P. Gomez-Romero, *Chem. Soc. Rev.*, 2018, 47, 2065–2129.