Electrochimica Acta 222 (2016) 194–202

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Facile and controllable construction of vanadium pentoxide@conducting polymer core/shell nanostructures and their thickness-dependent synergistic energy storage properties

Zhongqiu Tong[a,b,1], Shikun Liu[c,1], Xingang Li[d], Yanbo Ding[e], Jiupeng Zhao[c], Yao Li[a,*]

[a] College of Materials and Metallurgical Engineering, Guizhou Institute of Technology, Guiyang, Guizhou 550003, China
[b] Center for Composite Materials and Structure, Harbin Institute of Technology, Harbin 150001, China
[c] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
[d] Guizhou Construction Science Research & Design Institute Limited Company of CSCEC, Guiyang, Guizhou 550006, China
[e] School of Renewable Energy, Shenyang Institute of Engineering, Shenyang, 110136, China

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form 18 September 2016
Accepted 19 September 2016
Available online 20 September 2016

Keywords:
Metal oxides
conducting polymer
core/shell
thickness-dependent synergy
energy storage

ABSTRACT

Thickness- and morphology-controlled vanadium pentoxide/polyaniline (V_2O_5/PANI) core/shell hybrid nanofibers are fabricated by electropolymerization of PANI on V_2O_5 nanofibers for enhanced energy storage. By simply adjusting the electrodeposition time, the thickness of the PANI shells can be controlled from 5 nm to 47 nm, and the morphology can be changed from coaxial to branched. The influence of shell thickness on the improved Li-ion storage performance of the V_2O_5/PANI core/shell nanofibers is systematically investigated, and this enhancement of charge capability and cycling stability strongly varies with the shell thickness. Thickness-dependent synergistic electron transport, Li-ion diffusion distances, and shell mechanical strength mechanisms are also proposed. These results provide meaningful references for developing new functional core/shell materials and high-performance energy storage composite materials.

1. Introduction

Inorganic/organic hybrid materials stand at the important intersection between two fields of materials science, as these hybrids are creative alternatives for use in both academic research and innovative industrial applications [1,2]. Typically, rational combinations of conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), and poly(3,4-ethylenedioxythiophene) (PEDOT) with selected metal oxides having tailored structures are fascinating due to their underlying synergistic effects or added functionalities [1–7]. In recent years, one special kind of nanostructured hybrid materials has inspired worldwide research enthusiasm, those being metal oxide@CP core/shell nanocomposites. These nanocomposites not only reveal the electric, magnetic and optic mechanisms of their components [8–16], but their improved and unusual features also allow for their development in various applications, such as solar cells, electromagnetic shielding, sensors, catalysts, lithium batteries, supercapacitors, and electrochromism [8–21]. However, construction of high-performance metal oxide@CP core/shell nanocomposites is often challenging. Chief among these is the need to facilely and controllably synthesize nanocomposite with pre-determined architectures for developing advanced functional materials [15,22–24], because the synergy in and properties of these core/shell hybrids are strongly dependent on their shell thickness and morphologies [1–7], while the commonly used method of chemical oxidative polymerization is a difficult approach for preparing controllable CP shell nanostructures [8–24].

Because of its unique advantages of high energy density [25–27], the ability of the vanadium ion to change its oxidation state (V–II) [28,29], and its inexpensive cost (~$12 per kg), vanadium pentoxide (V_2O_5) is widely studied as an electrode material for aqueous alkali-metal ion (Li^+, Na^+) batteries [30–35] or pseudo-capacitors [36–43]. Due to its poor electronic conductivity, high dissolution rate in liquid electrolytes, and repeated volume expansion/shrinking along with ion intercalation/removal processes, its high-rate and long-term cycling electrochemical performance is somewhat lacking [30,36,37]. Integrating the features of V_2O_5 and CPs into a core/shell nanostructure is

---

[*] Corresponding author at: College of Materials and Metallurgical Engineering, Guizhou Institute of Technology, Guiyang, Guizhou 550003, China.
E-mail address: yaoli@hit.eu.cn (Y. Li).
[1] These two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.electacta.2016.09.098
0013-4686/© 2016 Published by Elsevier Ltd.

believed to synergistically improve the electrochemical performance of V_2O_5 materials [30,32,37]. For example, Qu et al. recently demonstrated that coating with a PPy shell is an effective way to improve the rate capability and cycling stability of V_2O_5 nanoribbons for supercapacitors [37]. Wang et al. reported the enhanced cycle stability of polypyrrole-coated $Li_xV_2O_5$ for aqueous Li-ion batteries [32]. However, when taking into account the energy storage difference between the CP and V_2O_5 [30–46], and evaluating the effect of CP shells on V_2O_5 core strain relaxation of volume expansion during Li^+ intercalation, studying the influence of CP shell thickness on the electrochemical performance of V_2O_5@CP core/shell nanostructures is necessary for better understanding their internal synergy. Unfortunately, rare corresponding researches are reported in the past.

In this work, using a V_2O_5 nanofiber architecture as the representative template, we demonstrate a novel approach to prepare metal oxide@PANI core/shell hybrids with controlled shell thickness and morphology by facile electrochemical polymerization. The growth mechanism and morphology evolution of the PANI shells are discussed. Then, the effect of the PANI shell thickness on the electrochemical performance of the V_2O_5@PANI core/shell hybrids is systematically investigated. Due to the coating process controlling the intrinsic CP growth mechanism, other metal oxide morphologies (such as V_2O_5 nanoparticle architecture) and CPs (such as PPy and PEDOT) are used to successfully fabricate core/shell structures. The V_2O_5@PANI core/shell hybrids show significantly improved charge capacity, rate capability, and cycling stability compared to pristine V_2O_5 nanomaterials. Moreover, the electrochemical performance of the core/shell hybrid is dependent on the shell thickness. A moderate shell thickness of approximately 13 nm leads the hybrid to exhibit maximum charge capacity performance, while hybrids with thicker shells show better cycling stability. Thickness-dependent synergistic electron transport, Li-ion diffusion distance, and shell mechanical strength mechanisms are proposed to explain these behaviors.

