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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PERFORMANCE OF NANOSTRUCTURED V_2O_5 THIN FILM DEPOSITED BY HYDROTHERMAL METHOD

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ABSTRACT: *In the present study, vanadium pentoxide (V_2O_5) thin films have been successfully deposited by a simple hydrothermal method at 180°C. These thin films were characterized for thermal, structural, morphological and surface wettability by using TGA-DTA, X-ray diffraction (XRD), Fourier transformation Raman (FT-Raman) spectroscopy, scanning electron microscopy (SEM) and contact angle measurement techniques. The electrochemical capacitor performance was examined by using cyclic voltammetric and galvanostatic charge-discharge method. The specific capacitance 286 F/g was obtained in 1 M Na_2SO_4 solution within the potential range of 0.2 V to 0.6 V versus SCE. The supercapacitor exhibited a good cycling performance and can be used to fabricate supercapacitor device.*

Keywords: *V_2O_5; hydrothermal method; thin film; supercapacitor.*

1. Introduction

Supercapacitors, are known as a new generation of electronic devices and have attracted much attention because of their simple principle, long cycle life, pulse power supply and high dynamic of charge propagation [1-2]. Supercapacitors are classified mainly into two types; first one electric double layer capacitor (EDLC) which stores charge electrostatically or non-faradaic and there is no transfer of charge between electrode and electrolyte. Second type is pseudo capacitor in which charge storage is faradaic through the transfer of charge between electrode and electrolyte [3]. Hybrid capacitor is the combination of EDLC and pseudocapacitor in which charge is stored using both faradaic and non-faradaic processes.

Vanadium oxides (V_2O_5) have been widely examined as an electrode material for electrochemical capacitors that use organic electrolytes. Vanadium also exhibits numerous oxidation states (II–V), but its poor electronic conductivity ($\sigma_{bulk} \approx 1x10^{-4}\Omega^{-1}m^{-1}$) renders the oxide unsuitable for use in high-rate electrochemical devices. V_2O_5 is the most attractive and promising material because of its layered structure [4-5] and received a research interest due to its potential applications in lithium ion batteries [6-8], catalysts [9-11], electrochromic devices (ECDs) [12-14] and supercapacitor [15-17]. V_2O_5 thin film is a promising material because of its high specific capacitance. Up to now V_2O_5 has been synthesized by different synthesis methods such as chemical vapor deposition [18-21], sol gel method [22], electrochemical deposition [23] and hydrothermal [24-25] etc. In present study, the hydrothermal method is used because hydrothermal is simple, inexpensive method is a low temperature (180°C) and a short reaction time (3 h) as compared to the conventional hydrothermal method. This technique to prepare V_2O_5 thin film using NH_4VO_3 as an initial material and HNO_3 pH control and this process needs no stirrer and surfactance. Neutral Aqueous electrolytes rechargeable supercapacitors have attracted much more attention because of their advantages like high ionic conductivity, low-cost, non flammability, no specific requirements for battery assembly and good safety [26-27]. V_2O_5 material has large theoretical capacity of 294 fg^{-1}, [28] which is rather higher than that of commonly used cathode materials, like $LiCoO_2$ (140 fg^{-1}), $LiMn_2O_4$ (148 fg^{-1}) and $LiFePO_4$ (170 fg^{-1}).

In the present work, V_2O_5 thin films are successfully deposited by a simple, inexpensive and novel hydrothermal method. The thin films are characterized for thermal, structural, surface morphological and wettability studies. The electrochemical properties of V_2O_5 thin film are examined using cyclic voltammetry (CV). Galvanstatic charge-discharge. The electrochemical reaction of V_2O_5 in neutral aqueous electrolyte is elucidated by analyzing the electrochemical behavior of V_2O_5 in 1 M Na_2SO_4 and their corresponding structure & composition changes during charge-discharge. Also V_2O_5 thin films are successfully deposited by hydrothermal reduction of NH_4VO_3 as an initial material. The thin films formation mechanism of orthorhombic V_2O_5 nanostructure is briefly discussed.

