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COMMUNICATION

Polypyrrole-coated hierarchical porous composites nanoarchitectures for advanced solid-state flexible hybrid devices

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Abstract
Design and fabrication of advanced functional materials is essential but still a challenge for current energy storage devices. Herein, polypyrrole coated highly porous vanadium oxide (V_2O_5@Ppy) nanorod and nanoplate arrays with large mass loadings, have been successfully constructed on carbon felt (CF) via a facile solvothermal reaction followed by in-situ polymerization technique. Interestingly, the structure of the V_2O_5 thin films can be simply tuned from porous nanoplates to nanorods with controlled calcination time. In addition, MnO_2 nanowires with Ppy coating were also grown on the CF substrates to form MnO_2@Ppy/CF electrode through the similar method. As integrate electrodes for energy storage devices, V_2O_5@Ppy/CF nanorods demonstrate more superior electrochemical properties compared to V_2O_5@Ppy/CF nanoplates. By virtue of their intriguing structural features and uniformly Ppy coating, a solid-state flexible hybrid device (SFHD) based on V_2O_5@Ppy/CF and MnO_2@Ppy/CF as the negative and positive electrode, respectively, manifests outstanding cycling stability (approximately 89% retention even after 20,000 cycles), excellent mechanical flexibility, and

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remarkable energy density (28.6 W h kg^{-1} at power density of around 200 W kg^{-1}), which makes it hold great potential to be unexceptionably flexible devices for portable and wearable electronics.

Introduction

With the rapid progress of nanomaterials and nanotechnology, wearable and protable electronics are becoming indispensable in the increasingly mobile society. Great efforts have been made to fabricate flexible devices in various fields, such as roll-up displays, artificial electronic skin, and so on. With the aim to create entirely flexible electronics, all of these devices need lightweight, flexible, and high-performance energy storage unites. In today's practical applications, electrochemical capacitors (ECs) [1,2] and batteries, as two major energy storage technologies, represent two extremes of the design space. To bridge the gap between ECs and batteries, hybrid devices (HDs), also known as hybrid combinations, provide a promising path [3,4]. Typically, such devices combine the advantages of both ECs and batteries by using a capacitor-type electrode to ensure high power density and battery-type electrode to enable high energy density. More importantly, compared to conventional ECs, HDs generally possess a wider working potential window, thereby further guaranteeing the energy storage capability. Consequently, a new avenue has been opened by HDs for the emerging high energy and power applications [5,6]. However, their role in flexible and smart portable devices barely satisfies the demands in mechanical flexibility and miniaturized in dimentions. Therefore, researchers are striving to explore advanced solid-state flexible HDs with both high power and energy densities, as well as excellent flexibility [7-9].

So far, great attentions on more safe and flexible HDs are devoted to build advanced integrate flexible hybrid electrodes with high energy and power densities for commercial implementation [10-12]. Since the hybrid electrodes largely determine the electrochemical performance of HDs, there has been extensive interest in the proper selection and hybridization of nanoarchitectures (phase composition, morphologies, size and uniformity) with precisely controlled structures [13-16]. It is well-accepted that the battery-type electrodes, usually metal oxides, are still limited by their intrinsic poor conductivity and suffer pulverization especially after long-term cycling. To address these issues, the most popular approach is to fabricate hybrid electrodes, which commonly combine metal oxides electrodes with various conductive polymer (polyaniline, Ppy) or carbon materials (CNT, graphene) [12,15,17]. Accordingly, it has been demonstrated that both the conductivity and capacitance of the hybrid configurations can be largely enhanced by coating a thin layer of conductive polymer on the surface of electrode materials, which not only possesses large capacitance and high electrical conductivity, but also can be easily polymerized [18-20]. Additionally, to meet the need for flexibile HDs, it should be taken into account about the flexibility of current collector. An advent of new concept is to disperse functional nanostructures with controlled morphologies and sizes on carbon frameworks or scaffolds such as graphene foam, carbon nanotubes coated textile, carbon cloth, to construct flexible integrate hybrid electrode [19,21,22]. These carbon frameworks act as backbones to faciliate the transportation of ions and electrons, thus leading to improved rate capability [23-25]. Baed on the above-mentioned aspects, a solid-state flexible HD, which consists of rationally designed hybrid nanoarchitectures, represents a new opportunity to achieve high power and energy applications.

Despite the significant development in functional nanomaterials, transition metal oxides (TMOs) still govern the landscape of active materials for electrochemical devices. In particular, vanadium oxides (V_2O_5) and manganese dioxide (MnO_2) exhibit significant predominance such as natural abundance, high theoretical capacitance, multiple oxidation states, and ease of synthesis [18,26-30]. In this regard, it is anticipated that introducing V_2O_5 as negative electrode and MnO_2 as positive electrode in a solid-state flexible HDs will becoming a promising energy storage technology. In the present study, we make the attempt to employ both of those possible optimization pathways (Ppy coated nanostructures on carbon felt) to enhance the performance of solid-state flexible HDs. Herein, Ppy coated hierarchical porous composites nanoarchitectures (V_2O_5@Ppy and MnO_2@Ppy) have been successfully built on carbon felt (CF) by a facile wet-chemical method followed by an in-situ polymerization Ppy on the surface of nanoarchitectures. Specifically, CF serves as the flexible current collector, mainly owing to its good mechanical flexibility, excellent conductivity, and great durability to bear shape deformation [31,32]. Moreover, the uniformly polymerized Ppy layer could not only effectively prohibit active mateirals (V_2O_5 and MnO_2) from corrosion in liquid electrolyte, but also provide an additional pathway for electron and ions transfer. Furthermore, it is found that the structure of the V_2O_5 thin films can be simply tuned from porous nanoplates to nanorods with controlled calcination time. Consequently, as integrate electrodes for energy storage devices, V_2O_5@Ppy/CF nanorods manifest more superior electrochemical properties compared to V_2O_5@Ppy/CF nanoplates. In addition, benefiting from the unique structural features, the as-prepared solid-state flexible HDs, which is based on V_2O_5@Ppy/CF anode and MnO_2@Ppy/CF cathode, exhibits outstanding cycling stability (approximately 89% retention even after 20,000 cycles), excellent mechanical flexibility, and remarkable energy density (28.6 W h kg^{-1} at power density of around 200 W kg^{-1}), which makes it hold great potential to be unexceptionably flexible devices for portable and wearable electronics.