



Interconnected three-dimensionally hierarchical heterostructures with homogeneously-dispersed V_2O_5 nanocrystals and carbon for high performance supercapacitor electrodes



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ABSTRACT

In this article, a simple “liquid phase impregnation template” strategy has been developed to synthesize hierarchically porous V_2O_5/C (HPVC) nanocomposites by using commercial V_2O_5 and phenol-formaldehyde (PF) resol as precursors and polystyrene opal microspheres as template. The amount of vanadium sol in the vanadium-PF precursor has a significant effect on the morphology and microstructure of the resulting HPVC nanocomposites. Due to the intact interconnected hierarchical network framework and the homogeneous dispersion of constitutive V_2O_5 nanocrystals and carbon phases, the optimal sample HPVC2 with higher surface area ($645 \text{ m}^2 \text{ g}^{-1}$) and mesopore surface area ($394 \text{ m}^2 \text{ g}^{-1}$) and an appropriate content of V_2O_5 (38.7 wt.%), is found to be the most efficient one as supercapacitor electrode with a high specific capacitance up to 492.1 F g^{-1} at a scan rate of 5 mV s^{-1} in the three-electrode system. When used as symmetric electrode, the HPVC2//HPVC2 supercapacitor exhibits a high energy density up to 87.6 Wh kg^{-1} at a power density of 497 W kg^{-1} , which greatly surpasses those of pure single-component counterparts and others reported V_2O_5/C composites. The present work conceptually provides a facile way for integrating transition metal oxide with carbon in hierarchically porous nanostructure to synthesize hybrid electrode materials for advanced energy storage/conversion devices.

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1. Introduction

As one of alternative energy/power sources for fossil fuels, supercapacitors have being the hotspot subject for energy storage devices over the past decades. In terms of charge storage mechanism, supercapacitors are generally assigned into two categories: electrical double-layer capacitors (EDLCs) with carbon materials and pseudocapacitors with transition metal oxides (TMOs) or conducting polymers [1]. Among the discovered pseudocapacitive TMOs, vanadium pentoxide (V_2O_5) has recently triggered increasing interests for supercapacitor electrode because of its low cost, abundance, high theoretical specific capacity (2120 F g^{-1}), layered structure for efficient ion diffusion, and variable oxidation states ($V^{2+} \sim V^{5+}$) with wide potential window for excellent reversible redox behavior [2,3]. Unfortunately, the relatively poor electrical conductivity, low specific surface area, structural instability, and high vanadium ions dissolution into

aqueous electrolyte often hamper the fully capacitive release of V_2O_5 . One typical solution is to synthesize special V_2O_5 nano-morphology or crystal structure, such as, hollow spheres [4], thin films [5], nanoribbons [6], nanosheets [7,8], nanoflowers, nanoballs, nanowires, nanorods [9,10], nanoporous network [11], nanofibers [12], and nanobelts, nanoparticles, microspheres [13], etc. However, the disconnected spaces between the nanostructures and structural fractures of V_2O_5 crystals would seriously limit the intrinsic electronic conductivity and thus deteriorate the cycle durability during the charging/discharging process. The other feasible strategy is to integrate varied V_2O_5 nanostructures with electrically conductive porous carbon materials to form guest-host V_2O_5/C composites. It is well recognized that the introduction of pseudocapacitive TMO into carbon material can significantly increase the whole electronic conductivity of the resulting hybrid. Porous carbon material with high specific surface area can act as scaffolds to support, stabilize, and disperse the pseudocapacitive TMO, and thus yielding more sites for charge storage. Positive synergic action of TMO and carbon would remarkably enhance the electrical, electrochemical, and mechanical performances of the resulting composite electrode. In addition, the EDLCs formed in the

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nanopores of carbon material contribute to the overall energy storage of composite [14–16]. So far, various forms of V_2O_5/C composites, including V_2O_5 /graphene [17–22], V_2O_5 /carbon nanotubes ($V_2O_5/CNTs$) [23–27], V_2O_5 /mesoporous carbon [28], V_2O_5 /carbon black [29], and $V_2O_5@C$ [30], have been successfully fabricated by different strategies. For example, Xu et al. report the synthesis of graphene/ V_2O_5 xerogel nanocomposites by hydrothermal method with a specific capacitance of 195.4 F/g in a 0.5 M K_2SO_4 aqueous solution [17]. Wu et al. fabricate a V_2O_5 /graphene hybrid aerogel through a chemical growth method and achieve a specific capacitance of 486 F g^{-1} with an energy density of 68 Wh kg^{-1} in a 1 M Na_2SO_4 aqueous solution [19]. Also, they apply mixed growth and self-assembly strategies to prepare V_2O_5 /MWCNT hybrid aerogels possessing a specific capacitance of 625 F g^{-1} and an energy density of 86.8 Wh kg^{-1} in the same electrolyte [25]. With a solvothermal treatment-annealing process, Li et al. prepare V_2O_5 /reduced graphene oxide nanocomposites, which exhibit a specific capacitance of 537 F g^{-1} and an energy density of 74.58 Wh kg^{-1} in a 8 M LiCl aqueous solution [20]. Kim et al. utilize polyacrylonitrile/ V_2O_5 in N,N-dimethylformamide to prepare a V_2O_5 /carbon nanofiber composite by an electrospinning method. The composite delivers a specific capacitance of 150.0 F g^{-1} with an energy density of 18.8 Wh kg^{-1} in a 6 M KOH aqueous solution [23]. Yu et al. synthesize V_2O_5 /CMK-3 composites by an ultrasonic method with a specific capacitance of 124 F/g in a 1 M KNO_3 aqueous solution [28]. Peng et al. prepare mesoporous V_2O_5 /Ketjin black nanocomposites via dip-dry of V_2O_5 sol onto pretreated-carbon. As a symmetric supercapacitor, the nanocomposite provides a maximum energy density of 56.83 Wh kg^{-1} with LiCl/PVA gel as the electrolyte [29]. Although some capacitive enhancements are achieved, there are open questions for these composites to be adequately addressed: (i) random distribution of constitutive V_2O_5 and carbon phases in composite, (ii) densely-packed V_2O_5 layers over carbon scaffold with limited accessible electrochemically active surface area, (iii) inappropriate pore size distribution with decreasing pore accessibility for ion diffusion. Therefore, it is still an urgent challenge to develop a scalable strategy for fabricating a new V_2O_5/C composite in which V_2O_5 may be more suitably integrated with carbon and efficiently utilized.

