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Preparation and capacitance behavior of manganese oxide hollow structures with different morphologies *via* template-engaged redox etching

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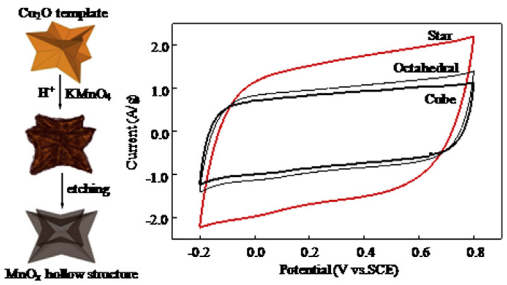
HIGHLIGHTS

- Amorphous manganese oxide hollow interiors are prepared by a redox etching process.
- Star-shaped amorphous manganese oxide hollow interiors show large specific surface area of 198 $m^2\ g^{-1}$.
- Capacitance of amorphous manganese oxide electrodes is connects with the specific surface area.
- Star-shaped amorphous manganese oxide hollow star electrode exhibits high specific capacitance of 366 F g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

A variety of amorphous manganese oxide electrode materials with uniform nonspherical hollow interiors are prepared *via* sacrificial template-engaged redox etching of the corresponding shape-controlled Cu_2O nanocrystals in $KMnO_4$ aqueous solution at room temperature. The obtained materials are characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and N_2 adsorption–desorption. The amorphous manganese oxide hollow materials not only well inherit the size and shape of Cu_2O nonspherical precursor, but also show a manganese average oxidation state of 3.7 and large specific surface area (about 198 $m^2\ g^{-1}$). The electrochemical measurements show that the capacitance of the as-prepared amorphous manganese oxide electrode materials with uniform nonspherical hollow interiors is connects with their specific surface area. The amorphous manganese oxide star hollow architecture exhibits not only high specific capacitance of 366 F g^{-1} at a scan rate of 5 mV s^{-1}, but also relatively good cycle stability (93.1% capacitance retention after 1000 cycles at a scan rate of 20 mV s^{-1}), which make it have a potential application as a supercapacitor electrode material.

1. Introduction

Electrochemical capacitor (EC) has emerged with wide application potential because it can provide higher energy density than conventional capacitors, and greater power density and longer cycling life than batteries through the use of high-surface-area electrodes and fast surface-charge-storage processes, which bridges the gap between conventional capacitors and batteries [1–3]. According to the mechanism of the energy storage, the electrochemical capacitor is classified as electric double-layer capacitor (EDLC) and faradaic pseudocapacitor [4, 5]. The double-layer capacitor is usually composed of the electrodes with high-surface-area because the non-faradaic capacitance of the electric

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double-layer stores energy by charge separation formed at the interface between the electrode and the electrolyte [5,6]. On the other hand, the faradaic pseudocapacitor based on transition metal oxides has attracted significant attention owing to its high specific capacitance, excellent reversibility and long cycle life [4,5,7]. Among these transition metal oxides, amorphous hydrated ruthenium oxide with remarkable pseudocapacitive behavior is one of the most attractive candidates for the electrode of electrochemical capacitors [7,8]. However, the high cost of ruthenium has limited its commercial use. Therefore, the investigate research for the cheaper metal oxides with equivalent characteristics is attracting attention.

Among the transition metal oxides with various valence states, manganese oxide is one of the most promising pseudocapacitance electrode materials due to its high specific capacitance, environmental compatibility and cost effectiveness [9,10]. Up to now, many manganese oxides with various structures and morphologies have been prepared *via* electrochemical and chemical routes, and their electrochemical properties have been investigated. The investigated materials mainly focus on the amorphous or poorly crystallized manganese oxides, single-crystalline manganese oxides and manganese oxide thin films because these material cathodes show ideally capacitive behavior such as large capacity, good electrochemical reversibility and high pulse-power property in a potential window of 1.0 V in Na_2SO_4 solution [11–18]. Moreover, it is well-known that manganese oxides with hollow structure have attracted considerable interest owing to its unique properties, such as large surface area, well-defined morphology, low density, and high energy storage ability [19–24]. In the past few years, a series of manganese oxides with hollow structure, including hollow nanospheres [20,23–25], nanotubes [26,27], hollow urchins [28,29], and hollow polyhedrons [30] have been synthesized. In general, two fabrication methods can be used to prepare these manganese oxides with hollow structure, which are a hard template method and template-free technology. Although the manganese oxides with hollow structure can be fabricated by hard template method, the removal of these templates such as monodispersed silica [21] or polycrystalline [31] by either thermal (sintering) or chemical (etching) methods is very complicated and energy-consuming, only the manganese oxide hollow structures with spherical or tubular morphologies can be obtained by a Ostwald ripening process [21,31], self-assembling [26] or Kirkendall effect [32]. Therefore, it is expected to develop a facile approach for preparation manganese oxides with hollow structure and different morphologies *via* nonspherical sacrificial templates. Compared with the widely reported templates, Cu_2O is one of the best corrosion-prone candidate sacrificial templates [33,34] because it has many advantages, such as the diversity in crystal morphology, low reduction potential (Cu^{2+}/Cu_2O = 0.203 V, vs SHE, SHE is abbreviated for standard hydrogen electrode) [35] and low prefabrication cost [36,37].

