Supercapacitor and nanoscale research towards electrochemical energy storage

Pai Lua, Dongfeng Xue a,b, Hong Yang c and Yinong Liu c

a School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China; b State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China; c Laboratory for Functional Materials, School of Mechanical and Chemical Engineering, The University of Western Australia, Crawley, WA 6009, Australia

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Electrochemical capacitors, also known as supercapacitors or ultracapacitors, have received much attention from research and development to industrialization, owing to their promise to deliver high levels of electrical power and offer long operating lifetimes. They are considered ideal candidates for energy storage in high-power applications. Benefiting from intensive nanoscale research in recent decades, remarkable improvements and development of supercapacitive energy storage systems have been achieved. Both the energy density and power density for supercapacitors have been substantially improved. In this review article, we endeavor to assess the profound impacts of nanoscale research on the development of supercapacitors, in terms of the substantial improvement of capacitive performance for electrode materials, and revolutionary advances in electrode and device configurations. In addition, recent progress in basic energy storage mechanisms and prototypes of supercapacitors are also reviewed, including a new kinetically-favored intercalation mechanism introduced for the first time. The review concludes with descriptions of the demonstration of already-realized practical applications of commercially-available supercapacitor devices, especially focusing on real usage in vehicles that are highly anticipated by future communities to further heighten the wide attention on clean energy storage systems.

Keywords: supercapacitor; nanoscale research; electrochemical energy storage; electrode material

1. Introduction

With the rapid depletion of fossil fuels and increasingly worse environmental pollution that the world faces as a result of fossil fuel consumption, the search for renewable and clean energy sources to substitute fossil fuels and for improved efficiency of energy utilization are acknowledged as important tasks. Advanced energy storage technologies have been developed to facilitate the efficient utilization of the produced energy. This is especially beneficial for the reduction of the emission of harmful gases (e.g. CO₂ and NOₓ) arising from the burning of fossil fuels. This has attracted wide attention as an intermediate step between the production and versatile utilization of energy [1].

Electrochemical energy storage is at the forefront of energy storage technology [2]. It is now playing a large part in our lives, ranging from portable electronics to hybrid...
vehicles. Electrochemical secondary batteries, fuel cells and supercapacitors are the three main types of electrochemical energy storage device. Each of the three types has its own distinctive technological advantages. Lithium-ion batteries and fuel cells have high energy densities, but are disadvantaged for some applications by having somewhat slow power delivery. Stimulated by the needs of high-power energy storage systems in a large spectrum of applications, such as electric and hybrid vehicles, supercapacitors have recently attracted much interest owing to their unique abilities to deliver high power release or uptake (10 kW kg\(^{-1}\)) in very short times (a few seconds) [3]. Compared with conventional electrostatic capacitors, electrochemical supercapacitors can store hundreds or thousands times more charge, making them more attractive for meeting the practical demands for energy storage.

In the past two decades, nanoscale research has opened revolutionary opportunities for improving the performance of supercapacitors [4]. It is well known that the size regime of ‘energy carriers’ for supercapacitors (electrolyte ions) falls into the domain of nanoscience and nanotechnology. More electrochemically active surfaces and interfaces are endowed by nano-engineering via the creation of nanoporous [5] and nanogranular electrodes [6]. These electrodes facilitate easy mass transport of electrolyte ions in the electrochemical process, thereby improving the capacitance and power density of supercapacitors. Recently, electrode configurations have been reformed by nanoscale design. Three-dimensional (3D) nano-architected supercapacitor electrodes have been devised to surpass the conventional two-dimensional (2D) ones [7]. Composite nanoelectrodes have also been designed to exert synergetic functions of individual components [8]. To satisfy the energy demand of flexible portable electronics, novel thin film nanostructured electrodes of high flexibility and robustness have been achieved [9]. In addition to the multiple benefits for electrodes, nano-engineering is also reforming the entire device configuration of supercapacitors. Some conceptual models have appeared [10], which may be anticipated as primary next-generation electrochemical energy storage devices.

Supercapacitors currently fill the gap between batteries and electrostatic capacitors. In this review, we will start with an introduction of basic energy storage principles of supercapacitors and their prototypes. Considering that nanoscale research has been playing a critical role in significantly improving the performance of supercapacitors, recent progress of supercapacitors benefiting from the nanoscale research will be highlighted in detail. After that, practical applications of supercapacitors will be reviewed.

2. Capacitive energy storage mechanism

Before the introduction of recent advances in electrode and device configurations, it is necessary to provide a brief overview of the way supercapacitors store electrical charge. To date, two main acknowledged energy storage principles of supercapacitors have been proposed: the electric double-layer principle and the surface redox reaction-based pseudo-capacitive charge storage principle. Besides these classical principles, one newly established kinetically-favored intercalation mechanism will also be discussed, which may stimulate new ideas for the design of novel electrode materials.

2.1. Electrochemical double-layer mechanism

The concept of an electrochemical double-layer capacitor (EDLC) was first described in a US patent in 1950s [11], which is the first proposed working principle for supercapacitors.
In this pioneering research, carbon with a high specific surface area was coated onto metallic current collectors and immersed into sulfuric acid electrolyte to collect the polarized charge. After that, aqueous-electrolyte capacitors were commercialized by NEC (Japan) in 1970s and applied in the energy storage field, initiating the wide usage of supercapacitors in commercial devices [11].

In general, an EDLC is an electrochemical capacitor that stores the charge electrostatically via reversible adsorption of electrolyte ions onto active materials that are electrochemically stable and have a highly accessible specific surface area, on which the charge is separated on polarization at the electrode–electrolyte interface [4]. Specifically, when the electrode is immersed in an electrolyte, driven by an external electric field, there will be a spontaneous organization of charges at the surface of the electrode and in the electrolyte, approaching the electrode to form electrochemical double layer. This charge collection process is schematically illustrated in Figure 1a. The two charged layers, i.e. the one at the surface of the electrode and the other within the electrolyte, behave as a conventional dielectric physical capacitor to store energy. The major difference is that the insulating barrier in a dielectric capacitor is replaced by electrolyte in a supercapacitor.

Since there is no Faradaic reaction in the EDLC, the electric energy in an EDLC is stored in aggregated charges at the surface of electrode material. The key to realizing superior performance is in using electrochemically stable electrode materials with high specific surface area and conductivity. Conductive carbon materials are the most appropriate candidates due to their low cost, good processing ability, superior electrochemical stability and conductivity. To seek carbon materials with large accessible surfaces is one of the main topics in capacitive energy storage research. Fortunately, nanoscience and nanotechnology have created a large spectrum of nanostructured carbons with high specific surface areas [12] that have played critical roles in improving the capacitive performance of EDLCs in recent years, such as nanoporous carbon (carbide-derived carbon, carbon nanotubes, etc.)

