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Single step hydrothermal synthesis of carbon nanodot decorated V_2O_5 nanobelts as hybrid conducting material for supercapacitor application

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ABSTRACT

Carbon nanodot (C-dot) decorated V_2O_5 (C-dot@V_2O_5) nanobelts are synthesized by single step, low cost hydrothermal route at low temperature by using V_2O_5 and glucose as precursors. We have not added any extra organic solvents or surfactants which are commonly used for the preparation of different nanostructures of V_2O_5. Electron microscopy analyses demonstrate that C-dot is entrapped inside V_2O_5 nanobelts which in turn enhance the conductivity and ion propagation property of this composite material. The C-dot@V_2O_5 nanobelts exhibit an excellent three electrode electrochemical performance in 1 M Na_2SO_4 and which showed a specific capacitance of 270 F g^{-1} at 1 A g^{-1}, which is ~ 4.5 times higher than the pristine V_2O_5 electrode. The electrochemical energy storage capacity of this hybrid is investigated towards solid state supercapacitor application also for the first time by employing electrophoretically deposited C-dot as the counter electrode and Li based gel as the electrolyte. The hybrid material delivers an energy density of 60 W h kg^{-1} and a reasonably high power density of 4.1 kW kg^{-1} at 5 A g^{-1} and good cycling stability and capacitance retention of about 87% was observed even after 5000 cycles. Above mentioned results clearly show that C-dot embedded hybrid, nanostructured transition metal oxides has great potential towards fabrication of electrodes for energy storage devices.

1. Introduction

Among various energy storage devices, supercapacitors or ultracapacitors have become one of the most promising candidate due to its high power density, faster charge discharge rates and excellent cyclic stability [1,2]. They have been used in wide range of applications such as large industrial machines, various portable electronic devices, hybrid electronic vehicles etc. Supercapacitor can be classified into electrochemical double layer capacitor (EDLC) and pseudocapacitor.

EDLC is considered as the electrical energy storage device with high power density, which store charges via reversible ion absorption at the electrode-electrolyte interface [3–5]. Carbon based materials are considered good for EDLCs due to their double layer capacitance which enhances the power density of the capacitor [6,7]. Even though carbonaceous materials provides high surface area and conductivity, the energy density of such capacitors is limited by the reduced double layer area [8]. On the other hand, pseudo-capacitors can provide high energy density, which are associated with a surface redox process on the surface of the electrode materials. For pseudo-capacitors fast faradaic redox reactions are responsible for the charge storage mechanism [9]. Conducting polymers and transition metal oxides are primarily used as the pseudocapacitance materials [10–12]. However, most of these pseudo capacitive materials show poor electrical conductivity and low power density. A better way to design a supercapacitor with both high energy density and power density is to construct a hybrid device that is composed of EDLC and pseudocapacitance within a single electrode.

Among various transition metal oxides V_2O_5 is considered as the well-established intercalation compound due to the following reasons: low cost, layered crystal structure, high energy density and multivalent oxidation states. V_2O_5 nanostructures such as wires, rods, belts, etc. offer high surface area, have been already used in different areas such as supercapacitor, lithium ion batteries, gas sensors, transistors etc [13–17]. As a supercapacitive electrode, the low electronic conductivity and low ion diffusion coefficient of V_2O_5 prevents the faster charge discharge rates. Combination of different carbon nanostructures such as activated carbon, graphene, nanotubes etc. with V_2O_5 can improve the conductivity of the composite and prevents the agglomeration of the metal oxide nanoparticles [18–20].

There are various reports based on V_2O_5 -carbon nanostructures for supercapacitor applications. All those hybrid compounds offer enhanced specific capacitance and improved electrochemical energy storage. In a previous report, graphene/V_2O_5 assembly offered a specific capacitance of 288 F g^{-1}, due to the combined effects of

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pseudocapacitance and double layer capacitance behavior [21]. In an another report, V_2O_5/functionalized multi walled carbon nanotubes hybrids exhibited excellent energy density ~ 57 W h kg^{-1} and a better rate capacity [22]. Incorporation of functionalized carbon nanotubes improves the surface area and conductivity of the composite which leads to the high energy and power density. Zhou et al. reported a bamboo like nanomaterial composed of V_2O_5 /polyindole decorated on the activated carbon cloth for supercapacitor application and it offered a high specific capacitance of 535 F g^{-1} [23].

