

Cite this: *RSC Adv.*, 2019, 9, 37882

# Improved pseudocapacitive charge storage in highly ordered mesoporous TiO<sub>2</sub>/carbon nanocomposites as high-performance Li-ion hybrid supercapacitor anodes†

Yujin Lee,<sup>a</sup> Seoa Kim,<sup>a</sup> Jeong Han Lee,<sup>b</sup> Kwang Chul Roh,<sup>b</sup> Eunho Lim<sup>\*c</sup> and Jinwoo Lee<sup>†a</sup>

A Li-ion hybrid supercapacitor (Li-HSCs), an integrated system of a Li-ion battery and a supercapacitor, is an important energy-storage device because of its outstanding energy and power as well as long-term cycle life. In this work, we propose an attractive material (a mesoporous anatase titanium dioxide/carbon hybrid material, m-TiO<sub>2</sub>-C) as a rapid and stable Li<sup>+</sup> storage anode material for Li-HSCs. m-TiO<sub>2</sub>-C exhibits high specific capacity (~198 mA h g<sup>-1</sup> at 0.05 A g<sup>-1</sup>) and promising rate performance (~90 mA h g<sup>-1</sup> at 5 A g<sup>-1</sup>) with stable cyclability, resulting from the well-designed porous structure with nanocrystalline anatase TiO<sub>2</sub> and conductive carbon. Thereby, it is demonstrated that a Li-HSC system using a m-TiO<sub>2</sub>-C anode provides high energy and power (~63 W h kg<sup>-1</sup>, and ~4044 W kg<sup>-1</sup>).

Received 6th September 2019

Accepted 6th November 2019

DOI: 10.1039/c9ra07157a

rsc.li/rsc-advances

## Introduction

High-power energy-storage devices have been regarded as indispensable systems for medium- and large-scale energy-storage applications such as electric vehicles (EVs) and smart grid technologies. This is because the medium- and large-scale energy storage applications require fast charging and discharging behaviors with long cycle lifetime.<sup>1,2</sup> An electric double-layer capacitor (EDLC), which is one of the typical supercapacitors, is the representative energy-storage device that provides highly excellent power abilities (2–5 kW kg<sup>-1</sup>) with stable cyclability.<sup>3–6</sup> However, in spite of its superb abilities, it suffers from low energy performance (~10 W h kg<sup>-1</sup>) due to its charge-storage mechanism being based on the physisorption of solvated ions at electrode/electrolyte interfaces.<sup>7–9</sup>

As its alternative device, Li-ion hybrid supercapacitors (Li-HSCs) composed of Li-ion battery (LIB) electrode materials as anodes and EDLC electrode materials as cathodes in a non-aqueous electrolyte containing a Li salt have been intensively researched and developed in recent years.<sup>10–12</sup> This is because that their electrochemical performance delivering both high

energy and power abilities with stable cyclability is highly attractive. Such unique characteristics result from asymmetric charge-storage mechanisms that Li<sup>+</sup> from the electrolyte inserts to the anode materials (faradaic reaction) and anions such as PF<sub>6</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> are physically adsorbed on the surface of the cathode materials (non-faradaic reaction) during the charge process.<sup>10</sup> However, because of the different charge-storage mechanisms between two electrodes, a kinetics imbalance issue is one of the major problems in Li-HSCs, which should be solved to develop high-performance Li-HSCs.<sup>13,14</sup> In other words, the reaction mechanism of the anode materials using ionic diffusion in a crystal framework of electrode materials is much more sluggish than that of cathode materials.<sup>15,16</sup>

To address this kinetics issue, two kinds of strategies have intensively been considered. One of the effective strategies is to reduce particle size of electrode materials in the nanoscale regime.<sup>15</sup> Well-nanosized electrode materials have a variety of merits such as shortened lengths for Li<sup>+</sup> diffusion/electron mobility (high-power ability) and enhanced electrode/electrolyte interface area (high capacity).<sup>17–19</sup> In addition, reducing particle size of electrode materials in the nanoscale leads to improved pseudocapacitive reactions associated with surface-controlled reactions, which is kinetically not limited by diffusion-controlled reactions.<sup>20</sup> Another strategy is to use attractive carbonaceous and Ti-based anode materials such as graphite and titanium dioxide (TiO<sub>2</sub>).<sup>21–24</sup> Particularly, anatase TiO<sub>2</sub> is one of the promising anode materials for Li-HSCs, because of its beneficial Li<sup>+</sup> insertion/extraction behaviors and a variety of merits. Firstly, it provides theoretical capacity of ~168 mA h g<sup>-1</sup> in the potential range of ~1.7 V (vs. Li/Li<sup>+</sup>) with

<sup>a</sup>Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science Technology (KAIST), Daejeon 34141, Republic of Korea. E-mail: jwlee1@kaist.ac.kr

<sup>b</sup>Energy and Environmental Division, Korea Institute of Ceramic Engineering and Technology (KICET), Jinju, Gyeongnam 52851, Republic of Korea

<sup>c</sup>Carbon Resources Institute, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea. E-mail: eunholim@kRICT.re.kr

