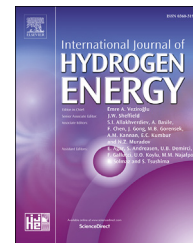




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# One step electrodeposition of V<sub>2</sub>O<sub>5</sub>/polypyrrole/graphene oxide ternary nanocomposite for preparation of a high performance supercapacitor

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## ABSTRACT

A new ternary nanocomposite based on graphene oxide (GO), polypyrrole (PPy) and vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) is obtained via one-step electrochemical deposition process. Electrochemical deposition of V<sub>2</sub>O<sub>5</sub>, PPy and GO on a stainless steel (SS) substrate is conducted from an aqueous solution containing vanadyl acetate, pyrrole and GO to get V<sub>2</sub>O<sub>5</sub>/PPy/GO nanocomposite. Characterization of the electrode material is carried out by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM). The electrochemical performance of the as-prepared nanocomposite is evaluated by different electrochemical methods including cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. Remarkably, V<sub>2</sub>O<sub>5</sub>/PPy/GO nanocomposite shows a specific capacitance of 750 F g<sup>-1</sup> at a current density of 5 A g<sup>-1</sup>, which is far better than PPy (59.5 F g<sup>-1</sup>), V<sub>2</sub>O<sub>5</sub>/PPy (81.5 F g<sup>-1</sup>) and PPy/GO (344.5 F g<sup>-1</sup>). Furthermore, V<sub>2</sub>O<sub>5</sub>/PPy/GO maintains 83% of its initial value after 3000 cycles, which demonstrates good electrochemical stability of the electrode during repeated cycling. These results demonstrate that the combination of electrical double layer capacitance of GO and pseudocapacitive behavior of the PPy and V<sub>2</sub>O<sub>5</sub> can effectively increase the specific capacitance and cycling stability of the prepared electrode. Also, a symmetric supercapacitor device assembled by V<sub>2</sub>O<sub>5</sub>/PPy/GO nanocomposite yielded a maximum energy density of 27.6 W h kg<sup>-1</sup> at a power density of 3600 W kg<sup>-1</sup>, and a maximum power density of 13680 W kg<sup>-1</sup> at an energy density of 22.8 W h kg<sup>-1</sup>.

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## Introduction

In the past decade, with the rapid increase of human population growth, energy depletion (such as fossil fuels) and environmental pollution, it is necessary to find eco-friendly, low

cost and high-performance energy storage devices. Supercapacitors or electrochemical capacitors show practical application potential due to their desirable characteristics of long life span, fast delivery rate and high power density [1–4]. Supercapacitors store electrical energy by two mechanisms: pseudocapacitance and electric double layer capacitance (EDLC).

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In EDLCs, charges are accumulated at the electrode-electrolyte interface. Generally, EDLCs are made of carbon-based materials such as activated carbon, carbon nanotube and graphene. Graphene, as a two-dimensional carbon material, is expected as a good candidate for supercapacitors, because of its several features such as large surface area, superior electrical conductivity and good electrochemical stability. However, graphene exhibits lower capacitive performance than the predicted value because of agglomeration of graphene sheets during its preparation, which greatly reduces the effective surface area of graphene sheets and ion diffusion rate [5–7]. It has been found that combination of carbon materials with pseudocapacitive materials (such as conducting polymers or transition metal oxides) can improve the capacitance of carbon-based supercapacitors [8–11].

Pseudocapacitors can store charges by fast redox reactions that take place at the interface of the electrode material and the electrolyte. Therefore, pseudocapacitors prepared using electroactive materials exhibit higher specific capacitance than conventional EDLCs. Pseudocapacitors are usually constructed from conducting polymers and transition metal oxides as the active electrode materials [12].

Many efforts have been devoted to studying conducting polymer-based supercapacitors, due to their good capacitive characteristics and low material cost [13]. Among various conducting polymers, such as polyaniline (PANI) [14], polyethylenedioxythiophene (PEDOT) [15] and polypyrrole (PPy) [16], PPy is a promising candidate for supercapacitor applications because of its high electrical conductivity, high specific capacitance, good processability, ease of preparation and low cost of its monomer [17].

However, the drawback of conducting polymers is instability during the continuous charge-discharge processes because the swelling and shrinkage of conducting polymers during doping/dedoping processes lead to mechanical degradation of the electrode material and decaying of the electrochemical performance [18–20]. In order to solve this problem, many researchers have suggested that the combination of conducting polymers and carbon material can improve the mechanical and electrical properties of their corresponding composites [18,21]. Fan et al. reported the in-situ polymerization of graphene nanosheet/carbon nanotube/PANI composite with the highest specific capacitance of 1035 F g<sup>-1</sup> [21]. Tsai et al. prepared graphene/PPy composite via electrochemical polymerization. The prepared composite exhibited a specific capacitance of 352 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> [19]. Wang et al. synthesized PPy/graphene oxide (PPy/GO) composite by one-step electrodeposition procedure and obtained a maximum specific capacitance of 387.6 mF cm<sup>-2</sup> at 0.2 mA cm<sup>-2</sup>. Also, PPy/GO composite electrodes maintained 84.8% of its initial capacitance value after 5000 cycles. Therefore, this composite showed an excellent capacitive behavior and good cycling stability [22].

