Pseudocapacitive effect and Li$^+$ diffusion coefficient in three-dimensionally ordered macroporous vanadium oxide for energy storage

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ABSTRACT

In order to act as extrinsic pseudocapacitor materials, nanoscale vanadium oxides are required to simultaneously exhibit a capacitance-based high power density and an intercalation-based high energy density. We have fabricated a three-dimensionally ordered macroporous (3DOM) structure with a wall thickness of 14 nm that fulfills the above requirements. The 3DOM vanadium oxide film exhibits high rate performance with 355 F g^{-1} at 0.5 A g^{-1} and 125 F g^{-1} at 15 A g^{-1}. The enhanced pesudocapacitive effect and Li-ion diffusion coefficient based on the 3DOM nanostructure, also contributes to the high rate capability of vanadia, which can be confirmed by cyclic voltammetry and chronoamperometry.

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1. Introduction

Vanadium oxides have been widely studied as electrochemical energy storage materials for supercapacitors and Li-ion batteries [1–7] because of their ability to undergo redox intercalation [6,8–10] and the various available oxidation states of vanadium (V–II) [10]. However, their small Li-ion diffusion coefficient and electrical conductivity [11–15] cause the intercalation process to be slow, seriously limiting their energy storage performance [16]. Nanostructured vanadium oxides can provide shortened Li-ion diffusion distances and increased surface areas, leading to efficient Li-ion intercalation and, therefore, to high energy density [17]. Another significant phenomenon that occurs with nanostructuring is the pseudocapacitive effect, originating from the fast faradaic processes occurring at the materials' surface, which can generate high power density [6,18–20]. Nanostructuring is of special significance for vanadium oxides because they are extrinsic pseudocapacitor materials [1,3,5,6,21–25]. The pseudocapacitance of nanostructured vanadia depends strongly on their contact area with the electrolyte. For example, aerogels exhibit almost perfect capacitive cyclic voltammetry (CV) curves [5], while electrospun nanorods exhibit CV curves with sharp and well-separated redox peaks [2].

Among the various nanostructures available, the three-dimensionally ordered macroporous (3DOM) structure is an important

nanoarchitecture for Li-ion storage materials [26–30]. Its bicontinuous structure provides intercontinuous voids for good electrolyte penetration, and continuous thin walls for effective electron transport and Li-ion intercalation. Typically, 3DOM structures are prepared from face-centered-cubic colloidal crystals. The sphere packing factor of 74% in colloidal crystal produces 3DOM materials with a similar porosity and a high surface area [26]. Furthermore, employing small diameter spheres results in 3DOM materials with thin wall structures that may exhibit pseudocapacitive behavior [1,5,6,21–25].

Herein, we have prepared 3DOM vanadium oxide films by electrodeposition within colloidal crystals. The films exhibit a significantly enhanced rate capability. Besides the typical advantages nanostructuring provides, CV and chronoamperometry have revealed that the observed improved performance is also the result of pseudocapacitive effect and improved Li-ion diffusion coefficient.

2. Experimental

Polystyrene colloidal crystals with a sphere diameter of 165 or 480 nm on indium-doped tin oxide substrates were grown by a controlled vertical drying method [31,32]. Anodic deposition of vanadia within the colloidal crystals was performed at 2 V versus Ag/AgCl from a 1:1 mixture of deionized water and ethanol containing VOSO$_4$ (0.25 M). After removing the template with toluene and drying at 120 °C for 6 h, 3DOM vanadia films were obtained. The 3DOM vanadia samples obtained from colloidal crystals with sphere diameter values

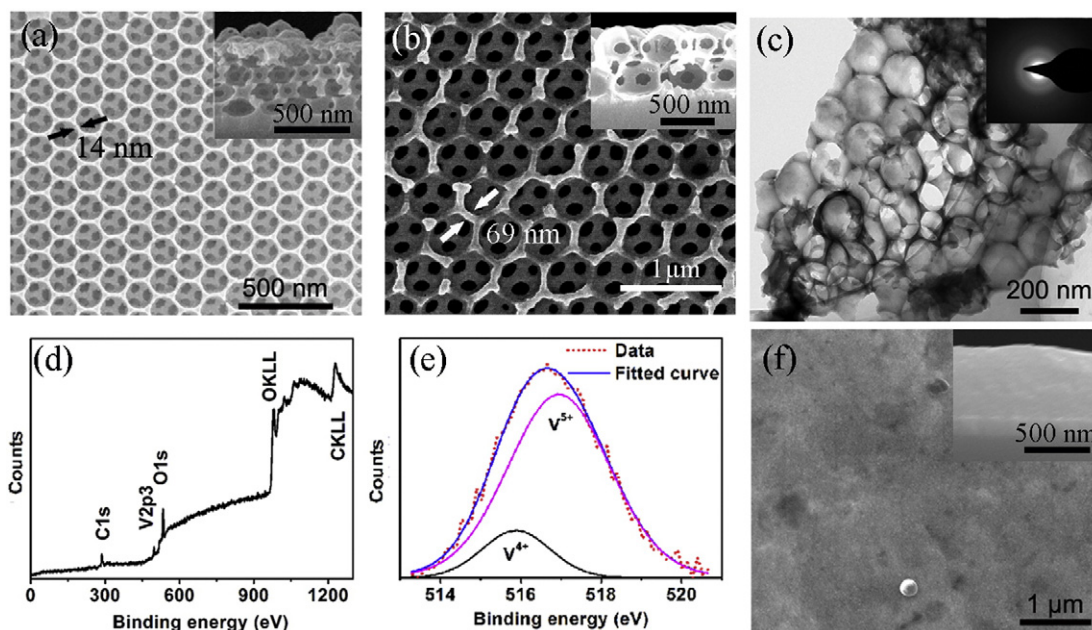* Corresponding author.
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Fig. 1. SEM images of (a) SD-165 nm and (b) SD-480 nm (side view in the inset). TEM image of (c) SD-165 nm (SAED pattern in the inset). (d) Wide-range XPS spectrum, and (e) V2p$_{3/2}$ core peak spectra of SD-165 nm. (f) SEM images of the compact vanadia film (side view in the inset).