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra07157a

small volume change (<4%) during cycling.<sup>21,25</sup> Therefore, compared to the graphite anode working in the potential range of ~0.2 V (vs. Li/Li<sup>+</sup>), it is free from Li-plating problem and can provide highly stable cycle performance.<sup>26,27</sup> Secondly, Li-HSCs using anatase TiO<sub>2</sub> anodes can use a cost-attractive and light-weight Al current collector in the anodic part instead of Cu current collector because alloying reaction between Li<sup>+</sup> and Al does not take place in the potential range of 1.0–3.0 V (vs. Li/Li<sup>+</sup>) for anatase TiO<sub>2</sub>. In addition, it is non-toxic and one of the highly abundant materials.<sup>28,29</sup> However, the drawback of anatase TiO<sub>2</sub> is its poor electrical conductivity and relatively low Li<sup>+</sup> diffusion rate.<sup>28,30,31</sup>

Here, to rationally design the anatase TiO<sub>2</sub> as anode materials for Li-HSCs, we synthesized mesoporous anatase TiO<sub>2</sub>/carbon nanocomposite (denote as m-TiO<sub>2</sub>-C) by using block copolymer assisted simple synthesis method. It is clearly demonstrated in this work that design of the synthesized mesoporous electrode material comprising both nanocrystalline anatase TiO<sub>2</sub> and conductive carbon is highly appropriate to solve drawback of the anatase TiO<sub>2</sub> and to maximize its electrochemical performance (high capacity and rate capability), which result from improved Li<sup>+</sup> diffusion kinetics with rapid electron transport. Furthermore, we proved that the well-designed m-TiO<sub>2</sub>-C is highly attractive as anode materials for Li-HSCs delivering high energy and power.

## Experimental

### Synthesis of m-TiO<sub>2</sub>-C

0.15 g of PEO-*b*-PS (poly(ethylene oxide)-*b*-poly(styrene),  $M_n = 27\,466\text{ g mol}^{-1}$ ) was dissolved in 4 mL tetrahydrofuran (THF). 0.9 mL of titanium isopropoxide (TTIP) with 0.3 mL of 35–37% hydrochloric acid (concentrated HCl) was added dropwise to the block copolymer/THF mixture solution with continuous stirring. After 1 h of stirring, the mixture solution was poured to the glass Petri dish. The solvent was evaporated overnight at 40 °C, and then dried at 100 °C. The as-synthesized transparent film was obtained and then, the collected power was heat-treated in Ar atmosphere at 700 °C for 2 h. Commercial TiO<sub>2</sub> purchased from Sigma Aldrich was employed for control group (denoted as com-TiO<sub>2</sub>).

### Materials characterization

**Structure and chemical characterization.** The structure and morphology of prepared samples were investigated using scanning electron microscopy (SEM; S-4200 field-emission, Hitachi) and high resolution-transmission electron microscopy (HR-TEM; JEOL JEM-2010). Nitrogen adsorption-desorption analysis was conducted with 77 K with Micromeritics Tristar II 3020 system to estimate pore size and specific surface area. To confirm the specific pore morphology, small-angle X-ray scattering (SAXS) patterns was detected using 4C SAXS beamlines at the Pohang Light Source (PLS). To investigate crystalline phase, X-ray diffraction (XRD) pattern was identified by D/max-2500 a diffractometer (Rigaku, Cu-K $\alpha$  radiation). The carbon content of m-TiO<sub>2</sub>-C was estimated using

thermogravimetric analysis (TGA; NETZSCH STA 449C). Electron energy loss spectroscopy (EELS) analysis was performed to identify containing elements using energy-filtering transmission electron microscopy (EF-TEM, JM-220FS).

**Electrochemical measurements.** For half and full-cell electrochemical tests, active materials including m-TiO<sub>2</sub>-C and com-TiO<sub>2</sub> (80 wt%) were homogeneously mixed with super-P carbon (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in *N*-methyl-2-pyrrolidone (NMP). The slurries were pasted on current collector using doctor blade. The prepared electrodes were dried at 60 °C for 6 h and then, 110 °C for 12 h in vacuum oven. Subsequently, the electrodes were roll-pressed. For half-cell test, 2032-type coin cells were fabricated with lithium metal as both counter and reference electrodes in Ar-filled glovebox. The mass loading of active materials used as anode materials were carefully controlled around 1.0 mg cm<sup>-2</sup>. The electrolyte was 1.0 M of LiPF<sub>6</sub> in mixture of ethylene carbonate/dimethyl carbonate (EC/DMC, 1 : 1 volume ratio, Panaxetec. Co., Korea). The activated carbon electrode used as cathode materials was prepared using commercially available MSP-20 (90 wt%), conductive carbon (5 wt%), and polytetrafluoroethylene (PTFE, 5 wt%). In the half-cell tests, the working voltages for anode and cathode materials were 1.0–3.0 and 3.0–4.5 V (vs. Li/Li<sup>+</sup>), respectively. In the case of full-cell, Li-HSC was assembled using m-TiO<sub>2</sub>-C as an anode and MSP-20 as a cathode and the weight ratio of anode and cathode active materials was controlled to 1 : 3.5 in working voltages of 0–3.0 V. The energy and power of the Li-HSCs was calculated by numerically integrating the galvanostatic discharge profiles using eqn (1) and (2) as follows.<sup>32</sup>

$$E = \int_{t_1}^{t_2} IV \, dt \quad (1)$$

where  $I$  is the constant current (A g<sup>-1</sup>),  $V$  is the working voltage (V),  $t_1$  and  $t_2$  are the start/end of discharge time (s) of Li-HSCs, respectively, and

$$P = \frac{E}{t} \quad (2)$$

where  $t$  is the discharge time (s). All electrochemical tests were conducted using the WBCS-3000 battery cyclor (WonA Tech, Korea).