Figure 1. Schematic drawing of the basic capacitive mechanisms: (a) electrochemical double-layer principle; (b) surface redox mechanism; and (c) one newly featured kinetically-favored intercalation mechanism.
and graphene sheets (GS). The numerous benefits from these well-tailored nanostructured carbons will be discussed in detail later. For porous carbon electrodes, it is noteworthy to understand the recently proposed electrochemical double-layer mechanism of microporous carbon electrodes [13]. Before the proposal of this mechanism, it was generally accepted that pores in the sub-nanometer regime would not be accessible for hydrated ions in aqueous electrolyte, especially in the case of solvated ions in organic electrolyte since the size of these ‘energy carriers’ is larger than 1 nm [14,15], and thus not beneficial for improving the capacitive performance in an EDLC. However, contradicting experimental evidence has been reported by many researchers that capacitance is increased in capacitors using carbide derived microporous carbon electrodes with sub-nanometer pore sizes [16,17]. It is implied that a de-solvated process is required first before forming the electric double-layer that will decrease the size of solvated ions, to meet the absorption condition in microporous electrodes. Thus, a novel electrochemical double-layer formation mechanism is established, which indicates that the partially de-solvated ions can enter the micropores in carbide-derived microporous carbon and line up to form an ‘electric wire in cylinder’ model of a capacitor [4]. It has been shown that incorporating micropores in carbon electrodes helps to improve the energy density of supercapacitors due to the increase of capacitance, on account of the effective collection of more adsorbed electrolyte ions during the polarization, while the power capability is not substantially improved via this design because of the slow dynamics of the pre-desolvation process and the diffusion of electrolyte ions into the micropores, which may be noticed in the design of carbon-based capacitive electrodes.

2.2. Pseudo-capacitive mechanism

Another type of supercapacitors is referred to as pseudo-capacitor. Unlike an EDLC, which exclusively relies on the reversible adsorption of electrolyte ions, pseudo-capacitors store energy mainly via fast and reversible electrochemical redox reactions between the electrodes and electrolyte ions. Benefiting from the fast reversible Faradaic charge transfer reaction, a higher energy density than EDLCs is delivered by pseudo-capacitors (1–5 F m\(^{-2}\) compared to 0.1–0.2 F m\(^{-2}\) for an EDLC). That is why more and more attention has been given to these later-developed supercapacitors. From the previous classical viewpoint, the pseudo-capacitive mechanism mainly points to the fast redox reaction carried out at the electrode surface. However, one kinetically-favored intercalation mechanism for mesoporous metal oxide electrodes with iso-oriented layered nanocrystalline domains has been reported in recent years. In this regard, both these pseudo-capacitive mechanisms will be discussed in this section.

2.2.1. Surface redox mechanism

The surface redox mechanism has been widely acknowledged in recent decades and has been found to operate in any type of pseudo-capacitive electrode. This mechanism is sketched in Figure 1b. In a pseudo-capacitor, electric energy is stored via Faradaic redox reactions between the electrolyte ions and the electrode, thus forming capacitance. Unlike electrochemical batteries, the bulk of the electrode in these capacitors does not participate in the electrochemical reaction, thus avoiding crystallographic and structural changes and leading to a superior stability during cycling as compared to batteries. Because the surface redox reactions occur only in the top few nanometers in the electrode’s surface, nanoengineering techniques play a significant role in enhancing pseudo-capacitive properties. Common approaches include decreasing the particle size to improve active material usage
and producing nanostructured electron conductive networks for pseudo-electrodes, ultimately to increase their conductivity and thus promote power delivery [19].

To date, the most used and promising surface redox mechanism-based electrode materials include metal oxides (RuO$_2$, MnO$_2$, NiO, Co$_3$O$_4$, Fe$_2$O$_4$, V$_2$O$_5$, etc.), metal hydroxides (Ni(OH)$_2$, Co(OH)$_2$, etc.) and conductive polymers (polyaniline (PANI), polypyrrole, etc.). They implement different redox reactions for different electrolyte ions. This remarkably affects the performance of supercapacitors in terms of specific capacitance, power character and working voltage window.

Of the pseudo-capacitor electrodes, RuO$_2$, an intensively studied pseudo-capacitive electrode with good conductivity, has been the focal point of both the academic and industrial communities in recent decades [3]. The fast and reversible electron transfer reaction on RuO$_2$ electrode accompanied by the electro-adsorption of protons in acidic electrolyte can be expressed by:

$$\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_2\cdot x(\text{OH})_x,$$

where $0 \leq x \leq 2$. In this electrochemical reaction, the valence of Ru may be varied from (II) to (IV). Although high specific capacitance of more than 700 F g$^{-1}$ can be achieved by X-ray amorphous hydrous RuO$_2$ [20], the high cost of RuO$_2$ has limited its wide practical use.

Inexpensive metal oxides have thereby been tried out in supercapacitive application to decrease the production cost of pseudo-capacitors. Some metal oxides have shown good capacitive properties with multiple surface redox reactions. MnO$_2$ was first tested as a pseudo-electrode in KCl electrolyte by Lee and Goodenough [21]. Since then it has attracted tremendous interest owing to its limited environmental harmfulness and wide voltage window in neutral aqueous electrolyte. A MnO$_2$ electrode stores energy according to the reversible reaction with electrolyte cations (K$^+$, Na$^+$, H$^+$), as expressed by:

$$\text{MnO}_2 + x\text{C}^+ + y\text{H}^+ + (x+y)e^- \leftrightarrow \text{MnOOC}_x\text{H}_y,$$

where $\text{C}^+$ denotes the cations.

Despite the high theoretical specific capacitance ($\sim$1370 F g$^{-1}$) manifested, which is endowed by the surface Faradaic charge transfer reaction, it is worth noting that to realize such high specific capacitance is not an easy task due to the poor conductivity of MnO$_2$. Nanoscale research now is helpful in solving this problem, which will be demonstrated in a later section.

In aqueous alkaline electrolyte, some metal oxides and metal hydroxides can also enhance electrode capacitive performance, such as Ni(OH)$_2$. The reversible redox reaction of Ni(OH)$_2$ electrode in KOH electrolyte is:

$$\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-.$$

Ni(OH)$_2$-based electrode materials in three-electrode tests normally exhibit high specific capacitance (up to several thousand Faraday per gram) at small current densities, whereas their disadvantage is also obvious, such as their narrow working voltage window (about 0–0.5 V) and poor rate performance.

Conductive polymer (CP) is attractive as a pseudo-capacitive electrode because of its high electrical conductivity and low cost. The surface redox reaction of CP can be described
as a fast and reversible p-doping (oxidation) and n-doping (reduction) process of electrolyte ions, as shown by

$$\text{CP} \rightarrow \text{CP}^n (A^-)_n + ne^- (\text{p-doping}), \quad (4)$$

$$\text{CP} + ne^- \rightarrow (B^+)_n \text{CP}^{n-} (\text{n-doping}), \quad (5)$$

in which $A^-$ and $B^+$ denote the electrolyte ions. Since the doping and dedoping processes involve the intercalation and de-intercalation of ions, CP pseudo-electrodes often degrade severely during cycling, which is a major obstacle limiting their further development.