of 165 and 480 nm were denoted as SD-165 nm and SD-480 nm, respectively. For comparison, template-free vanadia films were also prepared. The mass loading of SD-165 nm, SD-480 nm, and template-free film were ca. 0.42, 0.55, and 1.57 mg cm^{-2}, respectively.

Scanning electron microscopy (SEM) images were taken with a FEI Helios Nanolab 600i instrument. Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were recorded on a FEI Tecnai G2F30 instrument. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5700 ESCA system. The electrochemical properties were evaluated using a nitrogen-filled three-electrode cell with an electrochemical analyzer (CHI 660D) in 1M LiClO$_4$–propylene carbonate. A Ag/AgCl electrode was used as the reference electrode and a platinum plate was employed as the counter electrode. A Luggin capillary connected by a salt bridge was used to minimize iR-drop errors and to prevent contamination of the cell electrolyte.

3. Results and discussion

Due to the 3D ordered structure of the colloidal crystals, the SD-165 nm and SD-480 nm samples display honeycomb-like structures throughout their entire volume, with nanoscale walls with thickness of about 14 and 69 nm, respectively (Fig. 1a and b). Although powerful ultrasonication during the TEM-sample preparation partly destroyed its structure, the 3DOM nanostructure of SD-165 nm is still clearly observed (Fig. 1c). The presence of only amorphous rings in the SAED

pattern indicates that the as-deposited vanadia is amorphous. The XPS results of the 3DOM vanadia demonstrate its high purity and the presence of a mixture of V^{4+} (515.8 eV) and V^{5+} (516.9 eV) species (Fig. 1d and e) [33]. The template-free vanadia film exhibits a compact nature (Fig. 1f).

Fig. 2a, b, and c shows, respectively, the galvanostatic discharge/charge performance of SD-165 nm, SD-480 nm, and the compact films at 0.5, 1, 2, 5, 10, and 15 A g^{-1}. These films show featureless and symmetric discharge/charge curves, similar to the curves of other amorphous and nanocrystalline vanadia species [1,6,21–25], indicating that they are suitable materials for supercapacitors [6]. The 3DOM films exhibit a much higher specific capacitance (C_s) and rate capability than the compact film, and the 3DOM film with smaller pores (SD-165 nm) shows higher C_s values (Fig. 2d). At 0.5 A g^{-1}, the C_s value of SD-165 nm was calculated to be 355 F g^{-1}, higher than that of SD-480 nm and the compact film (240 and 187 F g^{-1}, respectively). When the current density reached a high value of 15 A g^{-1}, SD-165 nm still maintained a high C_s value of 125 F g^{-1}, whereas values of merely 74 and 22 F g^{-1} were obtained for SD-480 nm and the compact film, respectively. SD-165 nm exhibits superior charge storage performance compared to many other high-surface-area vanadia, such as nanosheets (314 F g^{-1} at 0.5 A g^{-1}), interconnected nanoporous networks (304 F g^{-1} at 0.1 A g^{-1}), and starfruit-like nanoparticles (216 F g^{-1} at 1 A g^{-1}) [25,34–39].

Besides the common advantages of nanostructures, such as large surface area and short Li-ion diffusion paths [40], the absence of plateau
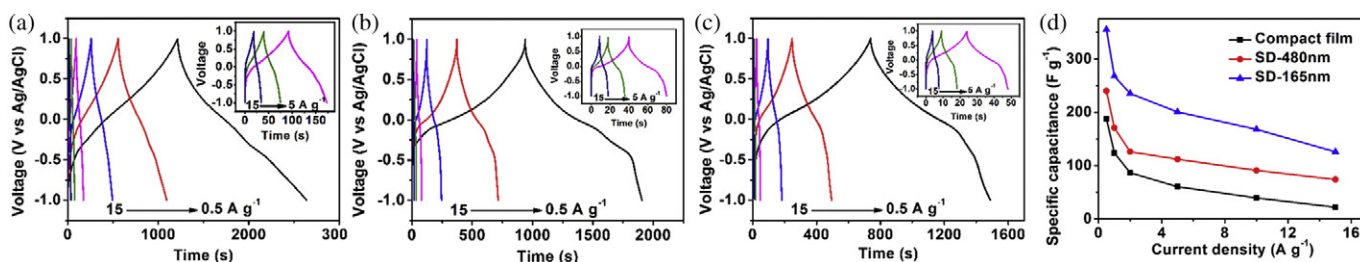

Fig. 2. Galvanostatic charge/discharge curves of (a) SD-165 nm, (b) SD-480 nm, (c) the compact film, and (d) variation of the specific capacitance with the current density for the three vanadia films.