## Results and discussion

### Material characterization

The m-TiO<sub>2</sub>-C was synthesized using a block copolymer-assisted synthesis method and schematic representation on the synthesis method is shown in Fig. 1. In brief, the Ti precursor (TTIP) and laboratory-made amphiphilic block copolymer (poly(ethylene oxide)-*b*-poly(styrene), PEO-*b*-PS) synthesized by atomic transfer radical polymerization (ATRP) were dissolved in tetrahydrofuran (THF). And then, to induce sol-gel reaction of TTIP, concentrated hydrochloric acid (HCl) was slowly added to the TTIP/block copolymer/THF mixture solution. The titanium oxide sol made by hydrolysis selectively interacts with the hydrophilic PEO part of PEO-*b*-PS *via* hydrogen bonds. During



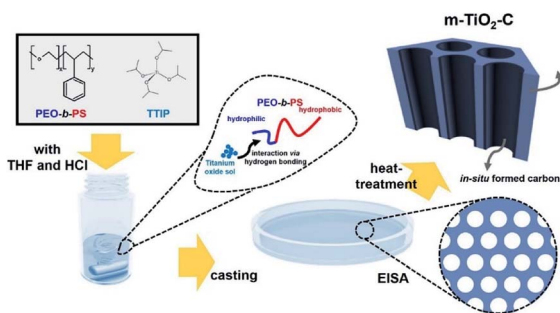


Fig. 1 Schematic illustration of the synthesis of m-TiO<sub>2</sub>-C.

the evaporation of organic solvent at 40 °C (evaporation-induced self-assembly, ESIA), highly ordered mesostructure is formed by self-organization of titanium oxide sol/block copolymer mixture.<sup>33–36</sup> After drying at 100 °C to induce the cross-linkage of titanium oxide sol, the as-synthesized TiO<sub>2</sub>/block copolymer composite was heat-treated at 700 °C under inert atmosphere (Ar condition). During heat-treatment, as-synthesized TiO<sub>2</sub> is converted to crystalline TiO<sub>2</sub>. In addition, PS part of PEO-*b*-PS is converted to mechanically stable and conductive carbon (*in situ* formed carbon in m-TiO<sub>2</sub>-C). For comparison, commercially available TiO<sub>2</sub> (com-TiO<sub>2</sub>) was employed.

Fig. 2a and b show that X-ray diffraction (XRD) patterns of m-TiO<sub>2</sub>-C and com-TiO<sub>2</sub> are in good agreement with anatase TiO<sub>2</sub> (JCPDS no. 21-1272) with no noticeable impurities. Their average crystallite sizes calculated using the Debye–Scherrer equation were ~14 (m-TiO<sub>2</sub>-C) and ~100 (com-TiO<sub>2</sub>) nm, respectively.<sup>37</sup> In addition, high-resolution transmission electron microscopy (HR-TEM, Fig. 2c) image of m-TiO<sub>2</sub>-C clearly shows the lattice fringes of anatase TiO<sub>2</sub> with (101) and (004) spacing of 0.353 and 0.238 nm, respectively, again indicating

that the crystal structure of m-TiO<sub>2</sub>-C well match the anatase TiO<sub>2</sub> phase. Mesoporous structure of m-TiO<sub>2</sub>-C is identified through scanning electron microscopy (SEM) image, N<sub>2</sub> adsorption-desorption technique, and small-angle X-ray scattering (SAXS) patterns. SEM image (Fig. 2d) shows highly ordered mesoporous structure with uniform pore size. Compared to m-TiO<sub>2</sub>-C, com-TiO<sub>2</sub> has irregular and larger particle shape/size without porosity (Fig. S1†). In addition, N<sub>2</sub> adsorption isotherm (Fig. 3a) of m-TiO<sub>2</sub>-C corresponds to type IV curve with a sharp adsorption at ~0.9 *P*/*P*<sub>0</sub>, indicating that uniform mesopores are predominant. The main pore size calculated using the Barret–Joyner–Halenda (BJH) method and specific surface area calculated using the Brunauer–Emmett–Teller (BET) of m-TiO<sub>2</sub>-C were ~13 nm and ~123 m<sup>2</sup> g<sup>−1</sup> (Fig. 3b), respectively, which is significantly higher than that of com-TiO<sub>2</sub> (<2 m<sup>2</sup> g<sup>−1</sup>). The mesoporous structural characterization of m-TiO<sub>2</sub>-C is further demonstrated by SAXS pattern (Fig. 3c). Scattering peaks of m-TiO<sub>2</sub>-C with a peak position ratio of 1 : 3<sup>1/2</sup> : 4<sup>1/2</sup> suggest that hexagonally ordered TiO<sub>2</sub> structure with a long-range order is well established.<sup>38</sup> To confirm the presence of *in situ* formed carbon in m-TiO<sub>2</sub>-C, thermogravimetric analysis (TGA) and electron energy loss spectroscopy (EELS) analysis were employed. TGA result (Fig. 3d) proves that the *in situ* formed carbon content in the m-TiO<sub>2</sub>-C is around 10 wt%. Furthermore, EELS analysis image (Fig. 4) directly shows the existence of *in situ* formed carbon in the m-TiO<sub>2</sub>-C, representing that Ti, O, and C are uniformly dispersed.

