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Review

Synthesis and application of nanocages in supercapacitors

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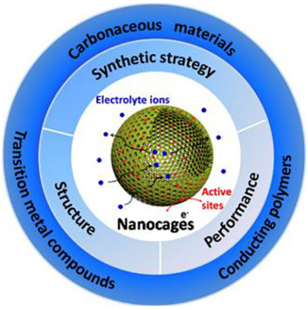
HIGHLIGHTS

- Nanocages are promising for electrode materials due to their unique nanoarchitectures.
- The structural parameters illustrating the nanocage are discussed.
- The synthesis methods of nanocages for SC applications are summarized.
- The SC performance of nanocages and its relationship with the structure are presented.

GRAPHICAL ABSTRACT

Recent development on the synthesis and electrochemical properties of nanocages for high-performance supercapacitors is reviewed.



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ABSTRACT

Supercapacitor (SC) is one of the most promising and rapidly growing energy storage devices owing to its high power density, fast electrochemical processes and long service life. A great deal of effort has been devoted to the development of high-capacity and high-stability electrode materials. Among various structures, nanocages of hollow or frame-like structures with pores on the walls have unique advantages for SC materials because they provide a large number of active sites for electrochemical reactions and facilitate the ion transfer during electrochemical processes. This paper summarizes the latest advances in SC electrode materials with nanocage structures, including carbon materials, transition metal compounds, conducting polymers, etc., by emphasizing the synthetic strategies and structure-performance correlations, and aims to provide guidance for the future design and fabrication of optimized SC electrode materials.

1. Introduction

Supercapacitors (SCs), also known as electrochemical capacitors, have become one of the most important electrochemical energy storage device in the past few decades. Their high power densities and fast charge/discharge processes hold great promise to bridge the gap between traditional capacitors and batteries [1–3]. With long cycle life, environmental benignity and safety [4,5], the SC has gained considerable interest as a promising candidate for energy storage in portable electric devices, hybrid electric vehicles and electric vehicles. Based on the energy storage mechanism, the SC can be generally classified as an electric double layer capacitor (EDLC) and a pseudo-capacitive SC [6,7]. The combination of the former two is called hybrid SC [8]. Important parameters for evaluating SC performance in terms of capacity and stability include specific capacitance (C, F g^{-1} or F cm^{-2}, revealing the energy storage ability) [1,9], energy density (E, W h kg^{-1} or W h L^{-1}, energy stored per unit mass or volume), power density (P, W kg^{-1} or W L^{-1}, illustrating the discharge speed), rate capability (capacitance retained at high current density), and cycling stability. The low energy density of current SCs is the major challenge for SCs

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being widely used under practical conditions. In this context, the development of high-performance SCs has become one of the central scientific tasks in the energy field in the past decades.

Downsizing of electrode materials to the nanoscale has become a promising approach to increase SC capacitance because nanostructured materials provide short pathways for charge and ion transport and have large surface to volume ratios to expose more electroreactive sites [10,11]. In addition, SCs using nano-electrode materials are also expected to achieve desirable properties such as light weight, flexibility, and transparency. Therefore, a great deal of research work has been devoted to the design and synthesis of nanomaterials with various compositions and structures for SC electrode materials. It has been found that the architecture, such as shape, size, and arrangement of the nanomaterials plays an important role in improving the SC performance of the electrode [12,13]. Up to now, nanoarchitectures of different dimensions have been explored for SC applications, including but not limited to nanoparticles, nanowires, nanobelts, nanofibers, nanotubes, nanosheets, nanofilms, and nanonetworks [14–16]. These nanoarchitectures each have their own pros and cons as SC electrode materials, which are determined by their structural characteristics. For instance, one-dimensional nanostructure are beneficial for electron transport and therefore may improve the rate capability [9,17]. Two-dimensional nanostructures provide large contact areas for the electrolyte, which facilitates rapid charge/discharge processes [9,18]. However, for zero-, one-, and two-dimensional nanostructures, the large surface energy brought by the small size of nanostructures makes them prone to aggregation, especially in electrochemical processes, thereby negatively affecting the stability of SCs. The use of low-dimensional nanostructures as building blocks to construct structures with higher-orders, can reduce the agglomeration of materials while maintaining the advantages of low-dimensional nanostructures and reduce the ‘dead area’ by forming interconnected pores [14].

