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Ultra-small vanadium nitride quantum dots embedded in porous carbon as high performance electrode materials for capacitive energy storage

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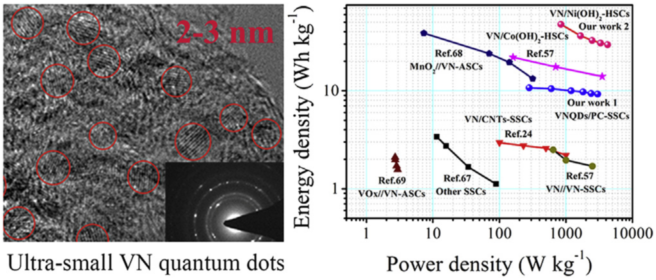
HIGHLIGHTS

- Ultra-small vanadium nitride quantum dots together with porous carbon were fabricated.
- Precursors were mixed in liquid-phase and thermal treated in nitrogen atmosphere.
- The hybrid material showed high specific capacitance and comparable energy density.

GRAPHICAL ABSTRACT



Ultra-small VN quantum dots

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ABSTRACT

Ultra-small vanadium nitride quantum dots embedded in porous carbon (VNQDs/PC) were fabricated by a thermal treatment process of $NH_4VO_3/C_3H_6N_6$ under nitrogen atmosphere. The specific capacitance of VNQDs/PC was 1008 mF cm^{-2} at a current density of 0.004 A cm^{-2}, whereas the VN/carbon hybrid material obtained by a solid-state blending of NH_4VO_3 and $C_3H_6N_6$ just exhibited a capacitance of 432 mF cm^{-2} at the same current density. By mediating the ratio of NH_4VO_3 and $C_3H_6N_6$, a maximum specific capacitance of 1124 mF cm^{-2} was achieved at a current density of 0.002 A cm^{-2} in aqueous 6 mol/L KOH electrolyte with the potential range from 0 to −1.15 V when it reached 1: 7 (wt./wt.). Additionally, symmetrical supercapacitor fabricated with synthesized VNQDs/PC presented a high specific capacitance of 215 mF cm^{-2} at 0.002 A cm^{-2} based on the entire cell, and exhibited a high capacitance retention of 86.6% with current density increased to 5 A g^{-1}. The VNQDs/PC negative electrodes were combined with $Ni(OH)_2$ positive electrodes for the fabrication of hybrid supercapacitors. Remarkably, at a power density of 828.7 W kg^{-1}, the device delivered an ultrahigh energy density of 47.2 Wh kg^{-1}.

1. Introduction

The growing serious environment pollution and energy crisis is forcing people to set a large and growing amount of sights on the development of clean renewable energy, such as wind power, solar power and even hydro-energy. However, the intermittent characteristic of such renewable energy cannot make them become continuously available on demand for powering the electrical grid, which prompts people to develop reliable and environmentally friendly approaches for energy conversion and storage [1–7]. Supercapacitors, also called electrochemical capacitors (ECs), have attracted significant attention as energy storage devices for

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applications such as starting automotives and the regenerating of brake energy to meet the requirements of long cycle life, fast charge and discharge and high power density [8,9]. As we all know, ECs can be divided into two distinct families: electric double-layer capacitors (EDLCs) and pseudocapacitors. The principal one, EDLCs mainly use porous carbon electrode materials with high accessible surface area and store charge in a thin double-layer at the interface between the electrolyte and the electrode [10–12]. However, EDLCs generally possesses high power capabilities but a low energy density based on the mechanism of the fast sorption and desorption of ions [13]. The second family of ECs, called as pseudocapacitors, is mainly based on fast and reversible surface redox (faradic) reactions that occur on electrode material surfaces or near surface [12]. Up to now, such pesdocapacitive behavior has been widely investigated for transition metal oxides (nitrides or sulfides) and conducting polymers in aqueous electrolytes [14–20].

Among these pesdocapacitive materials, transition metal nitrides [21–27], such as VN [23,27,28], Mo_xN [29,30], TiN [31,32], and WN [33], have attracted considerable attention for the applications as promising materials for electrodes of ECs owing to its excellent mechanical strength, high electronic conductivity, high specific capacitance [34]. Notably, according to the recent reports, a growing consensus and popular strategy for the development of pesdocapacitive materials is to design and synthesize nanoscale materials; and the increasing evidence manifests that electrochemical feature tend to be more capacitor-like when the crystallite is less than 20 nm [12,35,36]. Consequently, many works have been devoted to prepare nitrides, especially VN with different nanostructures [37–42]. Despite all these achievements, the simple and high efficient as well as scalable application of VN as SCs still limited due to costly, time-consuming and complex methods, for examples, chemical vapor deposition, laser atomic layer deposition, D.C. reactive magnetron sputtering, and electrospinning.