Recently, hierarchically porous (HP) materials have demonstrated impressive application prospects for electrochemical energy storage/conversion devices [31,32]. Generally, a multimodal HP material possesses the combined micropore, mesopore throughout a three-dimensionally interconnected macroporous monolithic framework. In comparison with unimodal porous materials, HP materials have shown superior electrochemical performance owing to the combining benefits of each pore size regime. The continuous macroporous network works as a reservoir storing and allowing electrolytes flow with low resistance, reducing diffusion time, and minimizing electrolytes diffusion distance from each pore. At the same time, the mesopores and micropores offer a larger accessible interior surface area for more ion transportation and charge accommodation [33–35]. On account of these merits of HP materials, it is reasonable to envisage that a hierarchically porous V_2O_5/C (HPVC) composite with interconnected hierarchical network framework and well-dispersed V_2O_5 nanocrystals would be a promising candidate for electrode material in supercapacitor application.

With the above elaboration as motivation, herein, we develop a simple and efficient approach to synthesize a novel HPVC nanocomposite by means of a “liquid phase impregnation template” strategy with a multicomponent (vanadium sol, phenol-formaldehyde (PF) resol, and Pluronic F127) alcohol solution as precursors. The structural characterization results show that appropriate weight rate of vanadium sol to PF resol is the key factor for constructing intact and channel-smooth HP

nanostructure. When used as supercapacitor electrode, the optimized HPVC2 with integrated three-dimensional interconnected macroporous framework, rich porosities, and an appropriate content of V_2O_5 (38.7 wt.%), exhibits low equivalent resistance, high specific capacitance, and excellent rate-capability in a three-electrode system. To simulate the real application of the nanocomposite, a symmetric two-electrode supercapacitor is also assembled and tested. The results demonstrate that the HPVC2//HPVC2 supercapacitor can deliver a high energy density up to 87.6 Wh kg^{-1} , which much precedes those of the reported V_2O_5/C composites.

2. Experimental

2.1. Synthesis of HPVC nanocomposite

The polystyrene (PS) colloidal crystal templates were synthesized as our reported work with an average diameter of ~ 320 nm (Fig. S1) [36]. As carbon source, the PF resol was prepared as described previously with a concentration of 50 wt.% in ethanol (PF/E) [37]. For a typical synthesis of vanadium precursor, 0.25 g of commercial V_2O_5 powder was firstly dispersed in 30 ml deionized water. Then, the suspension was stirred and heated to 60 °C to form a pale yellow solution. Afterwards, 5 mL of 30 wt.% H_2O_2 was added dropwise to the pale yellow solution and stirred for another 1 h, during which the temperature of the mixture was maintained at ~ 60 °C. After undergoing the exothermic reaction, the resulting solution became orange vanadium sol (VS), indicating the formation of diperoxovanadate anion $[VO(O_2)_2(OH_2)]^-$ [38]. Lastly, 1.5 g of PF/E and 0.2 g of Pluronic F127 were added to the cooled VS, and the mixture was further stirred overnight to obtain a homogeneous solution. By varying the amounts of VS, the vanadium-carbon precursors (VCPs) with different vanadium and carbon contents were prepared and denoted as VCP1, VCP2, and VCP3, respectively. The detailed preparation conditions and the corresponding sample codes are summarized in Table 1.

The HPVC nanocomposite was synthesized by soaking the PS colloidal crystal templates with the as-prepared VCP. After full infiltration, the templates were dried and thermally polymerized in vacuum at 100 °C for 24 h. Next, the obtained pieces were pyrolyzed under N_2 flowing at 400 °C for 2 h to remove the PS templates and then at 600 °C for another 6 h to pyrolyze the PF resol with a heating rate of 1 °C min^{-1} . In order to prevent the incomplete filling of the void spaces between the PS templates, the infiltration-drying steps were repeated at least for three times before N_2 -pyrolysis. This is an essential step to attain a monolithic HPVC nanocomposite and achieve uniform nanoscale V_2O_5 dispersion throughout the carbon nanoarchitecture. The final products were designated as HPVC1, HPVC2, and HPVC3, respectively. For comparison, the hierarchically porous V_2O_5 (HPV) and hierarchically porous carbon (HPC) were also prepared directly by employing the (VS +F127)/E and (PF+F127)/E as precursors following the aforementioned infiltration-drying-pyrolysis steps. The thermogravimetric analysis results showed that the weight loss of HPVC1, HPVC2, and HPVC3 were 82.4 wt%,

Table 1
Synthesis condition of VCP.

Sample	Precursor	VS (g)	PF/E (g)	VS/PF (g g^{-1})	F127 (g)	V_2O_5 (wt.%)
HPVC1	VCP1	1.0	1.5	0.67	0.2	17.6
HPVC2	VCP2	2.5	1.5	1.67	0.2	38.7
HPVC3	VCP3	4.0	1.5	2.67	0.2	52.1

* The VS was derived from 0.25 g V_2O_5 powder, 30 ml deionized water, and 5 mL of 30 wt.% H_2O_2 .

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