Among various forms of higher-order structures, nanocages have emerged as one particularly interesting class of nanoarchitectures for preparing electrode materials with high SC performance [19–21]. Nanocages are defined herein as hollow or frame-like structures with small openings/pores in the shells, which are constituted by nanosized building units. As illustrated in Fig. 1, some unique characteristics of nanocages make them particularly attractive for SC electrode materials compared to other nanoarchitectures: (i) porous shells with nanoscale thickness facilitate the contact between the electrode materials and the electrolyte, shorten the diffusion path of the ions, and increase the number of electroactive sites, and thus helps to increase the capacitance and rate performance; (ii) the hollow interior can act as a reservoir for ion storage, providing additional space and sufficient electrolyte ions for fast electrochemical processes and preventing the aggregation of encapsulated electroactive materials, thereby facilitating the electrochemical activity and stability of the material; (iii) the porous shell and hollow structure could also alleviate volume change during electrochemical processes, contributing to the cycling stability. In addition, enhanced electrical conductivity, rich accessible surfaces, various shell structures and adjustable compositions make nanocages compensate for the disadvantages of nanostructures of different dimensions. Although several reviews have covered the preparation and application of hollow structures for energy storage [19,21–27], there is currently no relevant review devoted specifically to nanocages for SC applications.

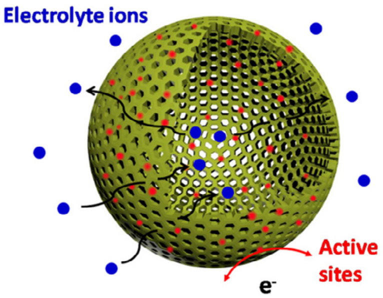

Fig. 1. Schematic illustration of the electrochemical processes in nanocages.

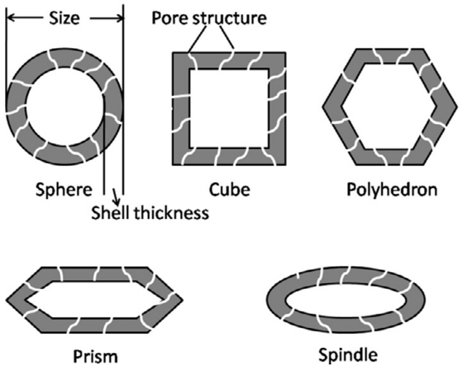

Fig. 2. Schematic illustration of structural parameters of nanocages with representative shapes of sphere, cube, polyhedron, prism, and spindle.

In this article, we started with a discussion on the structural parameters illustrating the nanocage as well as the characterization methods. Then we categorized and described the effective means of controlled synthesis of nanocages, summarized and compared the SC performance of nanocages made of different active materials, and finally looked forward to the future prospects of nanocages for SC electrode materials.

2. Structural parameters and characterization of nanocages

2.1. Structural parameters

There are mainly four parameters that define the structure of a nanocage, including the size of the nanocage, the thickness of the shell, the structure of the pores, and the shape of the nanocage, as shown in Fig. 2. Each parameter has its own degree of influence on the electrochemical processes of the nanocages, and these effects are mutually restricted and interrelated. In order to obtain better electrochemical performance, optimizing these structural parameters is a feasible approach.

The size of the nanocage is an important parameter determining its space. In theory, a nanocage with a smaller size has a higher surface area and can expose more active sites, however, due to the increased resistance between particles, they may show lower capacitance when assembled into electrodes. For example, polypyrrole (PPy) nanocages with a diameter of 100 nm have shown a higher resistance than those with a diameter of 200 nm, and exhibited a lower capacitance [28]. However, smaller-sized nanocages are mechanically stronger than those with larger sizes, and can withstand large volume change in electrochemical processes and are less likely to collapse [29,30]. Therefore, in order to balance the capacitance and stability, it is necessary to carefully consider the size of the nanocage in conjunction with the thickness of the shell and the building units.

The shell thickness of nancages has great influence on the transport of electrolyte ions. The thinner shell is more conducive to the penetration of electrolyte ions, and the thicker shell will make the diffusion path of electrolyte ions longer. Considering that the nanoscale structure with a very thin shell tends to collapse, a suitable shell thickness should be selected to achieve the internal/external mass transfer of the nanocage [31]. In addition, the thickness and size of the nanocage together determine the size of the hollow interior, which can act as reservoirs for electrolytes, which provide sufficient electrolyte ions for fast electrochemical processes.

The pore structure of the nanocage, including pore size, shape, and arrangement, has a great influence on the SC performance and the