2. Experimental

The commercially available AR grade ammonium metavanadate (NH_4VO_3) (98.0 % Loba Chemie Pvt. Ltd.), nitric acid (HNO_3) (69-72 % Loba Chemie Pvt. Ltd.) and sodium sulfate (Na_2SO_4) (99.0 % Loba Chemie Pvt. Ltd.) are used as received without further purification. All the chemicals are prepared in double distilled water. V_2O_5 thin films are deposited on stainless steel substrate surface from a bath of NH_4VO_3 solution. For deposition of good quality thin films the experimental conditions, such as pH of the reaction bath, reaction temperature and duration of the hydrothermal treatment are examined. In a typical synthesis, an appropriate amount of 0.5 M HNO_3 solution is added to 25 ml of 0.05 M NH_4VO_3 solution, to adjust pH in the range of 2–3. The solution is placed into a 50 ml stainless steel autoclave with a teflon liner and maintained at temperature 180 °C for 3 h and then cooled to room temperature naturally. The as obtained thin film washed three times in deionized water and finally annealed at 450 ^{0}C in air for 3 h to get pure V_2O_5 thin films.

The thermal analysis tests (TGA & DTA) conducted in nitrogen atmosphere at a heating rate of 10^o C/min, from room temperature to 1000^o C using an SDT Q600 Build 20 instruments. X-ray diffraction (XRD) pattern of final product recorded in the 2θ rang of 10° - 80° by using Cu Kα radiation (λ= 1.5418A^o) (Bruker D-8 diffractometer). Raman study carried out in the spectral rang of 100-1200 cm^{-1} using Bruker RAM. The surface morphological study of thin film carried out by using scanning electron microscope (SEM) (JEOL model 6360). The water contact angle of V_2O_5 film surface was measured using digital Goniometer (Rame-Hart NRL CA). The cyclic voltammetry (CV) & galvanostatic charge discharge measurement carried out using automatic battery cycle (WBCS 3000). The electrochemical characterization carried out in three electrode cell configuration by using graphite as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and & V_2O_5 thin film as a working electrode in 1 M Na_2SO_4 aqueous electrolyte.

3. Results and Discussions

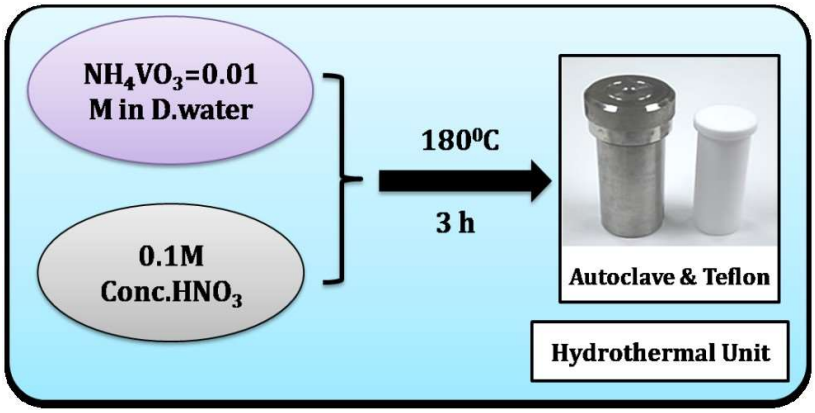

Fig. 1. Schematics of synthesis of V_2O_5 thin film by hydrothermal method

Fig.1. shows schematic of hydrothermal deposition of V_2O_5 thin film. The deposition is done by using aqueous solution of NH_4VO_3 in little amount of HNO_3 and pH is adjusted to ~2. The solution was put into a teflon liner with a stainless steel autoclave and cleaned substrate was immersed in to solution. The autoclave is put into a furnace and maintained temperature and after 3 h cooled down naturally. The process may involve chemical reaction (1).

$$2NH_4VO_3 + H_2O + HNO_3 \rightarrow V_2O_5 + 2NH_4NO_3 \text{ --------(1)}$$

The thickness of the V_2O_5 thin film is calculated by a gravimetric method. The typical working electrode is 0.120 mg in weight with a surface area of 1 cm^2 and its thickness was 357 nm, which was calculated by using the formula (2)

$$t = \frac{m_2 - m_1}{\rho \times A} \text{ ---------- (2)}$$

Where, 'm_1' is mass of electrode material before the deposition and 'm_2' is mass of electrode material after deposition, 'ρ' is the density of electrode material (3.36 gcm^3), 'A' is active area of the electrode material deposited on the steel substrate (cm^2) and't' is thickness of thin film electrode (nm).

Fig.2. shows TGA-DTA results performed in nitrogen atmosphere and were also carried out to determine

potential reactions during heat treatment at a heating rate of 10° C/min. The loss of water from the precursor is attributed to the observed endothermic peaks. The V_2O_5 exhibits two weight loss slopes, first weight loss is up to 110°C due to the loss of weakly bound water and retained weight 10.85 %. The second wave of weight loss extends up to 15.62 % around 450°C, which is an indication of the thermal decomposition of the precursor.

