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Facile synthesis of single crystalline mesoporous hematite nanorods with enhanced supercapacitive performance

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ABSTRACT

α-Fe_2O_3 nanorods with a length of 400–700 nm and a diameter of 20–80 nm, which have single-crystalline and mesoporous structure, could be obtained from these α-FeOOH precursors after calcining at 300 °C in air. The as-prepared single-crystalline mesoporous α-Fe_2O_3 nanorodes exhibited a large specific surface area and porosity, effectively increasing the contact area between the electrode materials and electrolyte, minimizing both the ionic and electronic transportation in the Fe_2O_3 during the charge-discharge process. The porous nanostructure facilitates the faster faradic reaction toward electrolytes and delivers highest specific capacitance (534 F g^{-1}) and an excellent long cycle life (upto 1500 cycles) in 1 M KOH electrolyte at current density of 4 A g^{-1}, demonstrating that the porous α-Fe_2O_3 nanorods can serve as an excellent electrode material for supercapacitors. It is believed that the single-crystalline mesoporous α-Fe_2O_3 nanorods are beneficial to the charge transfer in the electrode and to the ion transport in the solution during redox reaction.

1. Introduction

One-dimensional (1D) nanomaterials, such as nanorods, nanobelts, nanotubes and nanowires [1–6] have been the focus of much attention because of their improved chemical and physical performances over solid materials, as well as their intriguing applications in nanoreactors, catalysis [7,8] drug delivery [1,6] and energy storage for renewable energy sources [4,9]. Supercapacitors have attracted significant research attention as efficient energy storage devices in recent years due to their properties like high power density, excellent reversibility and long cycle life for time-dependent power needs of modern electronics and power systems [10–13]. Pseudocapacitors, which are based on reversible redox reactions at/near the surface of the electrode, show high specific capacitances and high energy storage characteristics [14,15] Fast faradic reaction leads to a high demand for the electron transport in the electrode and fast ion transport in the solution. Thus, the rational design and fabrication of high surface area-conductive electrodes with well-defined micro/nanoarchitectures for facile electron/ion transport are required for further enhancing electrochemical properties.

Transition metal oxides are considered as ideal electrode materials for pseudocapacitors as they can provide a variety of oxidation states for efficient redox charge transfer [10,16]. RuO_2 is well studied materials used as pseudocapacitive electrode materials with remarkable performance [17,18]. However, the high cost and toxic nature of RuO_2 limit its commercial application [19,20]. Thus there is a strong need to develop inexpensive and environmental friendly alternative electrode materials for supercapacitor applications. In order to meet the requirements of high power and energy density, 3d-transition-metal binary compounds (such as NiO, MnO_2, $Ni(OH)_2$, Co_3O_4) with various morphologies have been extensively explored [21–26]. Given that surface properties considerably influence the charge storage mechanism, the most active approach in supercapacitor research has been the development of electrode materials with improved surface properties [27]. Gogotsi et al. demonstrated that pore size significantly affects ion adsorption, enhancing the capacitance down to the solated ion size [28]. Several synthetic strategies are attempted to control the surface area, pore size and morphology and physicochemical properties of NiO and Co_3O_4 [29,30]. These studies revealed that parameters such as surface area and pore size, suitable surface morphology of traditional oxide play a significant role in exhibiting higher pseudocapacitance.

Hematite (α-Fe_2O_3) has been investigated for applications in lithium batteries, sensors, and catalysis [31–33]. It is also one of the promising materials for supercapacitors, because of its high

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specific capacitance, low cost and low toxicity [34,35]. However, the realized capacitance of α-Fe_2O_3 is considerably lower than the value expected. Because electrochemical properties of nanostructured materials strongly depend on its dimensionality, morphology, crystalline structure, and bulk density, extensive efforts have been focused on controlling the nanostructures of α-Fe_2O_3 for improving the capacitance properties [34–36]. For instance, nanostructured α-Fe_2O_3 film was electrodeposited anodically onto nickel substrate for ECs has been developed by Wu and co-workers [36]. They found that the electrochemical capacitive performance of the film depends on morphologies. Wang and co-workers developed a morphological–conserved route for the synthesis of mesoporous α-Fe_2O_3 nanostructures with controllable shapes for supercapacitors applications [34]. Highly ordered α-Fe_2O_3 nanotube arrays were fabricated through anodization method on iron foils for supercapacitors by Huang and co-worker [35]. Strikingly, the unique nanostructures of the α-Fe_2O_3 nanotube arrays also present remarkable rate capability and good cycling stability. In short, high performance supercapacitors generally require large surface area to increase the active sites for adsorbing electrons or for faradic reactions. For this purpose, producing suitable microporous or mesoporous structure in nanomaterials is a general strategy to improve the electrochemical properties. However, producing microporous or mesoporous structure generally accompanies crystalline order degradation, which also affects the electrochemical performance because the crystalline boundaries and defects influence electrons or holes transportation. So, producing microporous or mesoporous structure and at the same time, keeping single crystalline nature of the materials is a way to realize high performance supercapacitors. However, the synthesis of these novel structures is rather complex and difficult to control. Therefore, the design and synthesis of α-Fe_2O_3 with controlled shape and narrow size, distribution will continue to be a hot subject. To the best of our knowledge, there are few reports about single-crystalline mesoporous α-Fe_2O_3 structure as electrode of pseudocapacitor in different electrolytes.

