

Mesoporous Carbon Incorporated Metal Oxide Nanomaterials as Supercapacitor Electrodes

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Supercapacitors have attracted huge attention in recent years as they have the potential to satisfy the demand of both huge energy and power density in many advanced technologies. However, poor conductivity and cycling stability remains to be the major challenge for its widespread application. Various strategies have been developed for meeting the ever-increasing energy and power demands in supercapacitors. This Research News article aims to review recent progress in the development of mesoporous carbon incorporated metal oxide nanomaterials, especially metal oxide nanoparticles confined in ordered mesoporous carbon and 1D metal oxides coated with a layer of mesoporous carbon for high-performance supercapacitor applications. In addition, a recent trend in supercapacitor development – hierarchical porous graphitic carbons (HPGC) combining macroporous cores, mesoporous walls, and micropores as an excellent support for metal oxides – is also discussed.

oxides,^[7,8] carbonaceous materials^[9,10] and conducting polymers.^[11,12] Each type of electrode material has its pros and cons. For example, metal oxides can provide higher energy density than conventional carbon materials and better cycling stability than polymer materials, but they have a key weakness of poor conductivity. On the other hand, carbon materials have high power density and long cycle life, nevertheless, the low specific capacitance greatly limits their further application. Therefore, it has inspired attempts to develop novel electrode materials via the coupling of the oxides and carbon materials as electrode for supercapacitor.

In recent years, the huge progress in nanoscience and nanotechnology has provided an impetus for the development of

1. Introduction

One of the great challenges facing the current researchers is to provide low-cost and environmentally friendly high-power energy resources.^[1–6] Among the various energy storage systems, supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted intense attention because of their higher power density than batteries and higher energy density than conventional dielectric capacitors.^[1] They have found extensive applications which include consumer electronics, energy management, memory back-up systems, industrial power and mobile electrical systems. A typical example is the use of supercapacitors in emergency doors on an Airbus A380 (16 per plane), where the neediness of large scale implementation is also clearly proven.^[4] Many materials have been investigated as the electrode materials in supercapacitors, including transition metal

new supercapacitor electrode structures. The small size can significantly enhance the utilization of active materials and shorten the transport path of ion and electron. However, single-phased nanomaterials are still insufficient in performance because of their intrinsic weaker material properties in conductivity, cycling stability and mechanical stability in despite making them in the form of nanomaterials.^[13–16] As a result, heterogeneous nanostructured materials with multi-nanocomponents have been proposed. In this configuration, each component is tailored to meet different demands, e.g. high energy density, and high conductivity. The resulting materials exhibit synergistic properties by integrating the individual components, and greatly enhance the supercapacitive performance.^[16–20] Among the various hybrid approaches, the metal oxide-carbon combination has shown great potential. It is well-known that transition metal oxides, such as MnO_2 , have the advantage of low cost, environmentally friendly and high specific capacitance.^[21,22] Hence, an advanced approach is to hybridize the electrode materials by adding electrochemically active metal oxide materials to conductive carbon matrix. In this approach, it is essential to load and/or incorporate metal oxide nanoparticles to the nanostructured carbon materials, which can be carbon nanotubes, carbon aerogels, mesoporous carbons, graphene, etc.^[18,23–26] The metal oxide/carbon composites not only increase the utilization of the active materials, but also improve the electrical conductivity and mechanical strength of the composite materials. For instance, Zhang et al.^[18] have reported the MnO_2 nanoflower/carbon nanotube array (CNTA) composite electrode with hierarchical porous structure. The large surface area and superior conductivity of final structure are achieved by combining

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electrodeposition technique to a vertically aligned CNTA framework. This MnO_2/CNTA electrode presents high rate capability (50.8% capacity retention at 77 A/g), high specific capacitance (199 F/g and 305 F/cm³) and long cycle life (3% capacity loss after 20 000 charge/discharge cycles). The excellent electrochemical supercapacitive performance of the composite materials is mainly due to the superior electrical properties of the substrate, i.e. CNTA grown directly on the current collector, as well as the pseudo-capacitive behavior of the active materials. Recently, Zhu et al.^[26] also synthesized a composite of graphene oxide supported by needle-like MnO_2 nanocrystals (GO- MnO_2 nanocomposites) by using a simple soft chemical route in a water-isopropyl alcohol system. The electrochemical performance of the nanocomposites has been largely enhanced by the chemical interaction between GO and MnO_2 . These recent results have demonstrated that the metal oxide-carbon nanocomposite materials are indeed a class of promising electrode materials for high-performance supercapacitors.