2.2.2. Kinetically-favored intercalation mechanism

The intensive nanoscale research has reformed many classical theories in the scientific community. Recently, one kinetically-favored intercalation capacitive mechanism [22] has been proposed, benefiting from mesoporous metal oxide electrodes with iso-oriented layered nanocrystalline domains. It was found that intercalation of electrolyte ions into the crystallographically oriented mesopores, and thus the van der Waals gaps in bulk, is responsible for the high level enhancement of pseudo-capacitance. Generally speaking, intercalation into van der Waals gaps is a kinetically-slow process, which commonly occurs in electrochemical batteries. Only when the intercalation is kinetically facile and performed at the same time scale as the surface redox reaction can it be considered capacitive. Nano-engineering techniques can be employed to help reach this objective, by accelerating the diffusion-controlled kinetically limited process. MoO$_3$ thin films with interconnected iso-oriented crystalline mesopores were fabricated via a polymer directed assembly nanotechnology, of which the van der Waals gaps are incorporated in these channels. This nanostructure can readily meet the fast intercalation of Li$^+$ into the bulk of the electrode material by providing a ‘freeway’ for electrolyte ions into van der Waals gaps, making significant contributing to the pseudo-capacitance. This concept is shown in Figure 1c. The kinetically-favored intercalation mechanism was also found in mesoporous layered Group V transition metal oxide-based electrodes with the same nanoscale architecture [23]. Due to the contribution from intercalation mechanism, this type of T-Nb$_2$O$_5$ mesoporous films exhibited superior pseudo-capacitive properties over mesoporous amorphous films, which stored energy only via surface redox reactions. This newly featured kinetically-favored intercalation mechanism may afford new ideas to design novel nanostructured electrode materials for pseudo-capacitors.

3. Prototype devices

Electrode, electrolyte and current collector are the three main components of a supercapacitor. They are assembled into a sealed and stable device, providing electrical energy for the power system. The basic configuration of a supercapacitor is sketched in Figure 2. In this design, the positive and negative electrodes are immersed in electrolyte and separated by the separator, which is an ionic conductor but an electronic insulator. The electrode plays the most critical role in collecting charges in electrochemical processes via the above-demonstrated mechanisms.
As for the electrolyte, aqueous and non-aqueous organic media have both been used. Various inorganic aqueous electrolyte solutions are commonly employed, e.g. sulfuric acid, sodium sulfate and potassium hydroxide for acidic, neutral and alkaline conditions, respectively. When the supercapacitor is operated in aqueous electrolyte, high power characteristics are available due to the fast transport rate of electrolyte ions in aqueous solution. The stable voltage window of an electrode in aqueous electrolyte (≤1 V), however, is limited by the decomposition of water. In a supercapacitor, the energy density can be described by:

\[ E = \frac{1}{2}CV^2, \]

where \( E, C \) and \( V \) denote the energy density, specific capacitance and working voltage, respectively. It is found that the energy density is proportional to the voltage squared. Hence, the low decomposition voltage of water will result in low stored energy.

Organic electrolytes can be safely utilized in a wide voltage range, so that the cell voltage can be increased from 0.9 V to 2.5–2.7 V for an EDLC when aqueous electrolyte is substituted by an organic electrolyte. Although the specific capacitance of supercapacitors...
operating in organic electrolyte is lower, owing to its lower electrical conductivity, typically by orders of magnitude compared to an aqueous electrolyte, their energy density is still much higher due to the wide working voltage window. The current state of the art is the usage of organic electrolyte solutions in acetonitrile or propylene carbonate, such as those in electrochemical batteries; the latter particularly has become more popular due to its low flash point and low toxicity. Recently, tremendous efforts have been devoted to the investigation of environment-friendly and electrochemically stable ionic liquid electrolytes. An even higher voltage window of up to 4.0 V has been achieved for recent ionic liquid-based supercapacitors. Devices with 3 V, 1000 F specifications using carbon-based electrodes are already commercially available [24]. Besides the commonly employed carbon, some metal oxide electrode materials can also harvest pseudo-capacitance in ion liquid electrolyte. For instance, the pseudo-capacitive performance of MnO₂ in ion liquid was recently confirmed by Chang et al. [25,26]. It is also significant that another obvious advantage of ionic liquids is their high temperature stability, readily meeting the demand of energy storage devices at high temperature conditions, even at 60°C [27].

The current collector of a supercapacitor is a good electronic conductor. In conventional aqueous supercapacitors, Ni foam is normally employed as the current collector under neutral and alkaline conditions, whereas in acidic aqueous solutions metallic titanium is used instead. Supercapacitors designed for organic electrolytes commonly utilize treated aluminum foil or grid current collectors. Stimulated by the urgent demand of flexible portable electronics, some novel current collectors have appeared, such as the attractive carbon materials in the form of highly conductive nanotubes or graphene papers. They are inactive in aqueous electrolyte, very flexible and mechanically robust.

3.1. Symmetric devices

Symmetric device commonly refers to a supercapacitor that is composed of two electrodes with the same material and approximately the same electrode mass, as shown in Figure 2b. This type of supercapacitor is also the earliest prototype of electrochemical capacitor, dating back to the first patent of electrochemical capacitor with two identical activated carbon electrodes in the device. To date, carbon material-based EDLC electrodes are still the most commonly used in the format of symmetric configuration. One of the most prominent advantages is their high power characteristics. Recently, a single-walled carbon nanohorn/nanotube composite film electrode was reported [28]. Two of this type of electrodes, in connection with platinum mesh current collectors and a porous cellulose-based separator immersed in 1M Et₄NBF₄/propylene carbonate electrolyte, have been assembled in a dry argon environment, to form a symmetric device. The electrochemical test showed that this capacitor device exhibited extremely high power ability, of which the maximum power density can reach 990 KW kg⁻¹. The fast ionic transfer kinetics ascribed from the unique meso/macropore structure and good electronic conductivity of both graphitic carbon nanotubes (CNTs) and nanohorns are the main reasons for their high power characteristics. Pseudo-capacitive electrodes, such as metal oxides and conducting polymers, are now rarely tested in symmetric configuration since only a limited stable voltage window is available. This renders them less attractive compared to their asymmetric counterparts. Taking MnO₂ as an example, the operating voltage of MnO₂-based aqueous symmetric supercapacitor is generally limited to about 1.0 V. Although a symmetric device with graphene/PANI composite nanofiber electrodes has been reported [29], the main focus in this work was the flexible electrode itself, not the whole device that only had a 0–0.8 V working voltage range. Moreover, some pseudo-capacitive electrode materials
cannot be used in organic electrolyte, which makes these symmetric devices uncompetitive with carbon-based non-aqueous supercapacitors.

### 3.2. Asymmetric (hybrid) devices

A supercapacitor device can be constructed from two different electrode materials, thus forming an asymmetric supercapacitor, also known as a hybrid supercapacitor. The asymmetric systems can combine both the merits of two electrodes, offering an attractive alternative to improve the cell voltage, energy and power densities. There are three main approaches to the design of asymmetric supercapacitors: (1) two different pseudo-capacitive electrodes, (2) one pseudo-capacitive electrode with an EDLC electrode, and (3) one capacitor-like electrode with intercalation battery-like electrode.