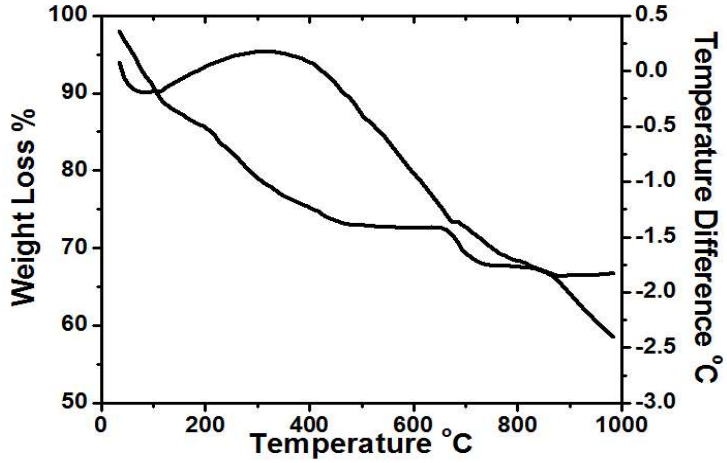

Fig. 2. TGA and DTA of (V_2O_5) thin film deposited by hydrothermal method

The formation of V_2O_5 phase is confirmed by an exothermic peak around 315° C in DTA spectrum. There is an endothermic peak around 675°C which may be due to the melting of sample and close to that of the reported melting point of V_2O_5.

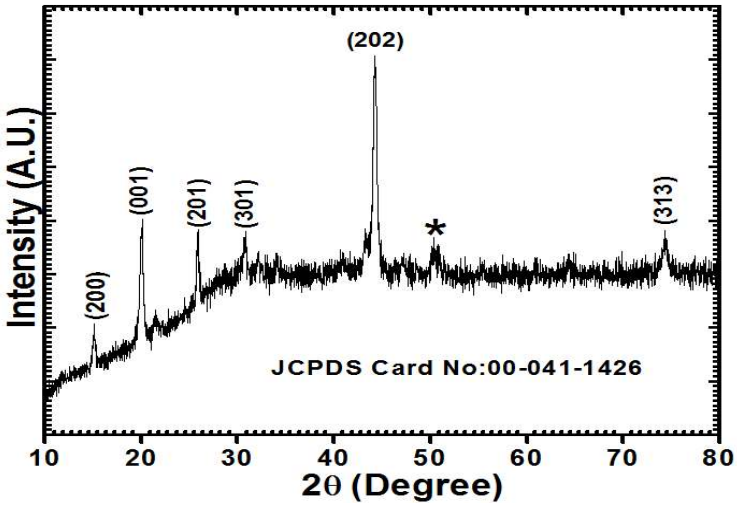

Fig.3. shows XRD pattern of V_2O_5 thin film on a stainless steel substrate.

It exhibit diffraction peaks along 2θ = 14.94, 19.77, 25.61, 30.93, 44.13, 74.59 degree and correspond to the lattice planes (200), (001), (201), (301), (202) and (313) respectively. The main diffraction peak indexed at 44.13° can be assigned to the (202) reflection. The diffraction peaks are in good agreement with standard JCPDS Card (no. 41-1426) of the V_2O_5 having orthorhombic crystal structure [29-38]. The * peak is due to the stainless steel substrate surface. The crystallite size is determining by using Scherer's formula (3)

$$D = K\lambda / \beta \cos\theta \text{ ---------(3)}$$

Where 'D' is crystalline size, 'K' is constant 0.9, 'λ' is wavelength of monochromatic X-ray (1.5418 Å) 'β' is full width at half maxima of the peak and 'θ' is diffraction angle. The crystallite size for (202) plane is found to be 24.21 nm.

