



Regular Article

Mesoporous transition metal oxides quasi-nanospheres with enhanced electrochemical properties for supercapacitor applications



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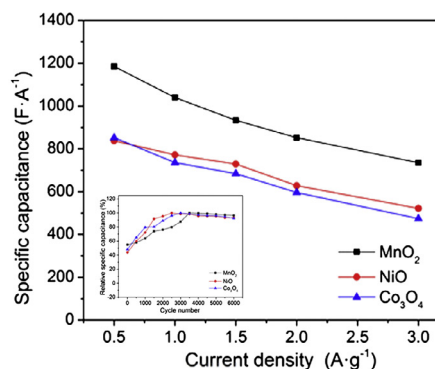
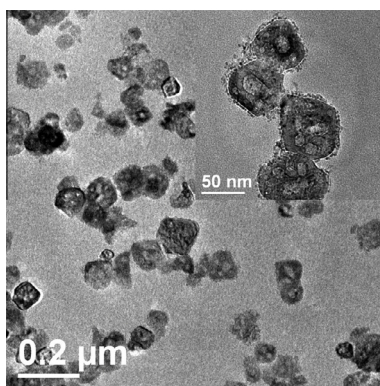
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HIGHLIGHTS

- Mesoporous MnO₂, NiO, and Co₃O₄ quasi-nanospheres were prepared.
- They showed the large specific surface area and narrow pore size distribution.
- They demonstrated the high capacity and excellent long-term stability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this report, we obtain mesoporous transition metal oxides quasi-nanospheres (includes MnO₂, NiO, and Co₃O₄) by utilizing mesoporous silica nanospheres as a template for high-performance supercapacitor electrodes. All samples have a large specific surface area of approximately 254–325 m² g⁻¹ and a relatively narrow pore size distribution in the region of 7 nm. Utilization of a nanosized template resulted in a product with a relative uniform morphology and a small particle diameter in the region of 50–100 nm. As supercapacitor electrodes, MnO₂, NiO, and Co₃O₄ exhibit an outstanding capacity as high as 838–1185 F g⁻¹ at 0.5 A g⁻¹ and a superior long-term stability with minimal loss of 3–7% after 6000 cycles at 1 A g⁻¹. Their excellent electrochemical performances are attributed to favorable morphologies with a large surface area and a uniform architecture with abundant pores. The associated enhancement of electrolyte ion circulation within the electrode facilitates a significant increase in availability of Faradic reaction electroactive sites.

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1. Introduction

Supercapacitors are an important bridge between conventional dielectric capacitors and high energy storage battery/fuel cell due

to their simple charge separation between electrode material and electrolyte, and are ideally suited to both fast energy storage and portable energy systems [1–5]. Because specific capacitance relies heavily on the microstructure and morphology of the electrode material, major research efforts have focused on the design of electrode materials with enhanced inner circulation of electrolyte ions and a high area at the electrolyte/electrode interface. Recent research indicates that nanosized morphological features

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introduce more electrochemically active sites and shorten the transport path length for both electrons and ions [6–9]. Consequently, the nanostructured electrode shows a significant enhancement of specific capacitance, charge/discharge ability, and cyclic stability. At present, transition metal oxides (TMO) have been extensively studied because of their favorable capacitive characteristics and environmental friendliness including NiO, Co_3O_4 , MnO_2 , V_2O_5 , and so on [10–16].

Among them, MnO_2 , NiO, and Co_3O_4 are the promising pseudocapacitive materials for supercapacitors due to their high theoretical capacity more than two times larger than that of graphite and are expected to meet the requirements of future energy storage work systems [17–25]. Subsequently, a series of MnO_2 , NiO, and Co_3O_4 with different morphology and structure were synthesized for improving their capacities as supercapacitor electrodes. MnO_2 nanorods obtain by Sawangphruk's group significantly improved the charge-storage performance with a maximum specific energy of 64 Wh kg^{-1} and power of 3870 W kg^{-1} [17]. The controlled MnO_2 nanostructures and ultrathin MnO_2 free-standing film exhibited the high specific capacitance (371 F g^{-1} at 0.5 A g^{-1} and 98 F g^{-1} at 50 A g^{-1} , respectively), which were prepared by replica molding and vacuum-assisted filtration technique, respectively [18,19]. NiO and Co_3O_4 in the form of nanoflakes, nanofibers, nanotubes, nanosheets, nanoparticles, and hollow fluffy cages were synthesized and they significantly improved the specific capacitance for supercapacitors application [20–25].

