



Two-dimensional Co_3O_4 thin sheets assembled by 3D interconnected nanoflake array framework structures with enhanced supercapacitor performance derived from coordination complexes



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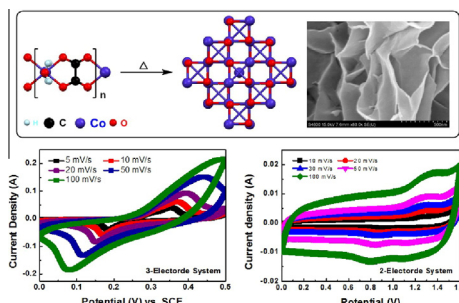
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HIGHLIGHTS

- 2D Co_3O_4 thin sheets were synthesized by simple pyrolysis of a $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ thin sheet precursor.
- The novel thin sheets synthesized at 500 °C for 6 h exhibit a high specific capacitance of 1500 F g^{-1} at 1 A g^{-1} .
- Excellent cycling stability of 99.3% capacitance retention after 2000 cycles.
- The asymmetric supercapacitor produced a high energy density of 15.4 Wh kg^{-1} at a power density of 0.8 kW kg^{-1} .

GRAPHICAL ABSTRACT



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ABSTRACT

Two-dimensional (2D) Co_3O_4 thin sheets assembled by 3D interconnected nanoflake array framework structures were first synthesized from nanoflake array-assembled porous cobalt-oxalate coordination complex thin sheets by means of direct pyrolysis in the air and the synthesis is simple and facile to implement scale-up for various application. The products exhibit excellent pseudocapacitive performance in an alkaline medium, holding great promise in supercapacitors (SCs). The electrochemical properties of the obtained Co_3O_4 thin sheets were evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge measurement (CP) and electrochemical impedance spectroscopy (EIS) in 2.0 M KOH solution. Temperature has an obvious effect on the performance of the products. Impressively, the thin sheets synthesized at 500 °C for 6 h used as electrode materials for SCs exhibit a specific capacitance as high as 1500 F g^{-1} at 1 A g^{-1} and even 828 F g^{-1} at 10 A g^{-1} , as well as remarkable cycling stability with 99.3% of its initial capacitance retained after 2000 continuous charge–discharge cycles at a current density of 5 A g^{-1} . In addition, the assembled asymmetric system using the obtained Co_3O_4 thin sheets at 500 °C for 6 h as positive electrode and activated carbon as negative one can produce a high energy density of 15.4 Wh kg^{-1} at a power density of 0.8 kW kg^{-1} . The hierarchical architectures of the products with hierarchical porosity and interconnected channels as well as the synergistic effect between their compositions provide several advantages including a large contact surface area, short ion diffusion path and good charge transport, which validate these thin sheets promising potential for a wide range of applications in energy storage.

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1. Introduction

With the increasing demand for clean and sustainable energy as well as the rapid-growth of portable electric equipments and hybrid electric vehicles, a great deal of efforts have been devoted to alternative energy conversion and storage systems with high efficiency, low cost, and environmental friendliness [1]. Supercapacitors (SCs), also called electrochemical capacitors or ultracapacitors, have been considered as one of the most promising options for next-generation power devices, mainly due to their higher power density than batteries and higher energy density than conventional electric double-layer capacitors (EDLCs) [2]. Store energy of SCs is through either ion adsorption of EDLCs or fast surface redox reactions of pseudocapacitors (PCs), as well as both of them [3]. And PCs can provide higher capacitance values than EDLCs. Therefore, the design and preparation of efficient and high-performance materials especially pseudocapacitive materials for electrical energy storage are expected to have a significant impact on practical applications.

The electrochemical performance and energy storage capacity of SCs is largely determined by the active materials in electrodes [4]. In general, there are three types of major electrode materials reported for SCs including metal oxides/hydroxides, carbon materials and conducting polymers [5]. In view of their high theoretic capacity, transition metal oxides can achieve much higher specific capacitance than the two others [6]. Furthermore, nanostructured transition metal oxides have been found to be an effective alternate to improve the charge storage of PCs because of their high surface area, short electron and ion transport pathway and enhanced interaction with the electrolyte ions [7]. Among various transition metal oxides with different valence states, cobalt oxide nanostructures exhibit many attractive advantages such as low cost, environmental compatibility, and especially the high theoretical specific capacitance, which render them competitive as electrode materials for PCs [8]. The specific capacitance of cobalt oxide electrodes is critically dependent on their surface and crystalline structure [9]. In order to improve the performance of PCs, it is desirable to develop novel cobalt oxide nanostructures with porous structures and highly active sites.