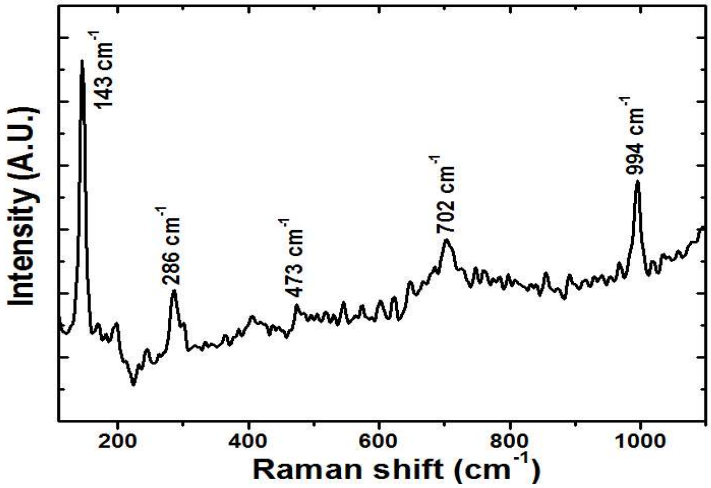

Fig..4. FT-Raman spectrum of V_2O_5 thin film deposited by hydrothermal method

The FT-Raman spectrum of V_2O_5 thin film is recorded over 110-1100 cm^{-1} and is shown in fig. 4. The Raman peaks observed in present spectrum at low and high frequency region. The spectrum shows well defined peaks at 143, 286, 473, 702 and 994 cm^{-1}. The most intense peak observed at 143 cm^{-1} is attributed to the skeleton bend vibration [39], while the narrow peak at 994 cm^{-1} corresponds to the terminal oxygen (V ≡ O) stretching mode [40]. Peak at 702 cm^{-1} is due to coordination of vanadium atom with the three oxygen atoms. The V-O-V stretching and bending modes are assigned to the frequency 286 cm^{-1} [41-42].

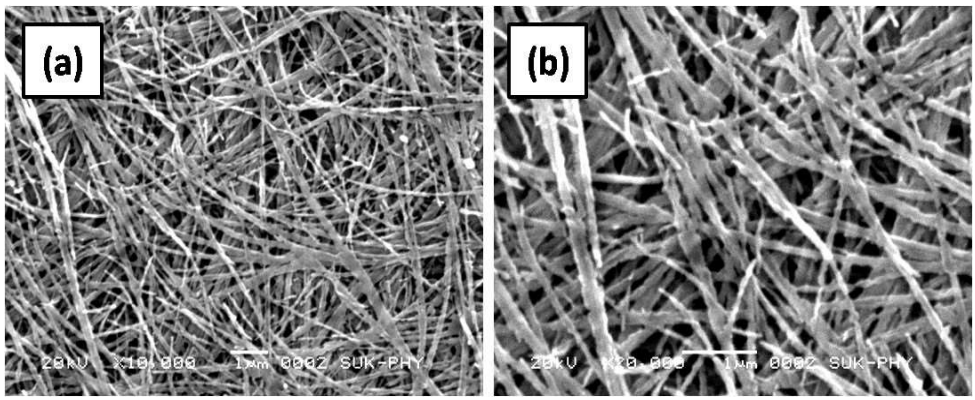

Fig.5. SEM images of V_2O_5 thin film with different magnifications

The surface morphological architecture of thin film is studied by using SEM. Figure 5 show high and low magnification images of V_2O_5 thin film. The SEM images show total coverage of substrate surface with V_2O_5 nanofibers. The fibrous networks have an average diameter of about 40 to 100 nm and length up to 6 - 7 μm. Such surface structure offer better performance in supercapacitor devices, because this surface provides efficiently minimum distance and time to travel charge carriers.

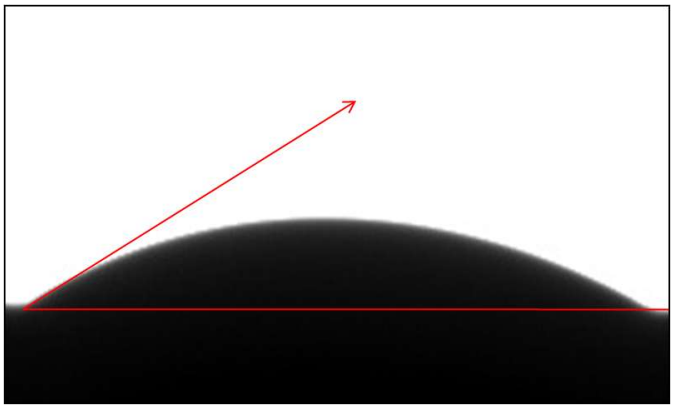

Fig.6. Contact angle image of V_2O_5 thin film surface (water droplet used as solvent)

Fig. 6. shows contact angle image of V_2O_5 thin film surface. Surface wettability test is investigated for the determination of hydrophilic ($\theta < 90^o$) or hydrophobic ($\theta > 90^o$) nature of thin film surface. If the wettability is high or low then strong or weak interaction between electrode and electrolyte solution refers to hydrophilic or hydrophobic nature of a V_2O_5 film surface. The V_2O_5 thin film exhibits contact angle of 20^o, which confirms super hydrophilic ($20^o > \theta$) nature. The super hydrophilic nature of film surface can give enhancement the electrochemical performance and good interfacial interaction between electrode electrolyte interfaces.