However, there still exist several major drawbacks for metal oxide-carbon nanocomposite materials, such as their relatively low weight fraction of metal oxide. As a result, their energy density in most cases is not optimal. Furthermore, the high cost of CNTs remains a great issue to the widespread uptake of CNTs-based supercapacitor technology. In this research news, we pay particular attention to another approach for enhancing electrochemical performance of metal oxide, such as the mesoporous carbon incorporated metal oxide ranging from 0D to 1D nanostructures nanocomposites. Furthermore, 3D hierarchical porous graphitic carbon (HPGC)-based composites for electrochemical capacitors which is the latest development in the field, will also be introduced.^[27,28] The latest results from various leading research groups are correlated to shed light for the future development of electrode materials in high performance supercapacitors.

2. Metal Oxide Nanoparticles (0D) Confined in Ordered Mesoporous Carbon Composite Electrodes

A major rate-limiting process is the electrolyte diffusion within the bulk electrode materials. It is essential to optimize the electrolyte transport paths without sacrificing electron transport.^[29] In this regards, ordered mesoporous carbon (OMC) materials are reckoned as desirable electrode material in energy conversion and storage due to their intriguing properties such as electrical conductivity, chemical inertness, high surface area, uniform pore size, and biocompatibility.^[30,31] In the construction of a metal oxide-carbon hybrid structure, OMC is considered as an ideal host for a host-guest electrode material. More significantly, the synthesis of metal oxide nanoparticles within carbon mesopores shows a confined growth process that can facilitate controllable growth of the nanoparticles to give them optimal dimensions. Thus far, many different nanoparticles have been reported to be incorporated inside OMC via various methods, such as ion-exchange methods,^[32] impregnation,^[33] sonochemical methods,^[34] etc.. A representative example was provided by Zhou et al.,^[34] where they successfully realized the synthesis of MnO_2 nanoparticles inside the pore channels

of OMC CMK-3 using a sonochemical method. The proposed process has been shown schematically in Figure 1a. The composite nanostructure was confirmed by transmission electron microscopy (TEM), as shown in Figure 1b. The MnO_2 nanoparticles were homogeneously dispersed in pore channels with uniform sizes of ~3–4 nm and no bulk aggregation of nanoparticles was observed on the outer surface, indicating the incorporation of MnO_2 was confined to the pores of CMK-3. The results showed that CMK-3 with 20 wt% loading of MnO_2 could deliver an enhanced discharge performance of 223 mA h/g at a relatively high rate of 1 A/g. Another example was that reported by Shi et al.,^[35] they reported a novel MnO_2 /mesoporous carbon composite structure, synthesized by embedding MnO_2 nanoparticles into the mesoporous carbon walls through the redox reaction between permanganate ions and carbons (Figure 1c). A large specific capacitance of over 200 F/g for the MnO_2 /mesoporous carbon composite and 600 F/g for the MnO_2 (Figure 1d) were achieved with high electrochemical stability and high reversibility. The enhanced performance was attributed to the well-defined geometry and pore size of the ordered mesoporous nanocomposites, which facilitated the rapid ion transport via the high surface area.