## Electrochemistry

Galvanostatic charge-discharge (de-lithiation and lithiation) test on m-TiO<sub>2</sub>-C was conducted in the potential range of 1.0–3.0 V (vs. Li/Li<sup>+</sup>), showing that the m-TiO<sub>2</sub>-C provides reversible charge capacity of ~198 mA h g<sup>−1</sup> at current of 0.05 A g<sup>−1</sup> (Fig. 5a). The typical plateau at a potential of ~1.7 V (vs. Li/Li<sup>+</sup>) demonstrates reversible Li<sup>+</sup> intercalation into anatase TiO<sub>2</sub>

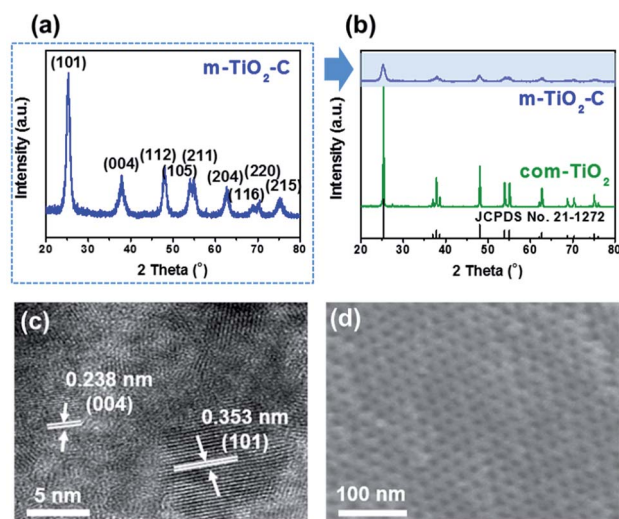


Fig. 2 (a) XRD pattern on m-TiO<sub>2</sub>-C. (b) Comparison of XRD patterns on m-TiO<sub>2</sub>-C and com-TiO<sub>2</sub>. (c) HR-TEM image of m-TiO<sub>2</sub>-C. (d) SEM image of m-TiO<sub>2</sub>-C.

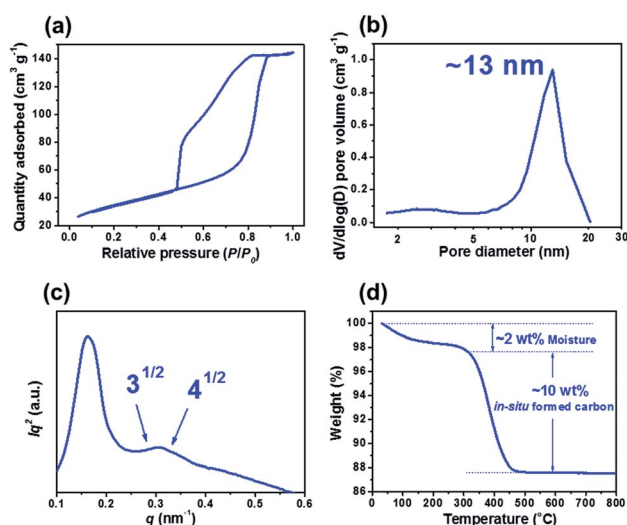


Fig. 3 (a) N<sub>2</sub> physisorption isotherm and (b) pore size distribution of m-TiO<sub>2</sub>-C. (c) SAXS pattern of m-TiO<sub>2</sub>-C. (d) TGA result of m-TiO<sub>2</sub>-C.





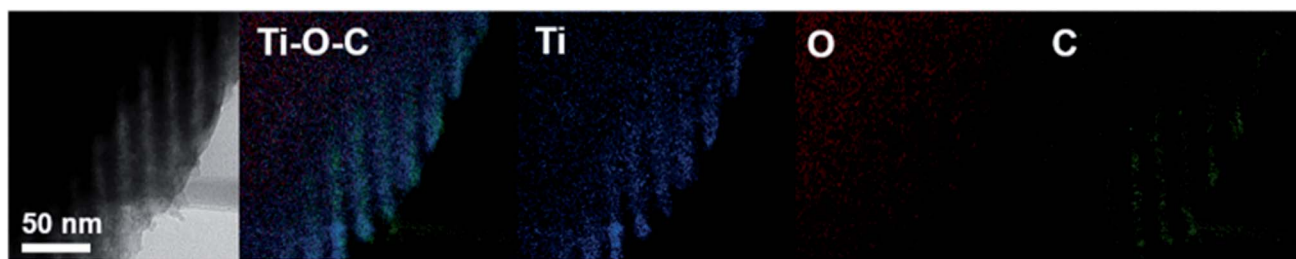


Fig. 4 EELS mapping images of m-TiO<sub>2</sub>-C.

lattice, where  $\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$  ( $0 \leq x \leq 0.5$ ).<sup>22,28,39</sup> Fig. 5b shows the specific capacity of m-TiO<sub>2</sub>-C is much higher ( $\sim 198 \text{ mA h g}^{-1}$ ) than that of com-TiO<sub>2</sub> ( $\sim 110 \text{ mA h g}^{-1}$ ) at current of  $0.05 \text{ A g}^{-1}$ . In addition, compared to com-TiO<sub>2</sub>, the m-TiO<sub>2</sub>-C showed much better rate capability with increasing currents from  $0.05$  to  $5 \text{ A g}^{-1}$ , also indicating that capacity retention of m-TiO<sub>2</sub>-C with increasing currents is significantly outstanding than that of com-TiO<sub>2</sub> (Fig. S2a†). Fig. 5c and S2b† shows that the galvanostatic charge–discharge curves of m-TiO<sub>2</sub>-C with increasing currents are well maintained with small overpotentials (reduced internal resistance) compared to those of com-TiO<sub>2</sub>. It represents that well-ordered structure with conductive *in situ* formed carbon is highly beneficial to improve electrochemical performances of anatase TiO<sub>2</sub>, mainly due to a variety of merits including (i) shortened diffusion lengths of Li<sup>+</sup>, (ii) superior electron mobility, (iii) easy penetration of electrolyte, (iv) plentiful charge-storage sites, and *etc.*<sup>34,40–42</sup> It should be noted that the m-TiO<sub>2</sub>-C exhibits better rate capability than other anatase TiO<sub>2</sub> anodes previously reported (Fig. S3†) and delivers highly stable cycle stability (capacity retention of  $\sim 94\%$  with  $\sim 100\%$  coulombic efficiency for  $\sim 350$  cycles) at the current of  $0.5 \text{ A g}^{-1}$  (Fig. 5d and S4†).<sup>43–47</sup> In addition, it shows