4. Supercapacitive performance

4.1. Cyclic voltammetry of V_2O_5 Thin Films

The hydrothermal deposited V_2O_5 thin film electrode is used in electrochemical capacitors and their performance is tested using cyclic voltammetry (CV). Fig.7. show cyclic voltammetry (CV) curve of V_2O_5 electrode at a scan rate of 10 mV/s within potential from -0.2 to +0.6 V vs. SCE in 1 M Na_2SO_4 electrolyte.

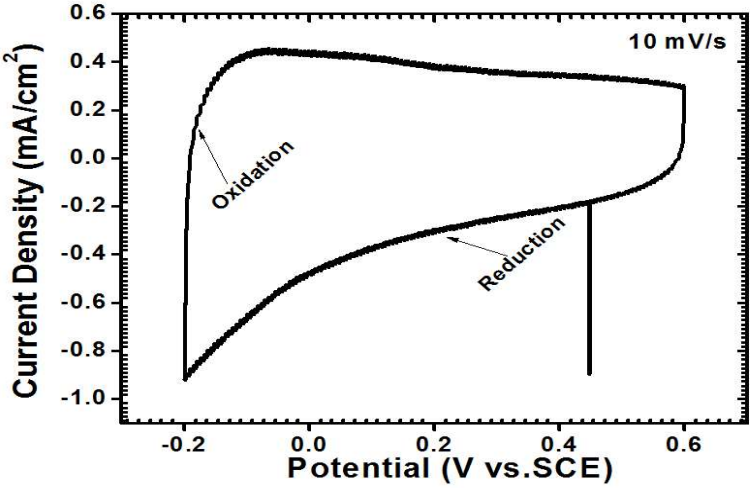

Fig.7. CV curves of V_2O_5 electrode in 1 M of Na_2SO_4 electrolyte

From shape of CV it is confirmed that capacitance arises from redox transition and EDLC within the electrode/electrolyte and electrolyte/electrode interface, respectively. The capacitance of film is calculated by using equation (4)

$$C = \frac{I}{dV/dt} \qquad (4)$$

Where 'I' is average current, 'dV/dt' is scanning rate of the electrode. The specific capacitance of the electrode is obtained by dividing the capacitance to weight (0.0001 g) dipped in the electrolyte. The specific capacitance of the electrode is found to be 286 F/g in 1 M Na_2SO_4 electrolyte.

4.2. Galvanometric Charge-Discharge Cycling Measurements

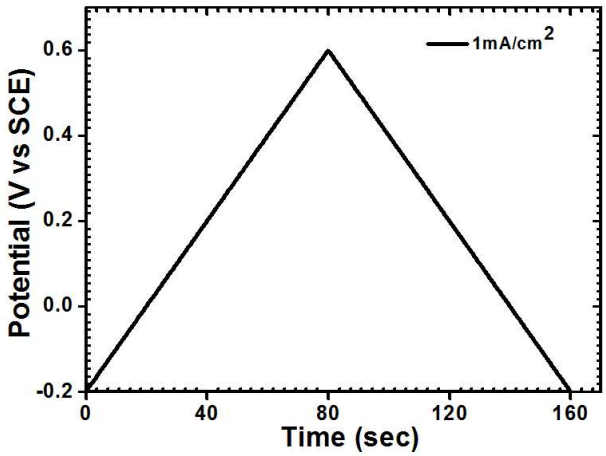

Fig.8. Charge discharge curve of V_2O_5 electrode in 1 M Na_2SO_4 electrolyte at current density of 1 mA/cm^2

The charge-discharge behavior of V_2O_5 electrode is studied by galvanometric charge-discharge method. Fig.8. represents charge-discharge behavior of electrode at current density of 1 mA/cm^2. The shape of the discharge curve does not show the capacitance characteristics of pure double layer capacitor. During discharging curves, linear variations of the time dependence of the potential (-0.2 to 0.6 V) indicate electric double-layer capacitance, which is the charge separation across the interface between the electrode and the electrolyte.

5. Conclusions

In summary, V_2O_5 thin films were successfully deposited onto stainless steel substrate by hydrothermal method. The XRD measurements confirmed that deposited V_2O_5 having orthorhombic crystal structure. The SEM analysis showed that the substrates were well covered with nanofibers. The electrochemical study revealed that the hydrothermal deposited V_2O_5 electrode had a specific capacitance of 286 F/g. Charge-discharge curves confirmed that capacitance was consisted from EDLC and pseudocapacitance. The hydrothermal method is a low cost and promisingly used for deposition of nanostructured thin film material for electrochemical supercapacitor.

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