3. Metal Oxide Nanowires (1D) Coated with Mesoporous Carbon Composite Electrodes

It is also noted that one-dimensional (1D) nanostructures with controlled size, crystallinity and chemical composition can provide faster redox reactions, and shorter diffusion paths for electrons and ions.^[13,36,37] Therefore, in recent years, coaxial nanowires, such as metal oxide/conducting polymers^[36] and metal oxide/CNTs,^[18] have been investigated. However, metal oxide/conducting polymers coaxial materials suffer from mechanical instability or poor cycle ability. On the other hand, composites with carbonaceous materials such as CNTs, carbon foam, and activated carbon, metal oxides have shown to have an enhanced electrochemical performance even when a low amount of metal oxide is incorporated in the carbonaceous materials.^[38] For example, Wang et al.^[39] reported the capacitive performances of MnO_2 nanoparticles confined inside CNTs (MnO_2 -in-CNT) and MnO_2 nanoparticles dispersed on the outer surface of CNTs (MnO_2 -out-CNT), respectively. Both configurations exhibited improved electrochemical performance, but the MnO_2 -in-CNT composite was noted to produce higher specific capacitance compared to that of MnO_2 -out-CNT. This is attributed to the enhanced electrical conductivity and the formation of $\text{Mn}_{(\text{IV})}/\text{Mn}_{(\text{III})}$ redox couples in MnO_2 -in-CNT composite, which was induced by the unique confinement inside CNTs. Nevertheless, it remains a challenge to develop composite electrodes with high content of metal oxide materials for high power demand applications such as electric vehicles.

Very recently, the author reported some new insight on the design of an ideal supercapacitor with both high energy and power densities.^[19,40,41] With manganese oxide as an example,^[40] a novel Mn_3O_4 /mesoporous carbon hybrid nanowires has been fabricated using dopamine as a carbon source, as illustrated in Figure 2a. It is noted that dopamine, a biomolecule that contains catechol and amine functional groups, can self-polymerize

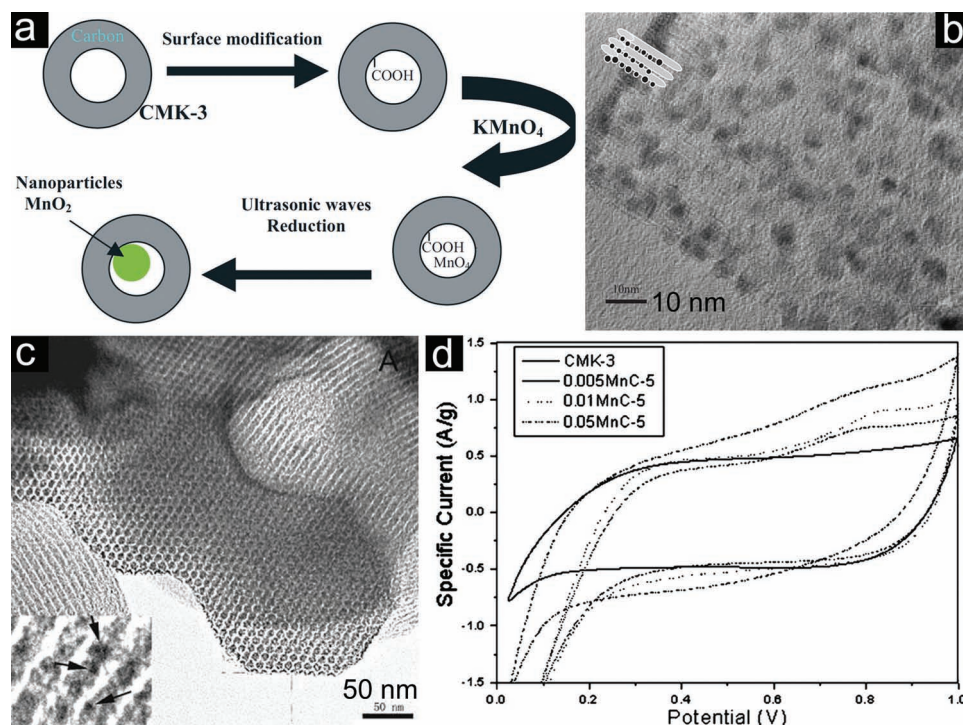


Figure 1. (a) The proposed formation process of MnO₂ nanoparticles inside the pores of CMK-3, and (b) CMK-MnO₂ structural model of the side view of the pore walls with nanocrystals formed along the pore channels of CMK-3. In the structural model, the gray area represents the carbon framework, and the black area represents nanoparticles. Reproduced from reference 34. (c) Novel MnO₂/mesoporous carbon composite with MnO₂ embedded into the mesoporous carbon walls, and (d) CV curves of the composites with different MnO₂ content in 2 M KCl at 5 mV/s. Reproduced with permission from reference 35. Copyright 2006, ACS.