In this work, we fabricate single-crystalline mesoporous α-Fe_2O_3 nanorods without any templates by calcining the α-FeOOH precursor in air. The single crystalline nature of α-Fe_2O_3 nanorods enables high electron mobility, which facilitates the transfer of electrons from the electrode surface sites to the substrate and helps to improve the electrochemical properties. Owing to single crystalline nature, the high surface area and porosity of the as-obtained α-Fe_2O_3 nanorods, the corresponding electrode material exhibits a high reversible capacity, and remarkable cycling performance.

2. Experimental

In this work, all chemicals are reagent grade and were used without further purification. In a typical synthesis procedure, Fe $(NO_3)_3 \cdot 9H_2O$ and KOH were used as the starting materials. The α-FeOOH nanorods were synthesized via a hydrothermal method as follows: firstly, 0.02 mol $Fe(NO_3)_3 \cdot 9H_2O$ and 0.08 mol KOH were each dissolved in 20 ml distilled water. Then, the KOH solution was dropped slowly into the $Fe(NO_3)_3 \cdot 9H_2O$ solution under vigorous stirring. The suspension solution was poured into a stainless-steel Teflon lined autoclave for the hydrothermal treatment, which was then filled with distilled water up to 80% of the total volume. The autoclave was sealed and maintained at 100 °C for 6 h. Finally, the

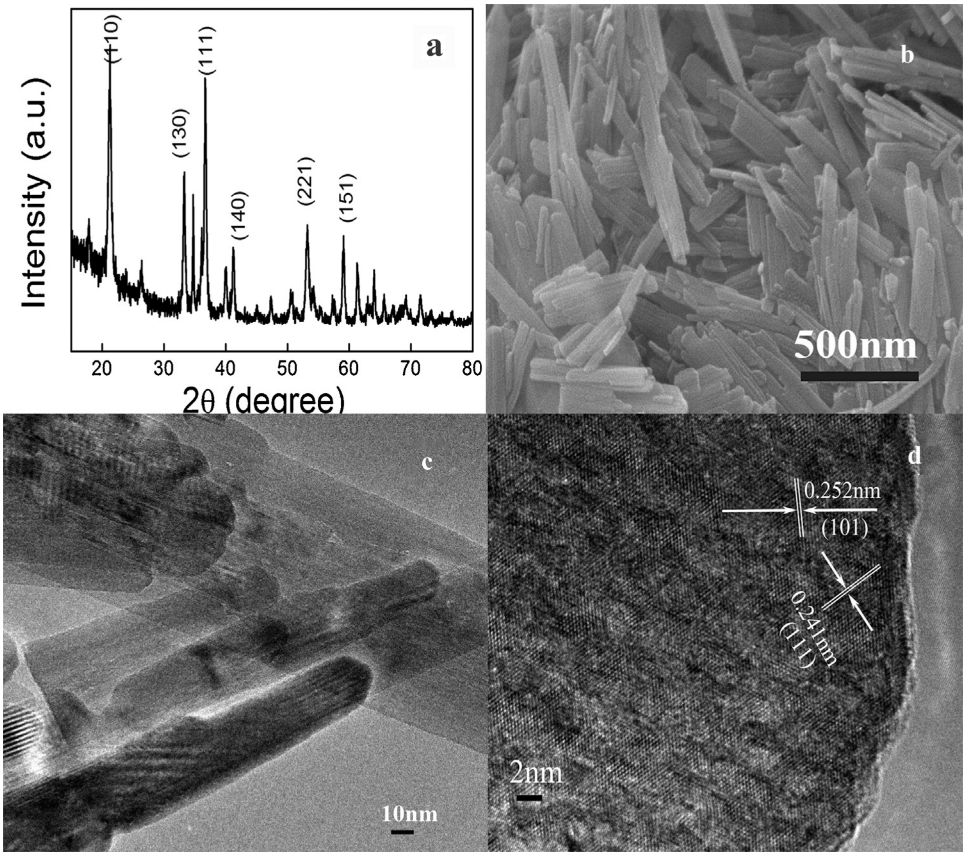

Fig. 1. (a) XRD pattern of the as-prepared α-FeOOH nanorods; (b) SEM image of the α-FeOOH nanorods; (c) TEM image of α-FeOOH nanorods; (d) HRTEM image of an individual α-FeOOH nanorod.