stable long-term cyclability at high current of  $3 \text{ A g}^{-1}$  for 1000 cycles (Fig. S4,† capacity retention of  $\sim 97\%$  with  $\sim 100\%$  coulombic efficiency). Because the excellent rate capability and long-term cycle stability are main factors for application to anodes of Li-HSCs, m-TiO<sub>2</sub>-C developed in this work could be the extremely potential Li-HSC anode material.

To further reveal the reason why m-TiO<sub>2</sub>-C provides superior electrochemical behaviors, we performed cyclic voltammetry (CV) tests on m-TiO<sub>2</sub>-C and com-TiO<sub>2</sub> conducted at sweep rates from  $0.1$  to  $1.0 \text{ mV s}^{-1}$  in the potential range of  $1.0$ – $3.0 \text{ V}$  (*vs.* Li/Li<sup>+</sup>) as shown in Fig. 6a and S5.† The pair of redox peaks ( $1.7$ – $2.0 \text{ V vs. Li/Li}^+$ ) of m-TiO<sub>2</sub>-C and com-TiO<sub>2</sub> at sweep rate of  $0.1 \text{ mV s}^{-1}$  well match the lithiation and de-lithiation reactions. In previous studies, it is well known that the anatase TiO<sub>2</sub> is influenced by the diffusion-controlled process with a two-phase process. Therefore, from  $i = av^b$  equation (where  $a$  ( $\text{mV s}^{-1}$ )) with CV tests,  $b$  value of anatase TiO<sub>2</sub> is close to  $0.5$ , indicating that the diffusion-controlled reactions is more dominant than

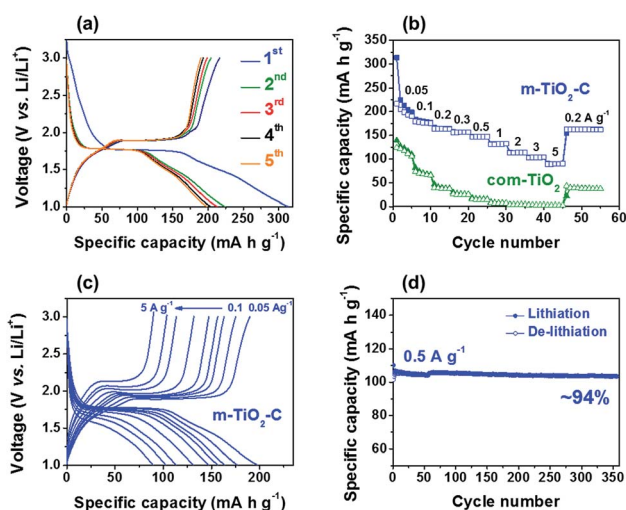


Fig. 5 (a) Galvanostatic charge–discharge profiles of m-TiO<sub>2</sub>-C at  $0.05 \text{ A g}^{-1}$ . (b) Comparison of rate capability of TiO<sub>2</sub> electrodes at different currents from  $0.05$  to  $5 \text{ A g}^{-1}$ . (c) Galvanostatic charge–discharge profiles of m-TiO<sub>2</sub>-C at various currents from  $0.05$  to  $5 \text{ A g}^{-1}$ . (d) Cycle performance of m-TiO<sub>2</sub>-C at a current of  $0.5 \text{ A g}^{-1}$ .

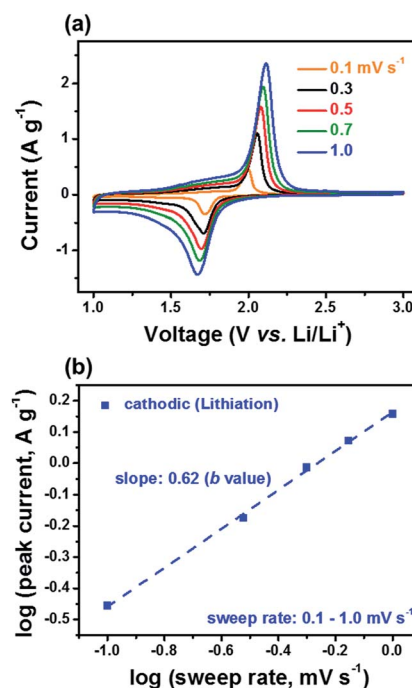


Fig. 6 (a) CV curves of m-TiO<sub>2</sub>-C at different sweep rates of  $0.1$ – $1.0 \text{ mV s}^{-1}$ . (b)  $\log(i)$  *vs.*  $\log(v)$  plot of cathodic peak current on m-TiO<sub>2</sub>-C electrode.