2. Experimental

2.1. Fabrication of V_2O_5@CP core/shell hybrids

We have previous published the preparation of V_2O_5 nanofibers on fluorine-doped tin oxide (FTO) substrates [47–50]. In brief, polystyrene colloidal crystal templates were grown on FTO substrates using a controlled vertical drying method. Anodic deposition of vanadia into the colloidal crystal template was performed at a constant potential of 2 V versus Ag/AgCl from a 1:1 mixture of deionized water and ethanol containing 0.25 M $VOSO_4$. After deposition, samples were immersed in a 1:1 mixture (v:v) of *N, N*-dimethylformamide and toluene for 24 h to remove the polystyrene templates. Finally, the as-prepared samples were dried at 110 °C for 3 h and then annealed in air at 450 °C for 4 h to obtain V_2O_5 nanofibers. V_2O_5 nanoparticles were obtained after the as-prepared samples were annealed at 375 °C for 7 h.

The V_2O_5 nanostructures acted as backbones for the growth of conducting polymer shells. Three typical conducting polymers (PANI, PPy, and PEDOT) were used, and the controllable growth of PANI shells was investigated in detail. The electrolyte for the electropolymerization of PANI was an aqueous solution containing 0.015 M aniline and 0.02 M camphorsulfonic acid. A three-electrode system was used for coating PANI onto the V_2O_5 nanofibers by applying a constant anodic current density of 1.5 mA cm^{-2}, using Ag/AgCl as the reference electrode and a Pt foil as the counter electrode. After being rinsed with deionized water, the products were dried at 60 °C for 24 h under vacuum. A series of timed electropolymerization (30 s, 60 s, 120 s, 180 s, and 240 s) was performed to obtain different degrees of coating, and the corresponding nanocomposites were labeled as V_2O_5/PANI30s, V_2O_5/PANI60s, V_2O_5/PANI120s, V_2O_5/PANI180s, and V_2O_5/PANI240s. An electropolymerization time of 60 s was used for coating PANI onto the V_2O_5 nanoparticles. Pristine PANI on FTO substrates was also prepared at 1.5 mA cm^{-2} for 240 s.

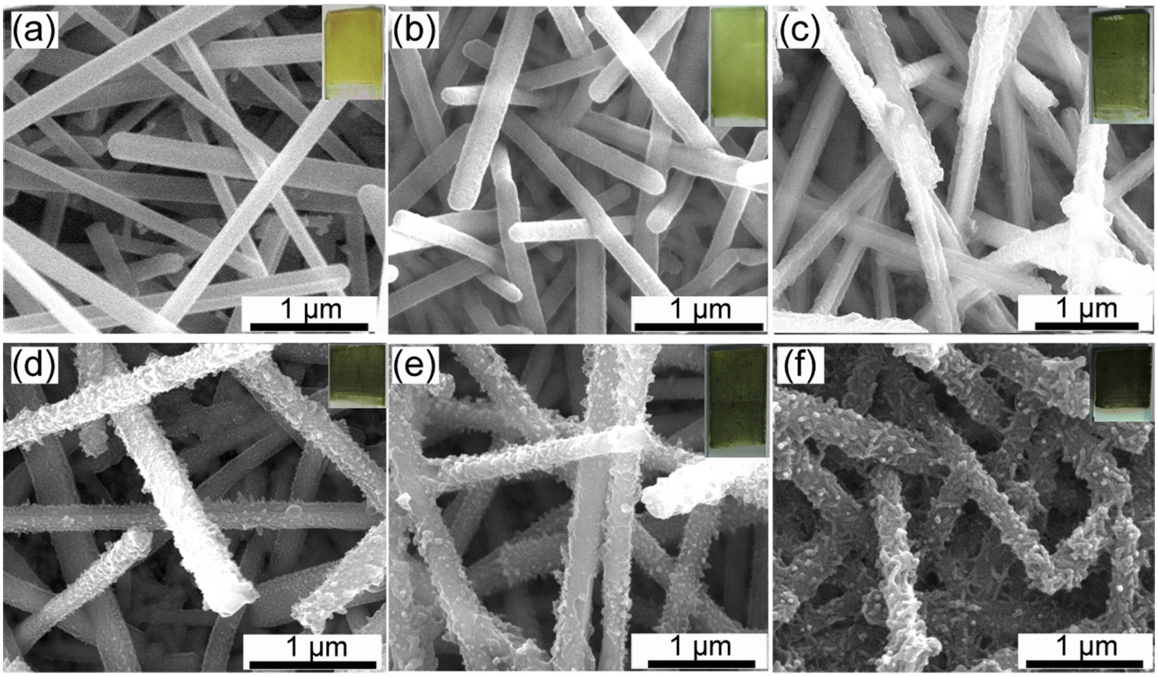

Fig. 1. (a) SEM images of the pristine V_2O_5 nanofibers. (b–f) SEM images of V_2O_5/PANI nanofiber core/shell hybrids under different electropolymerization times. (b) V_2O_5/PANI30s. (c) V_2O_5/PANI60s. (d) V_2O_5/PANI120s. (e) V_2O_5/PANI180s. (f) V_2O_5/PANI240s. The inset figures are photos of the samples.