In the present work, a facile one-step approach was developed to prepare a variety of amorphous manganese oxide electrode materials with different morphologies and uniform hollow structure *via* sacrificial template-engaged redox etching of the corresponding shape-controlled Cu_2O nanocrystals in $KMnO_4$ solution at room temperature. Because the Cu^{2+}/Cu_2O standard reduction potential (0.203 V, vs SHE) is much lower than that of $KMnO_4/MnO_2$ (1.679 V vs SHE), the redox reaction between Cu_2O template and MnO_4^- ions is thermodynamically feasible. Cu_2O nanocrystals in suspension could be oxidized by MnO_4^- ions at room temperature according to the following redox reaction:

$$Cu_2O(s) + 2MnO_4^- + 6H^+ \rightarrow 2Cu^{2+} + 2MnO_x + 3H_2O$$

and manganese oxide hollow structures with different morphologies were obtained by the complete consumption of Cu_2O template. The schematic formation process of the manganese oxide hollow structures with different morphologies is illustrated in Fig. 1. This bottom–up approach could be used to controllably prepare metal oxide hollow structures with different morphologies and sizes. The as-prepared amorphous manganese oxide hollow structure with star morphology shows large specific surface area and an ideal capacitive behavior.

2. Experimental

2.1. Material preparation

$CuCl_2 \cdot 2H_2O$, NaOH, PVP (polyvinylpyrrolidone), $CuSO_4 \cdot 5H_2O$, Na_2CO_3, $C_6H_8O_6$ (ascorbic acid), $C_6H_5Na_3O_7$ (sodium citrate), $C_6H_{12}O_6$ (glucose) and C_2H_6O (ethanol) were obtained from Chemical Reagent Ltd., China, in an analytical purity and used without further purification. Deionized water was used throughout the experiments.

2.1.1. Preparation of Cu_2O nonspherical templates

Cu_2O nanocubes were synthesized by the report method [36]. In a typical procedure, NaOH solution (2.0 mol L^{-1}, 5.0 ml) was added dropwise into $CuCl_2$ solution (0.01 mol L^{-1}, 50 ml) at 55 °C. After stirring for 0.5 h, ascorbic acid solution (0.6 mol L^{-1}, 5.0 mL) was added dropwise into the above solution. A turbid red liquid was gradually formed and the mixture was aged for 3 h, the resulting precipitate was collected by centrifugation and decanting, followed by washing with distilled water and absolute ethanol, and finally dried in vacuum at room temperature for 12 h, Cu_2O nanocubes were obtained. Cu_2O octahedrons were prepared by above similar method except adding given amounts of PVP (M_W = 30,000) immediately after dropwising the NaOH solution into the $CuCl_2$ solution. Star-shaped Cu_2O structure was synthesized *via* reducing the copper-citrate complex [37]. Typically, a mixture solution of 4.0 ml $CuSO_4$ (0.68 mol L^{-1}), 4.0 ml sodium citrate (0.74 mol L^{-1}), 4.0 ml anhydrous sodium carbonate (1.2 mol L^{-1}) and 5.6 ml glucose (1.0 mol L^{-1}) was diluted to 80 ml with deionized water, and then aged at 80 °C for 3 h. The obtained colloid solution was centrifuged, washed with deionized water and followed by ethanol, the star-shaped Cu_2O structure was obtained.

2.1.2. Preparation of amorphous manganese oxide hollow structures

0.6 mmol Cu_2O with different morphologies was added to 400 mL deionized water and stirred for 20 min to obtain a suspension. Then 30 mL of a mixed solution of $KMnO_4$ (0.05 mol L^{-1}) and hydrochloric acid (0.01 mol L^{-1}) was dropped into the suspension and stirred for 48 h, the obtained precipitate was collected by several rinse-centrifugation cycles and followed by immersing in ammonia solution (18%) for 10 h to remove the Cu_2O cores. The resulting product was collected by centrifugation, followed by washing with distilled water and finally dried in vacuum at 60 °C for 12 h, the amorphous manganese oxide hollow structures with different morphologies were obtained.

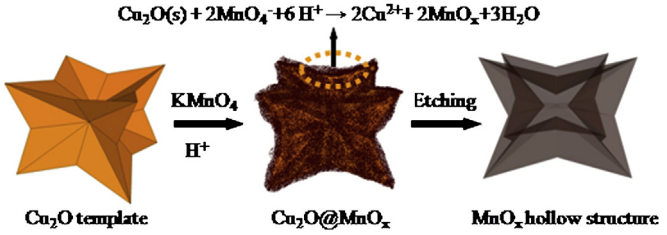

Fig. 1. A schematic formation process of the manganese oxide hollow structure with star morphology by template-engaged coordinating etching of Cu_2O.