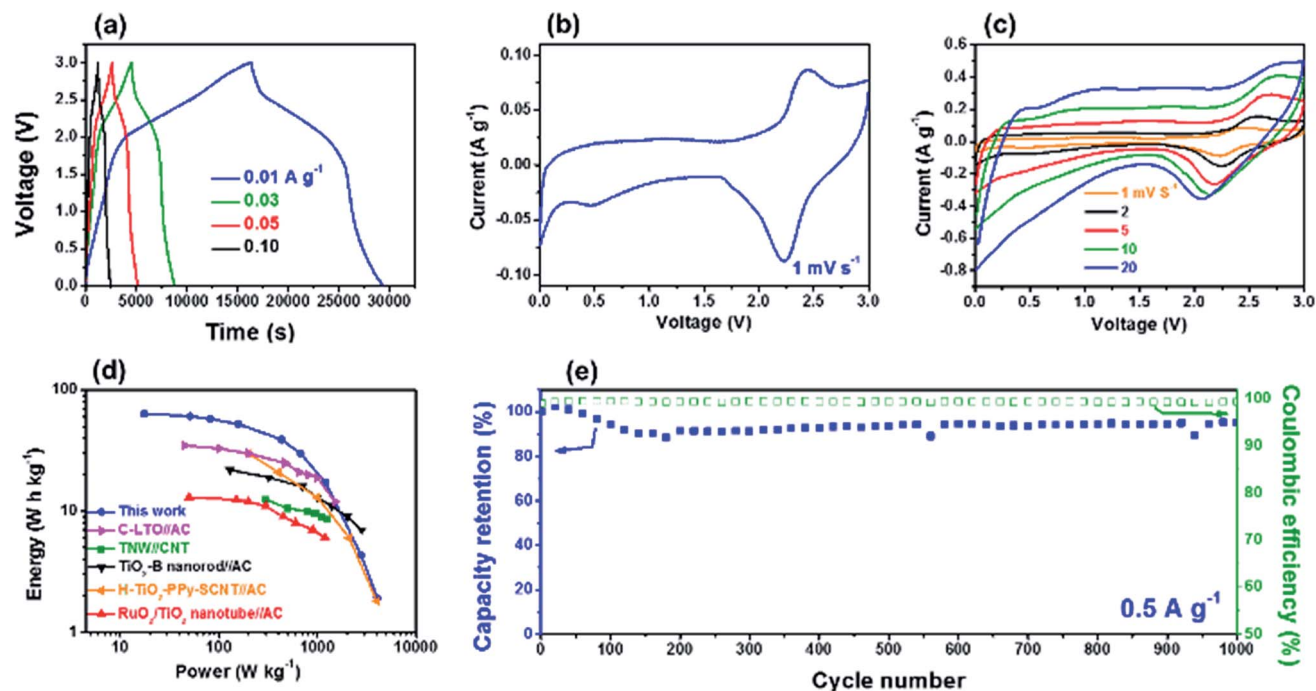


Fig. 7 (a) Galvanostatic charge–discharge profiles of the Li-HSC at different currents from 0.01 to 0.1 A g<sup>−1</sup>. (b and c) CV curves of the Li-HSCs at different sweep rates of 1–20 mV s<sup>−1</sup>. (d) Ragone plots compared with previously reported results. (e) Cycle performance of the Li-HSC at a current of 0.5 A g<sup>−1</sup>.

the surface-controlled reaction ( $b = 1.0$ ).<sup>20,48,49</sup> As shown in Fig. 6b and S6†,  $b$  value of m-TiO<sub>2</sub>-C obtained from peak currents of the lithiation process is around 0.62, indicative of that the charge-storage reaction mechanism in m-TiO<sub>2</sub>-C is influenced by both the surface- and diffusion-controlled reactions (improved pseudocapacitive reaction).<sup>49</sup> It is considerably contrast to that of com-TiO<sub>2</sub> showing severe deviation with increasing sweep rates from 0.1 to 1.0 mV s<sup>−1</sup> because of huge internal resistance. In addition,  $b$  values of m-TiO<sub>2</sub>-C obtained in potential range of 1.2–2.1 V (vs. Li/Li<sup>+</sup>) are also higher than 0.5 (Fig. S6†).

Before building Li-HSC system using the m-TiO<sub>2</sub>-C anode, electrochemical behavior of MSP-20 (commercially available activated carbon) as a cathode material for the Li-HSC was investigated by galvanostatic charge–discharge half-cell test. Fig. S7† shows that reversible specific capacity of the MSP-20 is ~60 mA h g<sup>−1</sup> at a current of 0.05 A g<sup>−1</sup> in the voltage range of 3.0–4.5 V (vs. Li/Li<sup>+</sup>). Considering the specific capacities and working voltages between m-TiO<sub>2</sub>-C anode and MSP-20 cathode, the Li-HSC system using m-TiO<sub>2</sub>-C anode and MSP-20 cathode was carefully assembled and its galvanostatic charge–discharge tests were conducted at various currents in the potential range of 0.0–3.0 V (Fig. 7a and S8†). Galvanostatic charge–discharge curves of Li-HSC using m-TiO<sub>2</sub>-C as anode and MSP-20 as cathode at current rates from 0.01 to 5 A g<sup>−1</sup> do not exhibit typical triangular shape, dissimilar to those of conventional symmetric SCs.<sup>50</sup> It is again confirmed from CV data at sweep rates of 1–20 mV s<sup>−1</sup> (Fig. 7b and c) that the CV profile does not follows a typical rectangular shape of conventional symmetric SCs. The galvanostatic charge–discharge and CV shapes of the