If two pseudo-capacitive electrodes with different working voltage windows are assembled into an asymmetric cell, the device voltage will be larger than their symmetric counterparts. On account of this, asymmetric supercapacitors have been widely studied. NiO has been confirmed to possess high specific capacitance in aqueous electrolyte; an obvious disadvantage, however, is the narrow working voltage region (about 0 to 0.5 V vs. SCE). To realize their practical use, a NiO/Ru0.35V0.65O2 asymmetric capacitor was devised [30]. Since Ru0.35V0.65O2 can exhibit pseudo-capacitive features within the electrochemical window of −1.0 to 0.1 V (vs. SCE) in 1M KOH, the assembled capacitor would afford good electrochemical capacitance behavior within the potential range from 0 to 1.7 V, for which the maximum specific capacitance and energy density were 102.6 F g−1 and 41.2 W h kg−1, respectively, delivered at a current density of 7.5 A cm−2. An asymmetric capacitor has also been proposed with conductive polymers as both the anode (styryl-substituted dialkoxyterthiophene) and cathode (polypyrrole) [31]. Metal oxide pseudo-capacitive electrodes are commonly assembled into asymmetric configuration with electrochemical double-layer based carbon materials. One typical prototype is the MnO2/activated carbon aqueous supercapacitor [32]. The cell voltage was 2 V, and an obvious improvement in energy density was realized compared with activated carbon-based EDLC. This type of supercapacitor only utilizes low-cost electrode materials, environment-friendly neutral aqueous electrolyte, making it a green alternative to an EDLC using acetonitrile-based organic solvents and fluorinated salts. One challenge faced by this system is to utilize organic electrolyte to realize higher cell voltage, thus further improving the energy density.

In the design of asymmetric capacitors, the rational selection of suited positive and negative materials is a key issue. Since the specific capacitance (SC) values of the positive and negative electrodes are different in an asymmetric device, the mass load balance should be first performed, according to:

\[
m_− = \frac{SC_+ ΔV_+}{SC_- ΔV_-} m_+, \tag{7}
\]

where \(m\), SC and \(ΔV\), respectively, indicate the mass, specific capacitance and working voltage window of the active electrode materials. It is worth noting that the SC values of positive and negative electrodes for calculation can only be taken at a certain current density or scan rate in the practical design. If the rate performances of the positive and negative electrodes are significantly different from each other, the optimum mass load balance will not be realized at any output current. Thus, selection of positive and negative electrode materials with comparable rate performance is an important design principle.
Besides considering their working voltage range so that no waste of electrode materials will be caused.

Since Amatucci et al. first proposed to integrate bulk Li-ion storage and double-layer storage to assemble an asymmetric capacitor (Li-ion supercapacitor) [33], this type of supercapacitor for achieving high power and high energy density simultaneously has attracted considerable attention. The basic configuration is shown schematically in Figure 2c, with an intercalation anode and capacitive cathode immersed in organic electrolyte. The most commonly employed intercalation anode materials are titanates with low strain, long cycling life and good safety reliability. One hybrid supercapacitor based on monoclinic TiO$_2$ anode and CNT cathode was reported recently [34], which can deliver 12.5 W h kg$^{-1}$ at a rate of 10 C. An ordered mesoporous carbon cathode and titania nanotube anode can also be incorporated in an asymmetric supercapacitor [35], for which the energy density and power density can reach 25 W h kg$^{-1}$ and 3 kW kg$^{-1}$. It is noteworthy that a Faradaic electrode leads to an increase of energy density at the cost of cycling stability. Thus, asymmetric supercapacitors may be only adaptive to fields where only medium cycle life is needed. Ultra-high rate capability like the EDLC and good cycling stability are the two main long-term objectives of asymmetric supercapacitors.

4. Benefits from nano-engineering

Indubitably, nanoscale research has enabled a revolution in the development of supercapacitors, which has not only led to substantial improvement of capacitive properties, but the reformation of electrode configuration, and even the device prototype. New nanomaterials created via nano-engineering have been gradually applied in supercapacitors, such as CNT, graphene, and many other unique nanostructures of carbon, metal oxide, and conductive polymer, etc. Besides the great impact from nanomaterials themselves, the revolutionary design principles of electrode and device configuration likewise open wide opportunities for supercapacitors. In this review article, we are mainly concerned with the introduction of nanoscale research-enabled enhancement of supercapacitors and with the demonstration of the real benefits from nanotechnology.

4.1. More electrochemically active surfaces and interfaces

4.1.1. Nanoporous electrodes

The size features of nano-engineering range from micrometers to sub-nanometer. In other words, more specific surface areas will be created via nanofabrication. Since the earliest establishment of EDLCs, increased specific surfaces for carbon electrodes were highly anticipated. Even in the subsequently developed pseudo-capacitors, higher specific surfaces are also beneficial for collecting more charge during the surface redox reactions. Nanostructured electrode materials that will endow more electrochemically active surfaces and interfaces have been being pursued in recent decades. Nanoscale research has provided many successful synthetic strategies towards nanoporous materials with large specific surface areas [36,37], which has further had profound effects on electrochemical energy storage. For instance, tailored nanoporous SnO$_2$ [38] or Co$_3$O$_4$ [39] via non-template nanofabrication can deliver high reversible capacity and good cycling performance as promising lithium-ion battery anodes. Likewise, nanoscale-engineered nanoporous capacitor electrode materials are now an intense research topic, which is briefly overviewed below.

With the development of EDLCs, in addition to the conventional activated carbon with broad pore size distribution, some novel nanoporous carbon materials have been tested
recently as capacitor electrodes, since the intrinsic mesopores readily match the spaces for forming an electrochemical double-layer via electrostatic adsorption of solvated ions in large areas. CNTs are the expected attractive candidate. Their important and promising characteristics for electrode materials are based on not only their large area of exposed surface, and thus large accessible storage spaces for electrolyte ions, but also their superior electrical conductivity, which significantly indicate their high-power applications.

Both single-walled and multi-walled CNTs have been tested as supercapacitor electrodes. In an earlier study, Niu et al. reported that multi-walled CNTs with a surface area of 430 m² g⁻¹ showed the maximum specific capacitance of 113 F g⁻¹ and a power density of 8 kW kg⁻¹ at an energy density of 0.56 W h kg⁻¹ [40]. In subsequent studies, it was found that single-walled CNTs with larger specific areas exhibited superior capacitive properties in comparison with multi-walled CNTs, and thus became the main focus in CNT-based capacitor electrodes.