at alkaline pH values and spontaneously deposit polydopamine conformal films on virtually any surface.^[42] The thickness of such a conformal coating can be precisely controlled with

a resolution of approximately 1 nm.^[42] It is exciting to discover that dopamine polymer can serve as a carbon precursor with an excellent carbon yield (~54% weigh retention even at

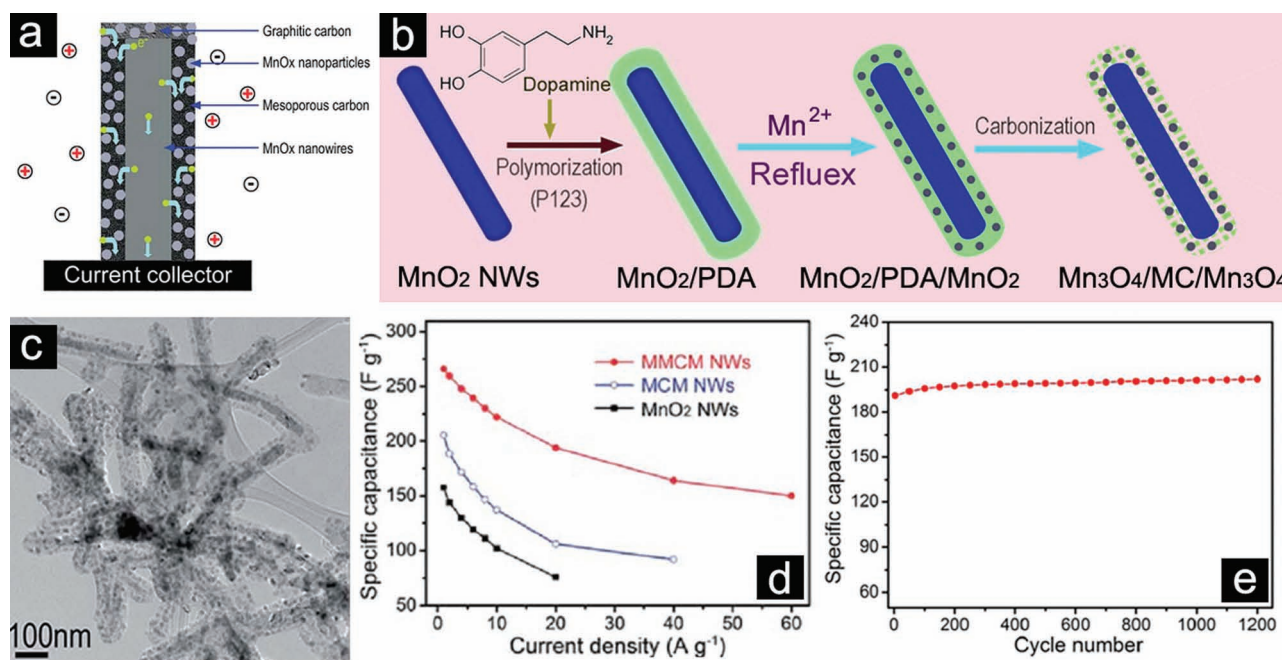


Figure 2. (a) Schematic image, (b) the formation strategy, (c) TEM image, (d) and (e) the corresponding supercapacitive performances of Mn₃O₄/MC hybrid nanowires. Reproduced with permission from reference 19,40. Copyright 2011, Royal Society of Chemistry.