Temperature programming is a simple and practical method for preparation of nanoscale VN. Glushenkov and Zhou et al. synthesized nanocrystallined VN by using temperature programming, which showed a specific capacitance of 161 F g^{-1} and 186 F g^{-1} [27,43]. However, the relatively low capacitance was a result of the relatively larger particle size and lower surface area due to aggregation and ineffective contact between VN nanoparticles. To resolve this problem, more recently, Shu and his co-workers reported a capacitance of 413 F g^{-1} at 1 A g^{-1} and the retention about 88% of its maximal capacitance at 4 A g^{-1} [42,44,45]. In the obtained materials, irregular VN nanoparticles in the range of 10–30 nm were separated by the carbon remains and without obvious agglomeration. Unfortunately, the size of VN nanoparticles is still large; and the manner of grounding V_2O_5 xerogel into fine particles and blending with melamine directly can lead to undermixing between V_2O_5 xerogel and melamine, causing a certain degree of wasting for nitrogen reagent and impurity of phase structure of the products. Another significant point to be considered is that although VN possesses high capacitance, their real contribution to the total charge storage depends strongly on the utilization of the active materials, which could be realized by dispersing nanosized VN particles onto high surface porous carbon substrates [46]. In such case, to improve the performance, it is often necessary to introduce nitrides nanoparticles in the high surface carbon matrix, which can effectively enhance the surface area as well as utilization of nitrides simultaneously, contributing to further enhancement for their application capability in capacitive energy storage. Unfortunately, to date, the materials of VN/C hybrid materials in which nanosized (the diameter even below 10 nm) VN particles doped in the carbon substrates uniformly was rarely reported.

Herein, we demonstrated a simple strategy for the straightforward preparation of the VNQDs/PC, where ultra-small quantum dots VN uniformly doped in the porous carbon substrates, via liquid-phase mixing of NH_4VO_3 and $C_3H_6N_6$ followed by a nitridation process in a furnace at 800 °C under a N_2 atmosphere. The facile strategy and unique doped structure accomplishes a number of significant goals for the VNQDs/PC, which include decrease of the waste of nitrogen reagent, avoidance of the agglomeration by the released ammonia, nitrogen, and other cyanide from melamine during pyrolysis, and highly enhancing the utilization of VN because of quantum size effect and corresponding high surface area. Notably, as the transformation from NH_4VO_3 to VN was gradual changing because of the various oxidation states (II ~ V) of vanadium, the self-nitriding effect of NH_4VO_3 can be realized through the ammonia released from NH_4VO_3 continued to react with generated vanadate intermediates during pyrolysis. Self-nitriding effect of NH_4VO_3 can not only effectively improve utilization of raw materials, but also contribute to form the unique structure of VNQDs/PC hybrid materials. Benefiting from the fascinating superiority originated from structure, the VNQDs/PC exhibited outstanding electrochemical performances with high capacitance, excellent electrochemical reversibility and good rate capability as electrode for ECs. Furthermore, such unique structure will not only serve as electrodes for ECs, but also be a promising material for the application of lithium ion batteries, catalysts and other fields in the future.

2. Experimental

2.1. Materials

Analytical grade ammonium metavanadate (NH_4VO_3) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. Dimethyl sulfoxide (DMSO) was purchased from Chengdu Kelong Inc. Melamine ($C_3H_6N_6$) and other reagents were of A.R. grade and received from Shanghai Mei Xing Chemical Reagent Factory, P.R. China. All chemicals (analytical grade) were used as received unless otherwise stated.

2.2. Synthesis of VN/C hybrid materials

Typically, 3.5 g $C_3H_6N_6$ was first dispersed in 45 mL mixed solvents of DMSO (15 mL) and H_2O (30 mL) by vigorous stirring at room temperature to obtain a homogeneous dispersion liquid (without bulky grain). Then, by changing the $[NH_4VO_3]/[C_3H_6N_6]$ mass ratio of 1: 5, 1: 7, 1: 9 and 1: 11, a certain amount of NH_4VO_3 was added slowly to the $C_3H_6N_6$ dispersion liquid and solution was stirred for another 1 h until fully mixed. After centrifugal separation, the blend was dried under vacuum at 60 °C overnight. The product was heated up to 800 °C in a tube furnace under N_2 atmosphere at 5 °C min^{-1} and kept at 800 °C for 2 h. Then, after the sample was cooled naturally, the VNQDs/PC hybrid materials were achieved.

2.3. Structure characterization

The microstructure of the as-prepared materials was characterized by FTIR method with a FTIR Nexus 670 (Nicolet American) instrument and transmission electron microscope (TEM, JEOL, JEM-2010, Japan). X-ray photoelectron spectroscope (XPS, physical Electronics UK) and X-ray diffraction (XRD, Rigaku D/MAX 2400 diffractometer (Japan) with CuKα radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 60 mA) patterns were used for the analysis of phase constitution. Further, energy dispersive X-ray (EDX) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to clarify the amount of each ingredient in the sample. Pore structure measurement was conducted by Nitrogen adsorption and desorption experiments at 77 K (Micromeritics, ASAP 2010 M, USA). The surface morphology of the samples were tested by field emission scanning electron microscope (SEM, JEOL, JSM-6700F, Japan).