At the current state of the art, a specific surface area up to 800 m² g⁻¹ is provided by commercial single-walled CNTs. Much larger specific areas can be further available in the lab research. Recently, super-grown single-walled CNTs [41] were reported to possess high capacitance, benefiting from their ultrahigh specific surface area [42]. One shortcoming of CNTs for capacitor applications is that the inner surfaces of nanotubes have rarely been used for forming an electrochemical double-layer because of their closed ends. To address this issue, the nano-engineering of open-ended CNTs is expected, to use the inner spaces of the nanotubes. Generally, oxidation processing of CNTs is needed. The optimization of oxidation conditions is highly critical and difficult to control since the capacitive properties of CNT-based electrodes will be damaged due to the introduction of deleterious defects. Hiraoka et al. reported that a specific surface area of more than 2000 m² g⁻¹ was realized for single-walled CNTs via an optimized oxidation processing [43]. The inner and outer electrochemically active areas can be simultaneously utilized. When tested in organic electrolyte, 24.7 W h kg⁻¹ in energy density and 98.9 kW kg⁻¹ in power density were delivered. Although the fabrication technologies of CNTs have been developed for a long period, the production cost of CNTs is still much higher than commercially available activated carbons, which cannot meet the demand for practical large-scale applications.

Graphene is one type of burgeoning special carbon material, which can be manufactured from graphene oxide (GO) in large quantities at low cost [44]. The production cost advantage and their intrinsic high electrical conductivity has stimulated intense interest in the development of graphene-based supercapacitors. However, despite considerable endeavor, their low specific capacitance is not desirable. The main reason for their low specific capacitance is that the theoretical high specific surface area of ∼2630 m² g⁻¹ is difficult to realize in graphene-based electrode materials due to the spontaneous aggregation tendency of graphene sheet (GS) during the fabrication procedure. To substantially enhance the specific capacitance of graphene-based electrode materials, Zhu et al. chemically activated the microwave exfoliated graphene oxide (MEGO) with KOH to produce nanoporous graphene [45], as sketched in Figure 3a. This activation process is similar to the commonly employed route to engineer activated carbons that is highly compatible with the current state art of electrode material production. The porous character (sketched in Figure 3b) endowed these electrode materials with high specific area up to 3100 m² g⁻¹. Superior capacitive performance was thus obtained, benefiting from the merits both of porous nanostructures and high electrical conductivity of graphene. This study opens a new route to enhance the capacitive performance of graphene used in organic electrolyte, and manifests a great potential for scalable industrial applications.
Carbide-derived nanoporous carbons have recently featured intensively since the establishment of the energy storage model of microporous carbon [13]. Selective leaching of the non-carbon element in the carbide with halogen will lead to the formation of microporous carbon materials, which is the basic engineering principle for carbide-derived nanoporous carbons. Taking the derived microporous carbon in [13] as an example, the reaction pathway can be expressed as

\[ \text{TiC} + 2\text{Cl}_2 \rightarrow \text{TiCl}_4 + \text{C}. \]  

This carbide-derived carbon nanofabrication technology readily allows the rational control over the pore size (\(\sim 0.5 \text{ to } \sim 3 \text{ nm}\)) [46] with narrow size distribution, and specific surface areas up to 2000 m\(^2\) g\(^{-1}\) [47].

A template strategy is a normally employed nanofabrication technique in nanoscale research. Nanoporous carbon can also be engineered via replicating the porous framework of template, which is denoted as templated carbon. This type of porous carbon with uniform pore size is commonly used as a supercapacitor electrode material. Since the micropores can contribute large EDLC supercapacitance for carbon electrode, considerable endeavors have been devoted to templated microporous carbon. Recently a novel type of zeolite-templated nanoporous carbon was devised for deriving high energy density [48]. Through filling the carbon precursor in the used FAU zeolite template and subsequent template elimination and carbonization, nanoporous carbon with unique pore structure was obtained. Benefiting from the three-dimensionally arrayed and mutually connected 1.2 nm nanopores formed in this carbon electrode, high specific capacitance of \(\sim 190 \text{ F g}^{-1}\) was realized in a symmetric device with the usage of organic electrolyte.
The combination of nanoscale template technology and silicon carbide-derived carbon nanofabrication was reported by Korenblit et al. [49] recently to achieve the preparation of nanoporous carbon with bimodal pores (both with mesopores and micropores), which totally contribute to the high specific surface area up to 2430 m² g⁻¹. In this study, the nanoscale template technique has led to the formation of mesopores, which act as a highway for ion transport at large discharge current density, and thus maintain the high power capability (85% capacitance retention at current densities up to 20 A g⁻¹). The micropores can contribute a lot to improve the energy density. The maximum specific capacitance of the assembled EDLC device with organic electrolyte is 170 F g⁻¹.

It is well known that pseudo-capacitive electrode materials possess larger specific capacitance compared with carbon materials. If the electrode materials are prepared as nanoporous aerogels, more electrochemically active surfaces and interfaces will be formed [50]. In this regard, to engineer nanoporous pseudo-capacitive metal oxide aerogels will benefit the creation of supercapacitors with ultrahigh energy density. Recently, a low cost epoxide-driven sol–gel nanofabrication process without using any expensive metal–organic precursors was employed to engineer NiCo₂O₄ aerogels with an average pore size of 2–5 nm [51]. When tested in a three-electrode cell using 1M NaOH solution electrolyte, a high specific capacitance of 1400 F g⁻¹ at a sweep rate of 25 mV s⁻¹ within a potential window of 0.04–0.52 V can be obtained.

4.1.2. Unique nanostructured electrodes with large electro-active areas

When the size of electrode materials is decreased, more specific surface area will be created. Nano-particulate electrode materials are attractive candidates for providing more active sites for electrostatic absorption in an EDLC or electron-transfer redox reaction in pseudo-capacitors. Recently, Choi et al. reported a new type of nanocrystalline vanadium nitride electrode material [52]. The nanometer-sized crystals increase the susceptibility for surface oxidation, while the high surface area of the nitride nanoparticles provides more redox reaction sites. It was shown that the high specific capacitance (1340 F g⁻¹ at a scan rate of 2 mV s⁻¹ in a three-electrode configuration) is not only the result of high specific surface areas, but also caused by a series of reversible redox reactions through hydroxy bonding confined to a few atomic layers of vanadium oxide on the surface of the underlying metallic nitride nanocrystals. This work presents a new direction to design tailored core/shell nano-particulate pseudo-capacitive electrodes.

One-dimensional nanostructured electrode materials have been intensely investigated in supercapacitor devices, which normally favor fast redox reactions, high specific surface areas and short diffusion paths for electrons and electrolyte ions. Unique MnO₂ nanowire networks were reported to possess superior capacitive properties [53], in terms of high specific capacitance of 279 F g⁻¹ at 1 A g⁻¹ and good cycling stability (1.7% loss after 1000 cycles). The ultra-thin nanowires with the diameters of ~3–7 nm helped improve the utilization of active materials, while the intertwined network has led to the formation of porous channels for the facile transport of electrolyte ions.