Presently, some research has already demonstrated an improvement in material energy storage density due to the mesoporous characteristics [5]. Larger specific surface area of mesoporous materials implies more faradaic active sites, higher contact area of the electrolyte accessible to the electroactive substance and thereby higher pseudocapacitance [26]. Meanwhile, the mesoporous structure can offer more channels for the electrolyte, leading to less electrochemical polarization and therefore minimal dissolution of metal oxide. Additionally, high porosity and ideal pore diameter can easily relieve the internal stress created during the charging and discharging processes, and protect the electrode from physical damage [27,28]. The limited studies of mesoporous materials such as mesoporous carbon [29], mesoporous flower-like $\alpha\text{-MnO}_2$ [30], and mesoporous CuO-NiO [31] for supercapacitors, have delivered the great capacitance performance and long-term retention. Recently, Wang et al. synthesized Honeycomb-like mesoporous NiO microspheres using a hydrothermal reaction followed by an annealing process demonstrate the highest specific capacitance of 1250 F g^{-1} at 1 A g^{-1} [32]. The 3D flower-like mesoporous $\alpha\text{-MnO}_2$, synthesized by the thermodynamically favorable redox reaction, is also recently reported to reach a high specific capacitance of 322 F g^{-1} at 1 A g^{-1} [33].

The construction of nanomaterials containing mesoporous structure shows enormous potential in the development of high performance electrode materials [34]. However, mesoporous TMO nanoparticles are hard to obtain, and published literature relating to their application for supercapacitors is relatively limited [35,36]. In this paper, we studied the synthesis and electrochemical properties of three kinds of TMO, MnO_2 , NiO, and Co_3O_4 , for the supercapacitors application. The general synthetic strategy is shown in Fig. 1. Mesoporous silica nanospheres were first synthesized using cationic surfactant as a template and gelatin as a suppressant via anion-hydrothermal process. Transition metal inorganic salt containing target material was introduced to the pore channels of mesoporous silica by impregnation. After annealing of the as-synthesized products, the resultant $\text{SiO}_2\text{@TMO}$ was alkaline etched to obtain the target product. Mesoporous TMO quasi-nanospheres possessing high porosity and ultrahigh relative active surface area have the ability to enhance the intercalation of ions and the utilization of electrode materials significantly. They therefore exhibit an ultra-high capacitance and long-term cycling stability when applied as electrode materials for pseudocapacitors.

2. Experimental

2.1. Materials

All starting materials are analytical grade and used without any further treatment. Cetyltrimethylammonium bromide (CTAB) and gelatin were purchased from Aldrich. Gelatin (type A, gel strength $\sim 300 \text{ g Bloom}$) was derived from porcine skin through acid treatment. Tetraethyl orthosilicate (TEOS), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH, ammonia, and absolute alcohol were obtained from Shanghai Chemical Reagents.

2.2. Synthesis procedure for mesoporous silica nanospheres

Mesoporous silica nanospheres were synthesized as our recently reported method [37]: 0.60 g CTAB with 0.30 g gelatin were made into a homogeneous solution using 50 ml deionized water and 50 ml ethanol at 38°C . 14.5 ml aqueous ammonia (26.5 wt.%) and 0.85 g TEOS were added to the solution successively and stirred for 2 h to give a white precipitation. The precipitate was collected by centrifugation, then washed with deionized water and ethanol several times, dried in vacuum at 60°C overnight, and finally heated to at 600°C for 6 h with a heating rate of 1°C min^{-1} .

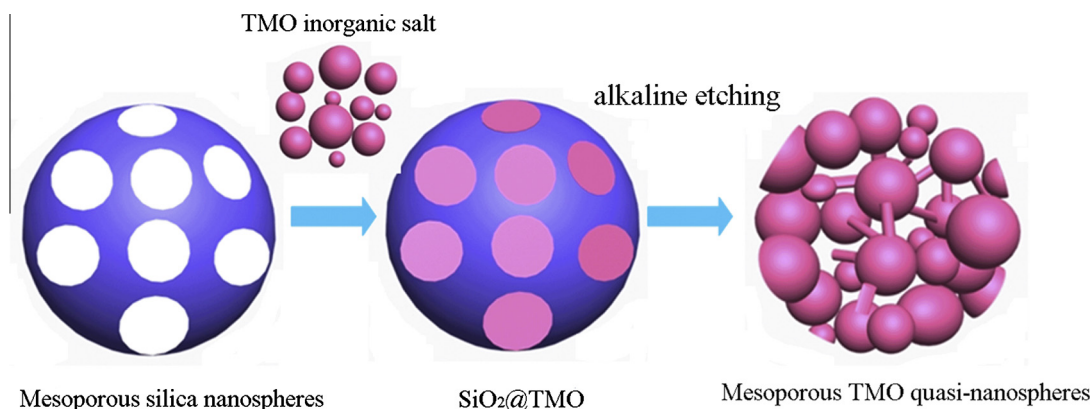


Fig. 1. Schematic illustration describing the formation of mesoporous TMO quasi-nanospheres.

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