Different types of transition metal oxides such as RuO<sub>2</sub> [23], MnO<sub>2</sub> [24–27], Co<sub>3</sub>O<sub>4</sub> [28], Fe<sub>3</sub>O<sub>4</sub> [29] and TiO<sub>2</sub> [30,31] have been shown as promising electrode materials for pseudocapacitors preparation.

Among various transition metal oxides, V<sub>2</sub>O<sub>5</sub> is believed to be a versatile material for fabrication of supercapacitor electrodes and Li-ion batteries, due to layered crystalline

structure, mixed valance states (V<sup>3+</sup>, V<sup>4+</sup> and V<sup>5+</sup>) and high theoretical specific capacity (2120 F g<sup>-1</sup> at 1 V). Also, facile synthesis, earth-abundant nature and non-toxic characteristics make it as a particularly promising candidate for supercapacitor applications [32–34]. However, the electronic conductivity and structural stability of V<sub>2</sub>O<sub>5</sub> are relatively low, which lead to slow rate of ions insertion/extraction [35]. Considerable efforts have been devoted to boost the electron diffusion rate of V<sub>2</sub>O<sub>5</sub> and further enhance its capacitive performances. Some approaches involve the formation of hybrids using conducting polymers or carbon materials with V<sub>2</sub>O<sub>5</sub> to overcome these problems [35]. For example, Qu et al. synthesized a core@shell structure of PPy grown on V<sub>2</sub>O<sub>5</sub> nanoribbons as an anode material for supercapacitor applications. This nanocomposite exhibited high energy density and long cycle life [36]. Mao et al. prepared V<sub>2</sub>O<sub>5</sub>@PPy nanocomposite as an electrode material for preparation of a supercapacitor with high specific capacitance and low inner resistance [37]. Also, two-dimensional (2D) heterostructures of V<sub>2</sub>O<sub>5</sub> nanosheet (V<sub>2</sub>O<sub>5</sub>NS) and reduced graphene oxide (RGO) electrode were synthesized by Alshareef et al. for supercapacitor applications. RGO/V<sub>2</sub>O<sub>5</sub>NS showed a specific capacitance of 635 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>. The capacitance of the heterostructures was almost 2.5 times higher than the 2D-V<sub>2</sub>O<sub>5</sub>NS alone. In addition, this nanocomposite revealed high energy and power density and excellent capacitance retention after 3000 cycles [33]. Balkus Jr. et al. developed a green method to prepare V<sub>2</sub>O<sub>5</sub> nanowire (VNW) and graphene composite without using any binder. The composite of VNW/graphene was used as the electrode material for preparation of a high energy density supercapacitor [38]. Also, Sharma et al. prepared graphene nanoribbons @ vanadium oxide nanocomposite by a facile hydrothermal route. In comparison to the bare nanosized metal oxide, this nanocomposite displayed good electrochemical properties for supercapacitor applications [32].

Since graphene, metal oxides and conducting polymers are the most important types of electrode materials for supercapacitors, the reasonable and credible combination of the three components would produce new electrode materials with considerably improved electrochemical performances. Therefore, combination of graphene and pseudocapacitive materials (such as transition metal oxides and conductive polymers) can enhance not only the capacitance of carbon materials, but also effectively improve the stability of the pseudocapacitive materials during charge-discharge processes. Several groups have studied graphene based ternary composites as the electrode material for supercapacitor applications like, graphene/Ag/PPy [39], graphene/SnO<sub>2</sub>/PEDOT [40], PPy/molybdenum trioxide/graphene [41], ZrO<sub>2</sub>/RGO/PPy [42] and GO/PPy/ZnO [43]. Therefore, from the above discussions, it can be seen that the composite of V<sub>2</sub>O<sub>5</sub>, PPy and GO (V<sub>2</sub>O<sub>5</sub>/PPy/GO) can be considered as a promising electrode material for preparation of high-performance supercapacitor.

In the present work, chronoamperometry method is used to carry out a one-step electrochemical deposition of V<sub>2</sub>O<sub>5</sub>/PPy/GO nanocomposite on stainless steel (SS) substrate. The resulting ternary nanocomposite shows high specific capacitance and good cyclability, which is due to the effective interactions between three components of GO, PPy and V<sub>2</sub>O<sub>5</sub>. For comparison, pure PPy, V<sub>2</sub>O<sub>5</sub>/PPy and PPy/GO are also prepared

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