In the above-demonstrated studies, the shape-controlled synthesis of nanostructures with large specific surface areas to create more electrochemically active accessible surfaces is the main focus. From this viewpoint, the research may be limited. Our group recently proposed a new idea to broaden the design principles of nanostructured electrode [54], on the basis of creating extra electrochemically active boundaries in the mixed-phase nanoparticulate pseudo-capacitive electrodes. As shown by the scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) characterization (Figures 4a and b), the MnO₂
nano-particulate electrode materials prepared via a mild chemical bath method are composed of both $\alpha$-MnO$_2$ and $\delta$-MnO$_2$. When the MnO$_2$ nanoparticle electrode was evaluated in a three-electrode cell, it is shown that the mixed-phase MnO$_2$ exhibited larger specific capacitance than both pure $\alpha$-MnO$_2$ and $\delta$-MnO$_2$ nanoparticles (see Figure 4c). Also, the mixed-phase MnO$_2$ is superior to mechanically mixed samples (see Figure 4d), implying that the active boundaries formed between the co-grown $\alpha$-MnO$_2$ and $\delta$-MnO$_2$ nanocrystallites are responsible for the substantial enhancement of capacitive performance.

4.2. Tailored electrode configurations

4.2.1. Nanostructured composite electrodes

Benefiting from the tremendous progress of nano-engineering techniques, a large spectrum of composite electrodes with controllable architectures has been achieved. The synergetic functionalities from every constitution will substantially enhance their electrochemical energy storage ability. A pseudo-capacitive electrode with high specific capacitance, such as metal oxide, is generally not a good electronic conductor, limiting the fast transfer of Faradaic charges and thus decreasing the capacitive properties, in terms of
specific capacitance, and rate capability. If these pseudo-capacitive electrode materials are combined with suitable conductive networks, the abovementioned disadvantages will be eliminated.

Nanostructured graphitic carbon materials with large accessible specific surfaces and low resistivity are commonly used to construct nanostructured composite electrodes in combination with pseudo-capacitive electrode materials. Two-dimensional GS, with one to several layers of carbon atoms, were recently investigated intensively as conductive component to derive novel nanostructured composite electrodes. Wang et al. achieved the growth of Ni(OH)$_2$/GS nano-composite via solution precipitation of Ni(OH)$_2$ nanocrystals on the pre-prepared GS [55]. As sketched in Figure 5, the surface defects and the residual functional groups on the GS surface favored the intimate connection of Ni(OH)$_2$ nanoplates on the underlying GS via chemical bond formation such that fast electron transport was easily realized in the electrochemical process. When tested by galvanostatic charge/discharge and cyclic voltammetry technologies in a three-electrode system, this composite electrode exhibited excellent rate capability (∼1335 F g$^{-1}$ at 2.8 A g$^{-1}$, 953 F g$^{-1}$ at 45.7 A g$^{-1}$) and cycling stability. To date, many pseudo-capacitive electrode materials have been composited with GS, such as nanostructured RuO$_2$/GS [56], Co$_3$O$_4$/GS [57], etc. However, the capacitive performance is somewhat not as ideal as expected. One main reason is the aggregation problem of graphene during composite processing so that some of the pseudo-capacitive electrode materials will be wrapped between the graphene components, which would lower their electrochemical activities. This may be the most prominent problem encountered in graphene-based composite electrodes.

CNTs present exceptional improvement of electrode performance due to their mesoporous and highly conducting networks. Using CNT and pseudo-electrode composite, the cell resistance can be substantially reduced and the transport of ions can be greatly enhanced. High specific capacitance, outstanding rate capability and cycling stability are thereby available. A hierarchical nanowire composite: V$_2$O$_5$/CNTs electrode was recently reported by Chen et al. [19]. A one-step hydrothermal crystallization technique was utilized to realize the growth of V$_2$O$_5$ nanowires intertwined with the CNT precursor. The interpenetrating networks of CNTs and V$_2$O$_5$ nanowire networks are hierarchically porous with high surface area and good conductivity, making them excellent electrode materials with high energy density and power density. When this composite was used as the anode in combination of a MnO$_2$/C cathode in an aqueous asymmetric device, 16 W h kg$^{-1}$ at a

![Figure 5. Schematic illustration of the formation of GS/Ni(OH)$_2$ nanocomposite electrode.](image-url)
power density of 75 W kg\(^{-1}\) and 5.5 W h kg\(^{-1}\) at a high power density of 3750 W kg\(^{-1}\) can be obtained, which is highly competitive with Ni-MH batteries.

The direct intimate growth of electrode materials on current collectors would avoid the addition of organic insulating binder, not only increasing the conductivity, but simplifying the electrode manufacture. Nanoscale engineering techniques open wide opportunities with respect to this point. The chemical vapor deposition technology has been widely employed to grow CNT arrays on metal substrates. In a typical study, Zhang et al. reported the growth of CNT arrays on Ta current collectors followed by electro-deposition of MnO\(_x\) nanoflowers on the CNTs [58], which together formed one type of binder-free composite electrode, as sketched in Figure 6. The CNT array-coated Ta substrate was employed as the current collectors to harvest the pseudo-capacitance of MnO\(_x\) nanoparticles, in which the high specific surface area of the CNT arrays can afford 3D room for active material rather than that of 2D metal current collectors. Also, the one-dimensional carrier route provided by CNT is one of the most optimum design principles to readily facilitate electron transfer. Thereby, high specific capacitance and rate capability are both supported by this nanoscale design.

Some other intensively investigated nanostructured composite electrodes are composed of pseudo-capacitive electrodes and non-carbon conductive components, such as

![Figure 6. Schematic design principle of binder-free CNT/MnO\(_x\) composite electrode material (CNT-coated Ta foil is used as the current collector without adding any insulating binder in this electrode configuration).](Image)
conductive metal oxide, conductive polymer and metal. SnO$_2$ nanowires synthesized via chemical vapor deposition were reported to have good conductivity of 5 to 74 S cm$^{-1}$ [59,60]. A SnO$_2$ nanowire/MnO$_2$ particle core/shell structured composite electrode was reported recently [61], in which the inner SnO$_2$ cores mainly play a critical role in collecting and transporting the electrons. Benefiting from this configuration, a specific capacitance (based on MnO$_2$) as high as 637 F g$^{-1}$ was obtained at a scan rate of 2 mV s$^{-1}$ (800 F g$^{-1}$ at a current density of 1 A g$^{-1}$) in a three-electrode system. MnO$_2$/poly(3,4-ethylenedioxythiophene) (PEDOT) coaxial nanowire composites were also tested as supercapacitor electrode [62]. The coaxial nanowires preserved 85% of their initial specific capacitance (from 210 to 185 F g$^{-1}$) as the current density increased from 5 to 25 mA cm$^{-2}$, surpassing both MnO$_2$ and PEDOT nanowires. In the above demonstration, although the pseudo-capacitance was harvested at full steam by the researchers, to reach the theoretical specific capacitance is still challenging and hardly realized for nanocomposite electrodes. Lang et al. broke through this barrier by preparing a nanoporous Au/MnO$_2$ nanoparticle electrode [63]. Via an electroless plating technique, the MnO$_2$ nanoparticles can be epitaxially grown on the inner walls of de-alloying formed nanoporous Au without aggregation. Benefiting from this unique nanostructure, the specific capacitance of 1145 F g$^{-1}$ normalized to MnO$_2$ that is close to the theoretical value was obtained, when the electrode is tested in a symmetric aqueous device. However, the high cost of Au conductive matrix would not be preferentially considered in scalable applications. Recently, porous Ni current collectors fabricated by selective dissolution of Cu in Cu–Ni alloy films were employed to help in harvesting the pseudo-capacitance of MnO$_2$ [64] and Co(OH)$_2$ [65]. This cost-effective strategy manifests the potential for practical use of these composite nano-electrodes.