Li-HSC are mainly due to combination of the faradaic reaction at the m-TiO<sub>2</sub>-C anode and the non-faradaic reaction at the MSP-20 cathode.<sup>22</sup> The maximum energy and power of the Li-HSC calculated using eqn (1) and (2) with galvanostatic charge–discharge curves were ~63 W h kg<sup>−1</sup> and ~4044 W kg<sup>−1</sup>, respectively. The Ragone plot on the trade of relationship between energy and combination of the faradaic reaction at the m-TiO<sub>2</sub>-C anode and the non-faradaic reaction at the MSP-20 cathode.<sup>22</sup> The maximum energy and power of the Li-HSC calculated using eqn (1) and (2) with galvanostatic charge–discharge curves were ~63 W h kg<sup>−1</sup> and ~4044 W kg<sup>−1</sup>, respectively. The Ragone plot on the trade of relationship between energy and power shows that its energy and power is much better than that of other results previously reported (Fig. 7d).<sup>43,51–54</sup> Finally, long-term cycle stability of the Li-HSC was investigated. Fig. 7e shows that the cycling stability of the Li-HSC at a current of 0.5 A g<sup>−1</sup> is well maintained with ~100% coulombic efficiency for 1000 cycles. The Ragone plot and cycle performance data imply that m-TiO<sub>2</sub>-C is highly suitable as the anode material for Li-HSC system.

## Conclusions

In summary, we reported the block copolymer assisted one-pot synthesis method of m-TiO<sub>2</sub>-C and its application for high-power anode materials of Li-HSC. The m-TiO<sub>2</sub>-C delivered high specific capacity (~198 mA h g<sup>−1</sup> at 0.05 A g<sup>−1</sup>) and rate capability (~90 mA h g<sup>−1</sup> at 5 A g<sup>−1</sup>) with stable cycle performance. Its electrochemical performance was superior compared to com-TiO<sub>2</sub>, mainly due to synergistic effects of



unique mesostructure and hybridization between anatase TiO<sub>2</sub> and *in situ* formed carbon. Thereby, the Li-HSC system using the m-TiO<sub>2</sub>-C anode possessed high energy and power abilities ( $\sim 63 \text{ W h kg}^{-1}$  and  $\sim 4044 \text{ W kg}^{-1}$ ) in the potential range of 0.0–3.0 V, implying that the energy-storage device (Li-HSC) can be a promising alternative to conventional symmetric SCs.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT [NRF-2017R1A2B3004648, and NRF-2018M1A2A2061987]. This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea [No. 20174030201600, and No. 20182010600430].