800 °C in an inert atmosphere).^[40] More significantly, the triblock copolymer P123 can be used as a structure-directing agent to generate the mesoporous structures with tunable pore sizes. These findings have offered a novel and simple approach to coat a layer of mesoporous carbon onto the surface of metal oxides. In addition, it has been reported that polydopamine has substantial functional groups, which can react easily with metal ion to form metal oxide-based compounds.^[42] The formation process, using MnO₂ nanowires as an example, was illustrated in Figure 2b. The TEM image (Figure 2c) confirmed the realization of the as-designed hybrid nanowires. The unique structure is noted to possess several major advantages: (1) the carbon layer coated on the surface of the MnO₂ nanowire overcomes the poor conductivity of metal oxide; (2) the mesoporous feature of the carbon shell not only ensures interaction between

the electrolyte and the active inner materials, but also digests the possible volume changes while cycling; (3) the small manganese oxide nanoparticles dispersed on the surface of the mesoporous carbon nanotubes can be almost fully utilized for the enhancement of capacitive performance. The hybrid nanowire with optimal carbon content exhibited superior capacitive properties in 1 M Na₂SO₄ aqueous solution, such as high specific capacitance (266 F/g at 1 A/g), excellent rate capability (56.4% capacity retention at 60 A/g) and outstanding cycling stability (without degradation after 1200 cycles). The energy densities achieved can be as high as 20.8 Wh/kg at a power density of 30 kW/kg. Using a similar approach, peapod-like metal Ni nanoparticles@mesoporous carbon core-shell nanowires^[41] were also synthesized considering Ni(OH)₂ nanowires could be reduced to the corresponding metal under carbon, which also

