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# Asymmetric supercapacitor based on vanadium disulfide nanosheets as a cathode and carbonized iron cations adsorbed onto polyaniline as an anode

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ABSTRACT

$VS_2$ nanosheets electrode material was successfully synthesized by the hydrothermal method, and the electrode material (C-Fe/PANI) based on the carbonization of Fe cations adsorbed onto polyaniline (PANI) was directly synthesized on a nickel foam (current collector) by pyrolysis of the iron-PANI mixture coated on nickel foam in a tube furnace under the $N_2$ atmosphere. The structural and morphological characterization of the as-synthesized electrode materials was carried out using X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The electrochemical behavior of each working electrode was analyzed in a three-electrode cell configuration using 6 M KOH electrolyte, and thereafter, a hybrid (asymmetric) device was successfully fabricated using $VS_2$ nanosheets as the positive electrode and C-Fe/PANI as a negative electrode. The fabricated $VS_2$//C-Fe/PANI asymmetric device was found to perform at a high applied potential difference of 1.7 V in 6 M KOH. At a current density of 2 A $g^{-1}$, this device exhibited high energy and power densities of 27.8 Wh $kg^{-1}$ and 2991.5 W $kg^{-1}$ respectively. In addition, a $VS_2$//C-Fe/PANI device showed excellent cycling stability with 95% capacity retention over 10,000 galvanostatic charge-discharge cycles at a current density of 5 A $g^{-1}$.

## 1. Introduction

Supercapacitors (SCs) which are also referred to as electrochemical capacitors (ECs) have attracted great interest for the important application in the area of electrochemical energy storage because of increasing demand for digital communication, electric vehicles and other electric devices at high pulse power level [1–7]. Since, SCs are high power-delivery storage devices which are able to discharge in a shorter time by exploiting their fast surface or near surface reactions and delivering high power compared to conventional batteries [2,8–10]. Though, SCs are high power-delivery storage devices (have high power density) they have low energy density especially compared to rechargeable batteries (Li-ion batteries) [2,11]. Accordingly, research focus in SCs is on improving their energy density (i.e. ~5–8 Wh $kg^{-1}$) without compromising their high power density (i.e. ~5–30 kW $kg^{-1}$), unlike in rechargeable batteries which already have high energy density in the range of 120–200 Wh $kg^{-1}$, the focus will be on improving the power density which is in the range of 0.4–3 kW $kg^{-1}$ [2,8,9,12]. Recently, asymmetric (hybrid) systems have been explored to increase the operating electrode potential to improve the energy density of the SCs. Generally, the behavior of the SCs is mainly influenced by the charge storage mechanism which is divided into two classifications, namely, the electric double layer capacitors (EDLCs) and pseudocapacitors [1,2,13]. In EDLCs, the predominant energy storage is achieved by double-layer capacitance, and in this charge storage process, there is no transfer of charges. On the other hand, in pseudocapacitors, the electrical energy is stored faradaically by electron charge transfer between electrode and electrolyte [2]. This is accomplished through electrosorption, reduction-oxidation reactions (redox reactions), and intercalation processes, called pseudocapacitance.

The electrochemical capacitors have three main categories of electrode materials which are carbon materials such as carbon nanotubes, transition metal oxides (e.g. $MnO_2$ and $RuO_2$), and electrochemically conducting polymers, for instance, polyaniline (PANI) and polypyrrole [14–17]. Among various pseudocapacitive materials that have been studied, PANI has attracted great attention

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as one of the most promising pseudocapacitive polymer material suitable for the next generation of supercapacitors. This is due to its attractive properties such as high pseudocapacitance, light weight, low cost, controllable electrical conductivity, high energy density, facile synthesis, and environmental friendliness [18–21]. PANI is often used as electrode material for supercapacitors and it has three oxidation states (leucoemeraldine, emeraldine salt, and pernigraniline) which contribute to its high specific capacitance [22]. Among its three oxidation states, the emeraldine salt has lower electronic conductivity than that of typical metals [23]. The need to develop high-performance SCs has led to the incorporation of metals and metal oxide particles into PANI to enhance its electronic conductivity [24]. It has been shown that iron-containing nitrogen-doped graphitic carbon materials, carbonized PANI in particular, achieve high electrocatalytic performance and exhibit high cycling stability [15,16]. Generally, carbonaceous materials with Fe cations have shown enhanced electrochemical performance as the negative electrode materials for SCs, including iron oxides and hydroxides [25–27]. Therefore, the synthesis of carbonized Fe-PANI hybrid material is promising for achieving high-performance SCs. In this study, Fe cations are found to be interesting since they can easily adsorb onto PANI by the complexation and electrostatic interactions due to the active binding sites present in functional groups on PANI [18,28–30].