Controlled synthesis of materials with well-defined morphology can offers excellent properties superior to those of their bulk counterparts and great promise for practical applications. Research results on two dimensional (2D) nanosheets with porous structures and pseudocapacitive performance have garnered considerable recent research attention and revealed that these materials are favorable to efficient ion and electron transport, and can better accommodate the structure change in the electrochemical reaction, which have great potential in energy storage devices [10]. Up to date, many strategies have been reported for the synthesis of 2D porous cobalt oxide nanostructures as electrode materials for PCs with the building blocks of nanosheets with diameter of tens and hundreds of nanometers. For instance, Qian's group reported mesoporous 2D Co_3O_4 nanosheets with specific capacitance of $92\text{--}85\text{ F g}^{-1}$ at $5\text{--}20\text{ mA cm}^{-2}$ through a facile binary-solution route and sequential thermal decomposition at atmospheric pressure [11]. Rao and his cooperators [12] demonstrated the synthesis of ultralayered Co_3O_4 structures with high porosity by a facile homogeneous precipitation process under hydrothermal conditions and the charge-discharge study shows that the material is capable of delivering very high specific capacitance of 548 F g^{-1} at a current density of 8 A g^{-1} and retains 66% of capacitance at 32 A g^{-1} , as well as excellent specific capacitance retention capability of ca. 98.5% after 2000 continuous charge-discharge cycles at high current density of 16 A g^{-1} . Gu and Tu et al. [13] reported mesoporous Co_3O_4 sheets from ionothermal and calcination strat-

egy, which exhibit superior cycling performance as PCs with specific capacitance of 238.4 F g^{-1} at 2 A g^{-1} and a higher strain accommodation capability due to its nanocrystallite constructed mesoporous sheet structure. Ji's group [14] investigated porous Co_3O_4 sheets induced by alternating voltage with maximum specific capacitance of 288 F g^{-1} at a current density of 1 A g^{-1} in 2 M KOH . More recently, our group [15] reported 2D multi-layer graphene-like Co_3O_4 thin sheets (CQU-Chen-Co-O-1) by direct hydrothermal decomposition of the mixed aqueous solution of cobalt (II) nitrate and acetic acid, which exhibited excellent pseudocapacitive performance with high specific capacitance of 1862 F g^{-1} at 1 A g^{-1} . The PCs store charge from fast and reversible redox reactions at the first few nanometers on the surface and controlling morphology of cobalt oxides to create porosity will improve the interface contact efficiency between active sites and electrolytes, to serve as reservoirs for electrolyte ions to facilitate ions and electrons transport, and to provide spaces for volume expansion during the cycling process [16]. Up to date, developing a simple and facile route for the controlled synthesis of 2D porous Co_3O_4 nanostructures with highly active sites is needed not only for academic research, but also for developing advanced energy storage materials.

From the viewpoints of the development of novel functional materials, coordination complexes (CCs) self-assembly of metal ions and organic ligands have been demonstrated to be a promising class of inorganic-organic hybrid materials with desired structures and potential applications [17]. Among them, the self-assembly of metal ion and oxalate dianion ($\text{C}_2\text{O}_4^{2-}$) in solution provides a rich variety of extended coordination networks for the design and synthesis of various CCs [18]. As one kind of novel inorganic-organic hybrid solids, metal-ox CCs have been widely used as precursors for the synthesis of metal oxide nanostructures [19]. For example, Shi's group [20] reported the synthesis of nanoporous manganese and nickel oxides with polyhedron particle morphologies, high surface areas and narrow pore distributions by controlled thermal decomposition of the oxalate CCs precursors. Coronado and co-workers [21] reported the synthesis of nanostructures of magnetic oxides from soluble molecular precursors of 2D polymetallic oxalate-bridged polymeric networks with general formula $[\text{M}^{\text{II}}(\text{H}_2\text{O})_2]_3[\text{M}^{\text{III}}(\text{ox})_3]_2(18\text{-crown-6})_2$ ($\text{M}^{\text{III}} = \text{Cr, Fe}$; $\text{M}^{\text{II}} = \text{Mn, Fe, Co, Ni}$; $18\text{-crown-6} = \text{C}_{12}\text{H}_{24}\text{O}_6$). Hor and his cooperators [22] presented the synthesis of intermetallic composite oxides by thermal decomposition of heterometallic MM' ($\text{M} = \text{Ba}^{\text{II}}, \text{Mn}^{\text{II}}$; $\text{M}' = \text{Cr}^{\text{III}}$) oxalato CCs. More recently, Pang et al. [23] reported the synthesis of porous ZnO-NiO composite micropolyhedrons by calcination of mixed oxalate CCs ($\text{Zn}_{0.9}\text{Ni}_{0.1}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$) at $400\text{ }^\circ\text{C}$ in air, which has a large specific capacitance 649.0 F g^{-1} in 3.0 M KOH solution and long-term stability of 99.1% of capacitance after 400 cycles. In recent years, many CCs especially coordination polymers (CPs) and metal-organic frameworks (MOFs) have been applied as precursors for the synthesis of nanostructured metal oxides used as electrode materials for SCs (in Table 1). Various metal oxide nanostructures including CeO_2 [24], mesoporous and nanoporous NiO [25–27] and how box, porous hollow and dendrite-like Co_3O_4 [28–31] synthesized from CCs, have been reported for electrode materials for SCs with high specific capacitances and good cyclical stability. However, little attention has been devoted to the synthesis of 2D metal oxide nanostructures from the metal-ox CCs and used them as electrode materials for PCs.

In the present work, we demonstrated the synthesis of 2D Co_3O_4 thin sheets assembled by 3D interconnected nanoflake array framework structures via a hydrothermal route followed by calcination treatment for the first time. Detailed structural characterization reveals that the obtained Co_3O_4 thin sheets at different temperatures are crystallized with a cubic phase spinel structure.

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