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Hydrothermal synthesis and electrochemical properties of hierarchical vanadyl hydroxide spheres with hollow core and mesoporous shell

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ABSTRACT

Hierarchical porous vanadyl hydroxide (VOOH) hollow spheres were successfully prepared using ammonium metavanadate as starting vanadium source materials through a facile hydrothermal method. Their morphology, structure and composition were characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, energy-dispersive X-ray spectrometry, elemental mapping, elemental analysis, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy and nitrogen adsorption-desorption isotherms. Brunauer-Emmett-Teller specific surface area of hierarchical VOOH hollow spheres measured 32 $m^2\ g^{-1}$, and their most probable distribution pore size reached 3.6 nm. Results demonstrated that hierarchical VOOH hollow spheres possessed macropores in their hollow interior and mesopores in shell. Electrochemical properties of hierarchical VOOH hollow spheres as supercapacitor (SC) electrodes were explored and investigated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. Results showed that hierarchical VOOH hollow spheres featured capacitive behavior based on pseudocapacitance, and exhibited specific capacitance of 93 F g^{-1} at current density of 0.2 A g^{-1}. Cycling stability was discussed in detail and indicated good rate capability of studied materials. VOOH hollow spheres are ideal material for SC electrodes in the present study.

1. Introduction

Driven by surging demands for portable electronics and renewable energy vehicles, increasing attention was paid to the field of energy storage systems in the past decades [1–10]. Among various energy storage devices, supercapacitors (SCs), also called electrochemical capacitors or ultracapacitors, drew tremendous interest because they can complement Li-ion batteries due to their excellent power output, exceptional cycling life, lightweight, ease of handing, and other features [11–13]. These unique properties make SCs potential power sources for the next-generation flexible and portable electronics, such as miniature biomedical devices, roll-up displays and wearable devices [11,14–16]. SCs store electrical energy by two mechanisms: non-Faradic process (electrochemical double-layer capacitors (EDLCs)) and Faradic process (pseudocapacitors (PCs)). EDLCs physically store charges by reversible ion adsorption at electrode electrolyte interface, and PCs chemically store charges by redox at surface vicinity (a few nanometers) [1]. Electrode materials for EDLCs comprise high-surface-area carbon-based materials, whereas PCs are made of conductive polymers and metal oxides/hydroxides [17]. Carbon materials exhibit low capacitance, especially at high charge-discharge rates. Metal oxides/hydroxides overcome this limitation and commonly exhibit high specific capacitance due to their more efficient energy storage mechanism. These materials feature potential as electrode material for SCs with high energy density [11,18–20]. Ruthenium dioxide is the most promising metal oxide candidate for SC electrodes owing to its high capacitance of 710 F g^{-1} [21]. However, ruthenium oxide is rare and expensive, thus severely limiting its

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practical application. Therefore, difficulty arises from development of new electrode materials for SCs with low cost [6].

In the past decades, some transition metal oxides and their derivatives were paid increasing attention for their application to SCs; these oxides include MnO_2 nanopillars [22], NiO nanoflakes [23], V_2O_5 [5,24], V_2O_5/PEDOT/MnO_2 nanosheets [25], V_2O_5/graphene [26], and other materials. Among these materials, vanadium oxides received tremendous attention as materials for energy storage in recent years [18,27–32] because of their low cost, multiple valences, layered structure and high specific capacity. However, vanadium-based materials, such as vanadyl hydroxide (VOOH), may bear scientific importance and novel chemical and physical properties but they are uncommonly reported. Thus, studies on VOOH are urgently necessary, and discovery of its potential applications features a challenge for materials scientists. Synthesis and properties of VOOH were insufficiently studied in previous reports [33–39]. In the present study, we emphasized on synthesis and electrochemical properties of VOOH as SCs electrodes. Xie et al. synthesized VOOH with various structures; these materials comprise hollow dandelions [33], lepidocrocite VOOH from single-shelled to double-shelled hollow nanospheres [34], quadrangular nanorods [35] and hollow nanourchins [36]. These reports focused on Li-ion batteries [33], synthesis and shape evolution [34], electrical switch material [35] and conversion to VO_2 [36,37]. Just recently, Shao et al. [38] used the template-free hydrothermal route developed by Xie et al. [34] to obtain low-crystallinity VOOH hollow microspheres, which exhibited outstanding rate behavior and long life for Na-ion storage. Ruan et al. [39] reported synthesis of groove-like VOOH nanostructures by in-suit Kirkendall effect and oriented attachment process and their application to Li-ion batteries. However, to the best of our knowledge, no report discussed electrochemical properties of VOOH and its application to SCs electrodes for energy storage.