4.2.2. Flexible thin film electrodes

Today, thin, lightweight and even flexible electronics are being pursued intensively, which has stimulated the investigation of flexible and durable energy storage devices for power generation. As a result, flexible thin-film electrodes are urgently needed. In recent years, nanoscale engineering technologies have brought many opportunities to fabricate high performance flexible thin-film electrodes. Nano-engineering has enabled tremendous progress in this field, as described in this section.

CNT thin films [66], also called bucky papers, always exhibit flexible characteristics, which have aroused tremendous interest. Flexible conductive papers that are obtained by conformal coating of CNTs on commercial papers were proposed by Hu et al. recently [9], which have been used as flexible electrodes in supercapacitors. In this study, when CNT inks were dropped on commercial paper followed by the simple conformal coating, the intrinsic porous and flexible character of commercial paper would allow the absolute adsorption of CNTs and endow the whole conductive paper with flexible features. Symmetric supercapacitors based on these conductive papers have shown excellent performance. When only the mass of CNT is considered, a specific capacitance of 200 F g$^{-1}$, a specific energy of 30–47 W h kg$^{-1}$, a specific power of 20 kW kg$^{-1}$ and a stable cycling life over 40,000 cycles were achieved. This type of low cost nano-engineering technology and flexible conductive paper may find many practical applications in energy-storage devices. Izadi-Najafabadi et al. reported a single-walled CNT/carbon nanohorn flexible electrode [28]. In this study, a self-supporting film was formed by evaporation of the solvent in the mixed CNT/carbon nanohorn solution. The long cylindrical CNTs played a role as binder in wrapping the nanohorn spheres, thus leading to a stable flexible film which can be bent
Flexible pseudo-capacitance-based electrodes have also been studied intensively. Some of them are composite films. Flexible MnO$_2$ nanowire/CNT film and In$_2$O$_3$ nanowire/CNT film were, respectively, used as the positive and negative electrodes to construct an asymmetric device [67]. The flexible composite films were fabricated by filtering the metal oxide nanowire solution through CNT films, after which the nanowires were trapped in the films. A 2 V potential window was provided by this asymmetric device, simultaneously with specific capacitance of 184 F g$^{-1}$, energy density of 25.5 W h kg$^{-1}$ and power density of 50.3 kW kg$^{-1}$. Not depending on the usage of CNT or CNT film, other flexible conductive substrates can be employed to fabricate flexible electrodes. Bao et al. reported a novel flexible Zn$_2$SnO$_4$/MnO$_2$ core/shell nanocable-carbon microfiber electrode [68]. In this study, a nanoscale bottom-up strategy was adopted to sequentially grow Zn$_2$SnO$_4$ and MnO$_2$ on flexible conductive carbon microfiber. Highly conductive Zn$_2$SnO$_4$ cores radially grown on carbon microfiber via vapor transport reaction facilitate the harvest of pseudo-capacitance from the outer MnO$_2$. As a result, a high specific energy of 36.8 Wh Kg$^{-1}$ and specific power of 32 KW Kg$^{-1}$ were available at large current density of 40 A g$^{-1}$ when the flexible electrode was tested in a three-electrode system.

Although flexible device prototypes have been devised by immersing flexible electrodes in liquid electrolyte, such as those reported in [9] and [63], for long-term durable applications, solid electrolyte may be more suitable by considering the safety factor. From this viewpoint, Meng et al. devised an all-solid-state paper-like polymer supercapacitor [69], based on the PANI/CNT flexible electrode [70] and polymer gel electrolyte, as sketched in Figure 7. It was shown that the CNT networks are coated with PANI to form a composite film electrode. To construct the all-solid-state device, two PANI/CNT nanocomposite thin films were immersed in H$_2$SO$_4$–polyvinyl aqueous solution for 10 min and allowed to be air-dried at room temperature. Afterwards they were finally pressed together under a pressure of $\sim$10 MPa; the flexible PANI/CNT electrodes were well solidified in the solid H$_2$SO$_4$–polyvinyl gel electrolyte. The devices can work normally even under its highly flexible (twisting) state. Normalized to the entire device, the specific capacitance of 31.4 F g$^{-1}$ was obtained, which is more than six times that of the current high-level commercial supercapacitor products.

Figure 7. Structural configuration of the flexible all-solid-state paper-like polymer supercapacitor.
4.3. Conceptual devices

Conventional supercapacitors that are highly desirable in electric vehicles and backup energy sources are heavy and bulky, which may not be suitable for powering future miniaturized electronics. To meet the development demand, not only the configuration of electrode should be reformed, but some revolutionary device prototypes of supercapacitors are needed. In this section, some recently established revolutionary device prototypes are introduced. Since the practical scale-up applications of these prototype devices have not been realized at the current stage, they are denoted as conceptual devices. Although the real applications may be found in several years or longer term, the innovative ideas represented by such devices must be beneficial for designing future capacitive energy storage systems.

Power clothes are a dream of human beings, which are assumed to be powered by the mechanical energy generated in daily actions. To realize this assumption, an intermediate energy storage system should be achieved as a critical component. If the cloth fiber could be used to generate and store electricity power, it would mark a significant progress toward power clothes. Recently, Bae et al. reported a conceptual fiber supercapacitor [10]. Nanowire-covered plastic wire and the surrounding entangled Kevlar fiber were the two electrodes used in this device, as sketched in Figure 8. On these two electrodes, Au films were pre-coated to act as the current collectors, and further as the substrate for ZnO nanowire growth, which endowed the electrode with large specific surface area and played the role in collecting charges. In the assembly of this device, it is noteworthy that direct contact of these two electrodes should be avoided by careful operation to avoid short circuit. Both liquid and solid gel electrolyte can be used to separate the electrodes without the usage of separator. The adoption of ZnO nanowires in this device is to benefit from the mature nanofabrication of ZnO nanowire arrays and its non-toxicity merit, which can be controllably grown on arbitrary substrates, especially at the low-temperature processing conditions that are adaptive to growth on fibers and fabrics. Using two fiber-based electrodes and 1M KNO₃ as the aqueous electrolyte, the supercapacitors exhibited specific capacitances of 0.21 mF cm⁻² and 0.01 mF cm⁻¹. Substituting the aqueous electrolyte with a gel electrolyte of PVA/H₃PO₄, high specific capacitances of 2.4 mF cm⁻² and 0.2 mF cm⁻¹ were delivered.