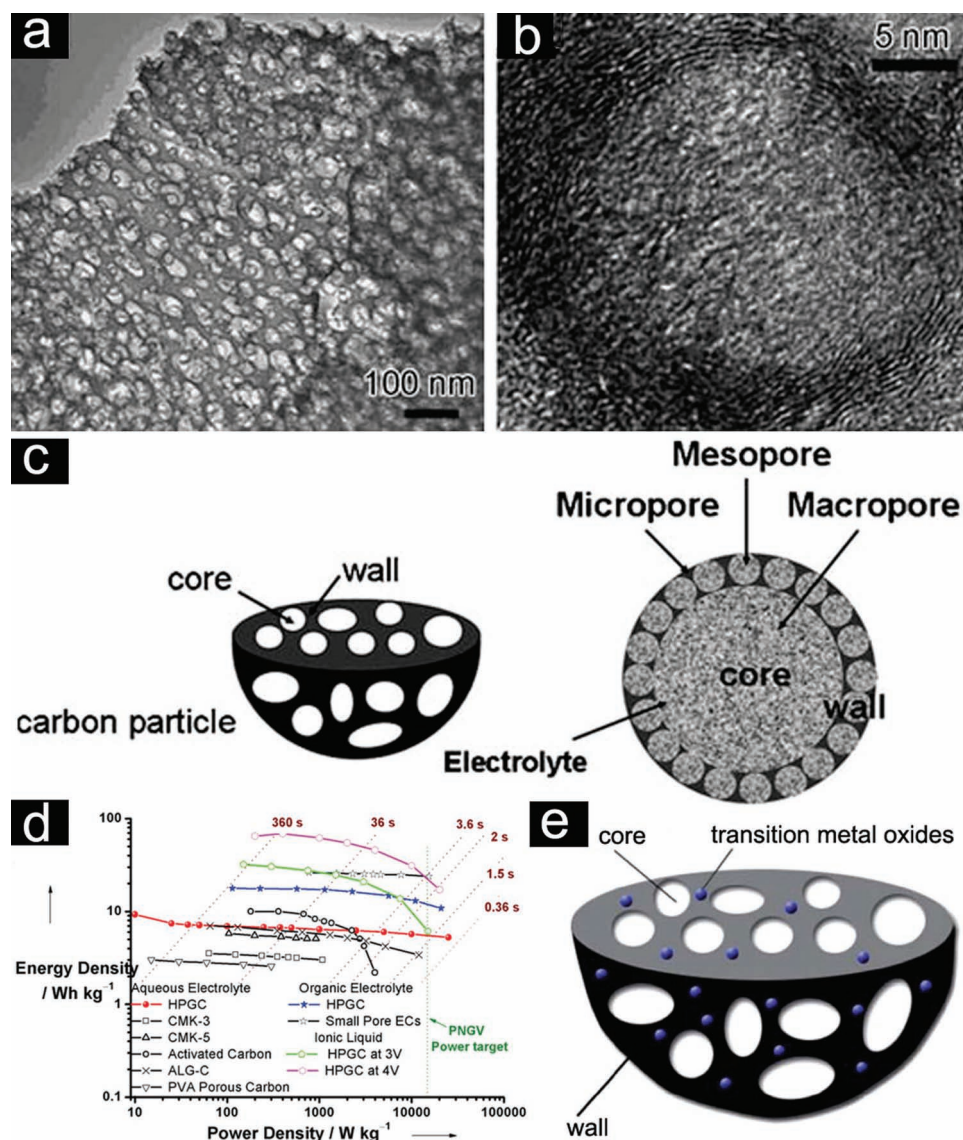


Figure 3. (a) Low- and (b) high-magnification TEM images of the as-synthesized HPGC, (c) schematic representation of the 3D hierarchical porous texture, (d) Ragone plot showing the position of the HPGC materials relative to other forms of carbon materials, (e) schematic diagram of the 3D hierarchical porous structure of metal oxide/HPGC composites. Reproduced with permission from reference 27. Copyright 2007, ACS.

exhibited a high specific capacitance with enhanced rate capability and cycle stability in 1 M KOH aqueous solution.

4. Hierarchical Porous Graphitic Carbon (HPGC)-Based Composite Electrodes

Since Song et al.^[43] and Lee et al.^[44] predicted theoretically that hierarchical pore structure may lead to a better rate performance of supercapacitors, numerous efforts have been devoted to the challenge of attaining these pore structures.^[27,45,46] The design of hierarchical porous structure is based on the different behaviors of electrolyte in pores with different sizes including macroporous cores, mesoporous walls and micropores (as illustrated in Figure 3c), which can result in high-performance electrode materials with short ion transport distance, low resistance, and large charge storage density.^[27] The physicochemical properties of the electrolyte in macropores can be viewed as similar to that of the bulk electrolyte with the lowest resistance. Furthermore, the ion-buffering reservoirs can also be formed in the macropores to minimize the diffusion distances to the interior surfaces. In addition, it is noted that the mesoporous walls can enhance the power performance at high power densities and accelerate the kinetic process of the ion diffusion in the electrodes, whereas micropores can effectively trap ions for high energy storage. Based on these intriguing advantages, Cheng et al.^[27] have synthesized 3D aperiodic hierarchical porous graphitic carbon as a potential electrode material for high power electrochemical capacitor applications, as shown in Figure 3a–d. The results have shown higher energy densities at high charge/discharge rates than previously reported high surface area carbons were achieved (Figure 3d). This new HPGC nanostructure is expected to combine with metal oxides as novel nanocomposite materials for high performance supercapacitors. Figure 3e illustrates the potential 3D hierarchical porous structure of metal oxide/HPGC composite.^[28] However, it is worth to point out that regardless of the type of carbon matrix, there exists a compromise among the composition of individual component, and an optimized mass ratio of ingredients, for every composite material.

5. Summary and Outlook

In summary, we have described recent advances in metal oxides based nanocomposites as electrode materials for supercapacitors applications. To overcome the poor conductivity and cycling stability of metal oxides, several strategies have been discussed. In view of the intriguing features of mesoporous carbon, we have specifically discussed porous carbon incorporated metal oxides nanocomposites as electrode materials. This includes metal oxide nanoparticles confined in ordered mesoporous carbon composites and 1D metal oxide nanostructures coated with mesoporous carbon composites. The resulting nanocomposite materials have been shown to exhibit synergic properties, greatly enhancing their supercapacitive behaviors, i.e., high energy density at high power density. The excellent electrochemical performances have made them one of the most promising electrode materials for electrochemical energy

storage devices. Furthermore, combining of macroporous cores, mesoporous walls and micropores, 3D hierarchical porous graphitic carbons (HPGC) have emerged to be the research focus in recent years. It is reckoned that HPGC can be an excellent support for metal oxides as electrode material for high performance supercapacitors. All in all, there is tremendous room still available in the design and synthesis of mesoporous carbon incorporated metal oxides nanocomposites as superior electrode materials for supercapacitor applications. It is believed that they will continue to contribute in the development of supercapacitors with a higher energy density and better cycling stability at high power density to meet the ever-increasing requirements of electrochemical energy storage devices.

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