## Notes and references

- B. Kang and G. Ceder, *Nature*, 2009, **458**, 190–193.
- M. H. Hsieh, G. A. Li, W. C. Chang and H. Y. Tuan, *J. Mater. Chem. A*, 2017, **5**, 4114–4121.
- J. Yan, Q. Wang, T. Wei and Z. Fan, *Adv. Energy Mater.*, 2014, **4**, 1300816.
- G. Zhang and X. W. Lou, *Adv. Mater.*, 2013, **25**, 976–979.
- G. F. Chen, Y. Z. Su, P. Y. Kuang, Z. Q. Liu, D. Y. Chen, X. Wu, N. Li and S. Z. Qiao, *Chem. - Eur. J.*, 2015, **21**, 4614–4621.
- S. Ghosh, S. Jeong and S. R. Polaki, *Korean J. Chem. Eng.*, 2018, **35**, 1389–1408.
- P. Simon, Y. Gogotsi and B. Dunn, *Science*, 2014, **343**, 1210–1211.
- D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P. L. Taberna and P. Simon, *Nat. Nanotechnol.*, 2010, **5**, 651–654.
- E. M. Jin, H. Lee, H. Jun and S. Jeong, *Korean J. Chem. Eng.*, 2017, **34**, 885–891.
- K. Naoi, S. Ishimoto, J. Miyamoto and W. Naoi, *Energy Environ. Sci.*, 2012, **5**, 9363–9373.
- C. M. Lai, T. L. Kao and H. Y. Tuan, *J. Power Sources*, 2018, **379**, 261–269.
- R. Yi, S. Chen, J. Song, M. L. Gordin, A. Manivannan and D. Wang, *Adv. Funct. Mater.*, 2014, **24**, 7433–7439.
- E. Lim, C. Jo, H. Kim, M. Kim, Y. Mun, Y. Ye, J. Hwang, K. Ha, K. Roh and J. Lee, *ACS Nano*, 2015, **9**, 7497–7505.
- E. Lim, W. Lim, C. Jo, J. Chun, M. Kim, K. Roh and J. Lee, *J. Mater. Chem. A*, 2017, **5**, 20969–20977.
- E. Lim, C. Jo and J. Lee, *Nanoscale*, 2016, **8**, 7827–7833.
- V. Aravindan, J. Gnanaraj, Y. S. Lee and S. Madhavi, *Chem. Rev.*, 2014, **114**, 11619–11635.
- Z. Wang, L. Zhou and X. W. Lou, *Adv. Mater.*, 2012, **24**, 1903–1911.
- Z. Yang, D. Choi, S. Kerisit, K. M. Rosso, D. Wang, J. Zhang, G. Graff and J. Liu, *J. Power Sources*, 2009, **192**, 588–598.
- A. K. Mondal, K. Kretschmer, Y. Zhao, H. Liu, H. Fan and G. Wang, *Microporous Mesoporous Mater.*, 2017, **246**, 72–80.
- J. Wang, J. Polleux, J. Lim and B. Dunn, *J. Phys. Chem. C*, 2007, **40**, 14925–14931.
- D. Deng, M. Kim, J. Y. Lee and J. Cho, *Energy Environ. Sci.*, 2009, **2**, 818–837.
- H. Kim, M. Cho, M. Kim, K. Park, H. Gwon, Y. Lee, K. C. Roh and K. Kang, *Adv. Energy Mater.*, 2013, **3**, 1500–1506.
- S. Ghosh, W. D. Yong, E. M. Jin, S. R. Polaki, S. Jeong and H. Jun, *Korean J. Chem. Eng.*, 2019, **36**, 312–320.
- W. Lee, S. Jeong, H. Lee, B. Kim, K. An, Y. Park and S. Jung, *Korean J. Chem. Eng.*, 2017, **34**, 2993–2998.
- L. Thirugunnam, S. Kaveri, V. Etacheri, S. Ramaprabhu, M. Dutta and V. G. Pol, *Mater. Charact.*, 2017, **131**, 64–71.
- Y. Liu and Y. Yang, *J. Nanomater.*, 2016, **2016**, 1–15.
- V. Etacheri, C. N. Hong, J. Tang and V. G. Pol, *ACS Appl. Mater. Interfaces*, 2018, **10**, 4652–4661.
- J. Shin, D. Samuelis and J. Maier, *Adv. Funct. Mater.*, 2011, **21**, 3464–3472.
- Y. Guan, T. Hu, J. Wu, L. Zhao, F. Tian, W. Pan, P. He, W. Qi, F. Li and K. Xu, *Korean J. Chem. Eng.*, 2019, **36**, 115–125.
- Y. Qiu, K. Yan, S. Yang, L. Jin, H. Deng and W. Li, *ACS Nano*, 2010, **4**, 6515–6526.
- J. S. Chen, H. Liu, S. Z. Qiao and X. W. Lou, *J. Mater. Chem.*, 2011, **21**, 5687–5692.
- F. Zhang, T. Zhang, X. Yang, L. Zhang, K. Leng, Y. Huang and Y. Chen, *Energy Environ. Sci.*, 2013, **6**, 1623.
- J. Hwang, C. Jo, M. Kim, J. Chun, E. Lim, S. Kim, S. Jeong, Y. Kim and J. Lee, *ACS Nano*, 2015, **9**, 5299–5309.
- C. Jo, Y. Kim, J. Hwang, J. Shim, J. Chun and J. Lee, *Chem. Mater.*, 2014, **26**, 3508–3514.
- J. Lee, M. C. Orilall, S. C. Warren, M. Kamperman, F. J. DiSalvo and U. Wiesner, *Nat. Mater.*, 2008, **7**, 222–228.
- J. Hwang, J. Kim, E. Ramasamy, W. Choi and J. Lee, *Microporous Mesoporous Mater.*, 2011, **143**, 149–156.
- A. D. Krawitz, *Introduction to Diffraction in Materials Science and Engineering*, Wiley, New York, 2001, p. 168.
- M. Templin, A. Franck, A. D. Chensne, H. Leist, Y. Zhang, R. Ulrich, V. Schadler and U. Wiesner, *Science*, 1997, **278**, 1795–1798.
- Y. Guo, Y. Hu and J. Maier, *Chem. Commun.*, 2006, **26**, 2783–2785.
- Y. Ye, C. Jo, I. Jeong and J. Lee, *Nanoscale*, 2013, **5**, 4584–4605.
- C. Jo, J. Hwang, H. Song, A. H. Dao, Y. Kim, S. Lee, S. Hong, S. Yoon and J. Lee, *Adv. Funct. Mater.*, 2013, **23**, 3747–3754.
- E. Kang, Y. Jung, G. Kim, J. Chun, U. Wiesner, A. C. Dillon, J. Kim and J. Lee, *Adv. Funct. Mater.*, 2011, **21**, 4349–4357.
- G. Tang, L. Cao, P. Xiao, Y. Zhang and H. Liu, *J. Power Sources*, 2017, **355**, 1–7.
- E. Lim, H. Shim, S. Fleischmann and V. Presser, *J. Mater. Chem. A*, 2018, **6**, 9480.
- H. Wang, C. Guan, X. Wang and H. J. Fan, *Small*, 2015, **11**, 1470–1477.



- 46 T. Brousse, R. Marchand, P. Taberna and P. Simon, *J. Power Sources*, 2006, **158**, 571–577.
- 47 V. Aravindan, M. V. Reddy, S. Madnavi, S. G. Mhaisalkar, G. V. Subba Rao and B. V. R. Chowdari, *J. Power Sources*, 2011, **196**, 8850–8854.
- 48 V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, H. D. Abruna, P. Simon and B. Dunn, *Nat. Mater.*, 2013, **12**, 518–522.
- 49 H. Lindstrom, S. Sodergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt and S. Lindquist, *J. Phys. Chem. B*, 1997, **101**, 7717–7722.
- 50 K. Karthikeyan, S. Amaresh, V. Aravindan, H. Kim, K. S. Kang and Y. S. Lee, *J. Mater. Chem. A*, 2013, **1**, 707–714.
- 51 H. Jung, N. Venugopal, B. Scrosati and Y. Sun, *J. Power Sources*, 2013, **221**, 266–271.
- 52 Q. Wang, Z. Wen and J. Li, *Adv. Funct. Mater.*, 2006, **16**, 2141–2146.
- 53 V. Aravindan, N. Shubha, W. Chui and S. Madhavi, *J. Mater. Chem. A*, 2013, **1**, 6145–6151.
- 54 Y. Wang, W. Wang and Y. Xia, *Electrochim. Acta*, 2005, **50**, 5641–5646.