In this study, we successfully prepared hierarchical porous VOOH spheres with hollow core and mesoporous shell by a facile and template-free hydrothermal method. Investigations focused on electrochemical properties of VOOH hollow microspheres as electrode materials for SCs.

2. Materials and methods

2.1. Synthetic route

All analytical grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without any further purification. VOOH hollow sphere synthesis comprised two steps. In a typical synthesis, 0.234 g NH_4VO_3 and 45 mL distilled water were mixed in a 100 mL beaker and then strongly stirred. Subsequently, 1 mL of 1.0 mol L^{-1} HCl solution was dropped to the above solution. After the solution turned transparent yellow, 3 mL $N_2H_4 \cdot 3H_2O$ was added, and resulting mixture was stirred for 30 min at room temperature. In this process, transparent solution formed a suspension, with its color evolving from yellow to gray. Gray precipitation comprised $V(OH)_2NH_2$ solid spheres. This suspension was transferred to a Teflon-lined stainless steel autoclave, sealed, and maintained at 120 °C for 4 h. Products were filtered off after reactions, washed with H_2O and ethanol several times to remove any possible residues, and dried in vacuum.

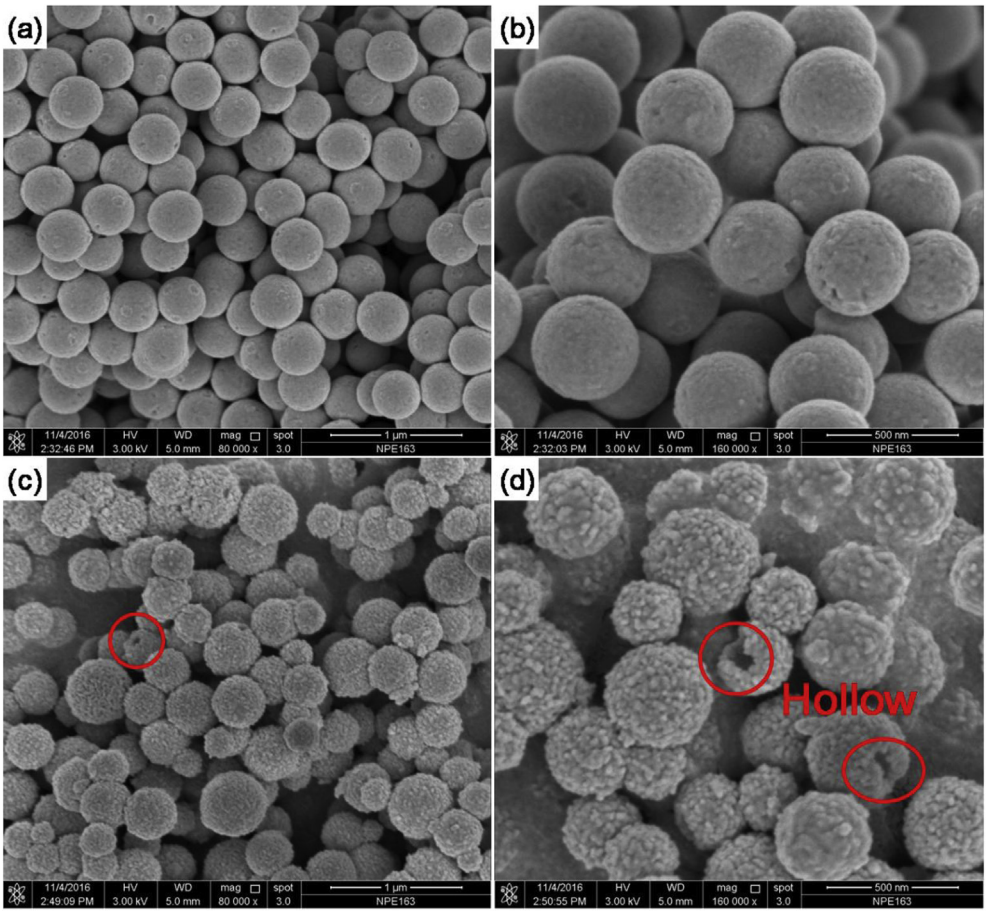

Fig. 1. FE-SEM images of the samples: (a and b) the precursor $V(OH)_2NH_2$ spheres; (c and d) VOOH hollow spheres.