Until now, transition metal oxides/sulfides and layered transition-metal dichalcogenides (TMDs) such as $MoS_2$, $VS_2$, $WS_2$, $FeS_2$, $CoS_2$, and $NiS_2$ have been successfully established as new paradigm in the chemistry of nanomaterials especially for nanotubes and fullerene-like nanostructures as well as the graphene analogs and have been extensively investigated as the positive electrode materials for SCs due to their high faradic capacitance [31–35]. On the other hand, $VS_2$ has not received much attention in two electrode supercapacitor devices. However, it has been investigated for applications in SCs due to its promising electrochemical performance. Recently, Feng et al. [36], reported all-in-solution route to synthesize $VS_2$ phase for the first time, taking advantage of an intermediate intercalated compound precursor of $VS_2 \cdot NH_3$. This report clearly demonstrated that $VS_2$ nanosheets are highly conductive and have a high specific capacitance, showing promising signs for 2D material to be utilized in energy storage devices. Masikhwa et al. [37], reported the design of an asymmetric supercapacitor based on 3D interconnected activated carbon as the negative electrode and mesoporous $VS_2$ nanosheets as the positive electrode material. The report suggests that pairing hybrid materials could be an excellent method to produce SCs with high energy and power densities.

Although studies about $VS_2$ electrode for supercapacitor applications have been reported in the literature, there are rare studies done on the binder-free electrode material based on carbonized Fe cations adsorbed onto PANI (C-Fe/PANI) and until now there are no reports on $VS_2$//C-Fe/PANI asymmetric cell device. Herein, we report on asymmetric supercapacitor based on $VS_2$ nanosheets as a cathode and C-Fe/PANI as an anode. This study focuses on structural, and morphological characterization of the as-synthesized electrode materials and the electrochemical properties of $VS_2$//C-Fe/PANI asymmetric device. The $VS_2$//C-Fe/PANI asymmetric device was found to perform at a high applied potential difference of 1.7 V in 6 M KOH. At a high current density of 2 A $g^{-1}$, this device exhibited energy and power densities of 27.8 Wh $kg^{-1}$ and 2991.5 W $kg^{-1}$ respectively. In addition, a $VS_2$//C-Fe/PANI device showed excellent cycling stability with 95% capacity retention for 10 000 galvanostatic charge-discharge cycles at a current density of 5 A $g^{-1}$.

## 2. Experimental

### 2.1. Materials

All the reagents used in this work are of analytical grade and were used as received without further purification. For $VS_2$ nanosheets synthesis: Sodium orthovanadate (1 mM $Na_3VO_4$, purity 99.98%) and thioacetamide (5 mM $C_2H_5NS$, purity ≥99%), were purchased from Sigma Aldrich. For C-Fe/PANI synthesis: Aniline hydrochloride ($C_6H_5NH_2 \cdot HCl$, purity ≥99%), ammonium persulphate ($(NH_4)_2S_2O_8$, purity ≥99%) and iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, purity ≥99.95%) were also purchased from Sigma Aldrich. Polycrystalline nickel foam (Ni-F) used as a current collector which is a 3D scaffold template with an areal density of 420 g $m^2$ and thickness of 1.6 mm was purchased from Alantum (Munich, Germany).

### 2.2. Synthesis of $VS_2$ nanosheets using hydrothermal method

$VS_2$ nanosheets were synthesized by the hydrothermal method as shown in Scheme 1(a). In the synthesis, 1.65 g of 1 mM $Na_3VO_4$ and 3.37 g of 5 mM $C_2H_5NS$ were dissolved in 120 mL of deionized water and stirred for 1 h at room temperature using a magnetic stirrer. After stirring, the resultant solution was transferred into a sealed, 150 mL Teflon-lined, stainless-steel autoclave and kept at a temperature of 160 °C for 24 h and then cooled naturally down to the room temperature. Subsequently, the obtained precipitate was filtered and washed with deionized water several times and dried at 60 °C overnight. Finally, the recovered product of $VS_2$ nanosheets was obtained as displayed by micrograph in Scheme 1(a).

### 2.3. Synthesis of C-Fe/PANI

For PANI synthesis: 0.2 M aniline hydrochloride was added to a 50 mL solution of 1.0 M HCl, and in a separate beaker 0.25 M solution of ammonium persulphate was added to 1.0 M HCl. The prepared solutions were kept for 1 h at room temperature, thereafter, they were mixed and stirred for about an hour and left to polymerize. After polymerization, PANI precipitate was collected on a filter (after been washed several times with 100 mL of 0.2 M HCl, and acetone) and dried at 60 °C overnight. Furthermore, PANI was used as a substrate for adsorbing Fe cations. Briefly, 0.2 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.0125 g of PANI were dissolved in 50 mL of ethanol and sonicated in ultra-sonication bath until the ethanol was almost completely evaporated. Thereafter, the slurry was coated on nickel foam (current collector) which was loaded in a tube furnace and heated to 850 °C and pyrolyzed for 2 h under the $N_2$ atmosphere. After pyrolysis, the as-synthesized sample which shows homogeneously dispersed nanograin particles (Scheme 1(b)) was used as the negative electrode (i.e. without a binder).

### 2.4. Structural, and morphological characterization

The crystallite structure analysis of the as-synthesized $VS_2$ and C-Fe/PANI materials was carried out using X-ray diffraction (XRD) XPERTPRO diffractometer (PANalytical BV, Netherlands) with theta/2 theta geometry, operating with a cobalt (Co) tube at 50 kV and 30 mA. A T64000 micro-Raman spectrometer (HORIBA Scientific, Jobin Yvon Technology) with a 514 nm laser wavelength and spectral acquisition time of 120 s was used to characterize the as-synthesized electrode materials. The Raman system laser power was set as low as 3 mW in order to minimize heating effects. Fourier transform infrared (FT-IR) spectroscopy performed in the range of