In electronic devices, micro-energy powering systems with sizes ranging from tens to hundreds of micrometers are poised to provide integration of power sources. Although micro-batteries are commercially available [71], they always suffer from limited cycle life, poor low-temperature kinetics and many other limitations. Micro-supercapacitors have been being investigated intensively to complement or substitute micro-batteries at

![Figure 8. Schematic illustration of one conceptual fiber-based supercapacitor.](image)
high power conditions and long-term application [72]. Recently, Lee et al. proposed a micro-supercapacitor prototype based on carbide-derived carbon films [73]. In this study, conventional micro-fabrication technologies, e.g. the vapor phase transport method and lithography technique, were employed to engineer this micro-supercapacitor. Firstly, thin carbide films were deposited on the substrate. Then a low-temperature chlorination processing was adopted to produce carbide-derived porous carbon film. Finally, masking and Au current collector sputtering followed with etching of exposed carbon film led to the formation of the film micro-device. All of the fabrication techniques are compatible with chip production, providing such micro-supercapacitors with extremely potential for powering the integrated circuits in the micro-electromechanical systems. Analogous to this integrated micro-supercapacitor, onion-like carbon based micro-devices were described by Pech et al. [74]. In this micro-device an ultrahigh rate capability with powers per volume that can be comparable to electrolytic capacitors was realized, broadening their numerous applications.

5. Applications of supercapacitors

High power delivery and uptake are readily afforded by supercapacitors with about hundreds to many thousands of times the power that a similar-sized battery can deliver. This energy storage device is needed in a large spectrum of applications, especially in high power demand fields such as power buffers, power saving units and even energy recovery. Supercapacitors were first commercially available on the market in 1978 as small farad-sized devices to provide memory back-up power for computers [75], and subsequently also used as the memory back-up units for toys, cameras, video recorders and mobile phones [76,77]. Devices of a few tens of farads can be fully charged or discharged in less than 2 min, with long cycling life, readily meeting the above-described applications. Recently, a large device, i.e. a series/parallel assembly of 100 F, 2.7 V cells, has been practically applied and was integrated into the safety doors of airplanes (Airbus A380) for emergency door opening.

The main aim of developing supercapacitors is to extend their applications in transportation in future years, such as for powering electric and hybrid vehicles, in which the peak power is normally obtained from supercapacitors [78]. Although there is a debate on whether or not the high-power lithium-ion batteries devised recently [79] are more advantageous to substitute supercapacitors, supercapacitors are still the most potential candidates for high-power providers on account of their safety and stability considerations. Not less than several minutes are still needed for charging high-power batteries, while in supercapacitors the much shorter time of $\sim$1 s is enough for fully charging. Due to the bulk energy storage mechanism of batteries, at large working current, the stability and cycling life will be substantially decreased. As for supercapacitors, they can be operated at high-power conditions over 100,000 cycles. A number of projects on hybrid-electric vehicles have been proposed using EDLCs [80,81]. The ISE Corporation in the US has developed a 360 V capacitor unit, which consists of 144 Maxwell cells (2600 F) in series [82]. This type of supercapacitor has been utilized in hybrid vehicles in combination with combustion engines and hydrogen fuel cells, which mainly takes charge of providing peak power (over 300 kW) during vehicle acceleration and recovering energy during braking. It has been shown that hybrid buses using supercapacitors with low emission of harmful gases can achieve 25–30% better fuel economy than diesel-powered buses and are consistently better than hybrid buses using batteries. In addition to carbon-based EDLCs, asymmetric capacitors have also been commercialized with specific energies of $>10$ W h kg$^{-1}$ [83],
which are likewise suitable for transportation applications. In the next-step development of supercapacitors applied in transportation, it is necessary for researchers to explore low-cost devices with high energy density that can not only be employed to provide peak power but can be utilized to complement batteries or reduce the usage of expensive fuel cells as one of the main energy sources in driving electric vehicles.

6. Summary and outlook

In this review article, our main goal was to assess the nanoscale research-enabled substantial development of supercapacitors, in addition to the necessary introduction of the basic working principles, prototypes and applications of supercapacitors. It is remarkable that many merits have been afforded by nano-engineering to promote the enhancement of supercapacitor technologies. The newly featured kinetically-favored intercalation mechanism has been proposed as absolutely benefiting from the fine nanofabrication technology, via which the crystallographically oriented mesopores required can be engineered at high quality. As for the enhancement of capacitive ability, more electrochemically active surfaces and interfaces can be created via nanofabrication, which readily increase the electrochemically active sites for energy storage. Nano-engineering has also brought enormous revolution in electrode and device configurations that help harvest the capacity in an optimum way and broaden the application opportunities of supercapacitors, such as in lightweight durable devices and micro-energy sources in micro-electromechanical systems.

To increase the energy density of supercapacitors, simultaneously maintaining their high power characteristics is the main research focus both today and in future. Comparable energy density with the current Li-ion batteries is highly expected for supercapacitors in the next short-term development step. Nano-engineering is confirmed to be beneficial for improving the specific capacitance of capacitors, hence resulting in high energy density. Well-tailored composite nano-architectures with synergetic compositions would be one of the most potential candidates to derive high specific capacitance electrodes since the high pseudo-capacitance of the electrode can be further harvested in this way, and likewise the good rate capability and long-term cycling life can be guaranteed. It is noteworthy that in some cases the high specific capacitance delivered by some lightweight nanocomposite electrodes is only ensured by their low active mass load, such as that prepared by deposition of a thin layer of active material on conductive networks. The applications of these electrode-based capacitor devices in high-energy supplying areas (e.g. hybrid or key electric vehicles) must be limited due to the low mass load of electrode materials. It is also worth noting that some pseudo-capacitive electrode/conductive matrix composite electrodes are not suitable for application in organic electrolyte; their technical importance is as the electrode in aqueous asymmetric capacitor devices. One main obstacle in utilizing advanced nanostructured electrode and device configurations for energy storage is that the high nanofabrication cost towards the nanostructured electrode materials and conductive networks is contrary to their commercial generalization. It is implied that the development of energy- and cost-effective nanofabrication technologies towards electrode materials with high specific capacitance is a primary task at the current stage. Additionally, other routes to improve the energy density including the increase of working voltage window by using stable organic electrolyte, especially the charming ion liquid, and the development of hybrid (asymmetric) devices, should be further developed.

A new future development trend for supercapacitors is to develop durable supercapacitors based on the nanostructured flexible electrodes. Some prototypes like CNT paper capacitors and the PANI/CNT thin film-based all-solid-state capacitor have
manifested cost-effective fabrication of commercially potential flexible devices, whereas the available energy density in these devices has not reached the demand for normally used portable electronics. To integrate more energy in the flexible devices, the incorporation of more pseudo-capacitive materials with high capacitance may be a good alternative. The intensely investigated printable micro-supercapacitor is another intriguing outcome of nanoscale research and supercapacitor technology. In the development of smart online sensors and drug delivery systems, micro-supercapacitors would play critical roles as energy sources.

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