Carbon dots (C-dots) belongs to new class of carbon nanomaterials, and these materials have attained extensive scientific interest due to their fascinating properties such as stability, low toxicity, good electrical conductivity, ease of synthesis etc. Moreover it is quite cheap also [24,25]. This class of materials are capable of showing strong luminescent characteristics, which can be tuned by tuning the excitation wavelengths. Most importantly C-dots can act as electron acceptors as well as electron donors [24]. It was used in wide range of applications such as sensors, solar cells, bio-imaging, catalysis etc [26–29]. Liu et al. had reported C-dot as the electrode materials for supercapacitor for the first time [30]. A symmetric micro-supercapacitor was fabricated by electrodeposition techniques. The results were promising for fabrication of high performance supercapacitor based on C-dots. There are also few reports based on hybrid supercapacitor based on C-dots [31].

In the present work, a facile, cost effective and single step hydrothermal method is utilized for the synthesis of C-dot decorated V_2O_5 (C-dot@V_2O_5) hybrid nanostructures as electrode materials demonstrating good power and energy densities. The nano-structured hybrid is prepared by employing V_2O_5 and glucose as the precursors, without the addition of any other oxidizing or reducing agent or any other surfactants. Glucose acts as an oxidizing agent at high temperature, which leads to the formation of V_2O_5 nanobelts. At the same time glucose is pyrolyzed and underwent reduction which in turn leads to the formation of carbon dots. The carbon dots have been decorated inside the V_2O_5 nanobelts which significantly improves the electrical conductivity. The V_2O_5 nanobelts are also involved in faradaic reactions and render high energy density. These conductive C-dots help to provide high power density to the C-dot@V_2O_5 composite. These C-dot@V_2O_5 based hybrid nanostructures has demonstrated a specific capacitance value of 270 F g^{-1} at 1 A g^{-1}. The solid state device delivers an energy density of 60 W h kg^{-1} at a current density of 1 A g^{-1} and a reasonably high power density of 4.1 kW kg^{-1} at 5 A g^{-1} and good cycling stability and capacitance retention of about 87% was observed even after 5000 cycles.

2. Experimental section

2.1. Materials and chemicals

Vanadium pentoxide (V_2O_5), glucose, sodium sulphate (Na_2SO_4), propylene carbonate (PC), *N*-methyl pyrrolidine (NMP) and acetone were obtained from Merck. Lithium perchlorate ($LiClO_4$, purity > 98%) and poly (methylmethacrylate) (PMMA) were procured from Sigma-Aldrich. Deionized water (DI) is obtained through Millipore Direct-Q3 system. Transparent SnO_2:F (FTO) coated glass substrate with a sheet resistance of about 15 Ω sq^{-1} were purchased from Sigma-Aldrich, washed with soap solution, flushed with copious amount of water and finally rinsed with acetone before use.

2.2. Synthesis of C-dot decorated V_2O_5 nanobelt

Molar ratio of V_2O_5 and glucose is fixed as 0.75:1 and dispersed in a 40 mL of DI water and then stirred vigorously for 1 h at room temperature. The resulting yellow colored suspension is transferred into a 50 mL Teflon lined autoclave and is maintained at a temperature of 140 °C for different time intervals of 5 h, 12 h and 24 h in a vacuum oven. Obtained products are then centrifuged, washed and dried at 60 °C for 12 h. The final precipitates were dark green in color. The obtained yield of C-dot@V_2O_5 at 24 h is estimated to be ~ 76–80%. For comparison, control experiments without the addition of glucose and glucose alone also was carried out separately at 140 °C for 24 h.

2.3. Fabrication of electrodes for supercapacitor

The working electrode paste is prepared by mixing electroactive material (V_2O_5 or C-dot@V_2O_5) in few drops of N-methyl pyrrolidine (NMP). It is then coated over FTO and dried at 120 °C for 12 h in vacuum oven. The active material loading is maintained in the range of 1.2–1.5 mg. The electrophoretically deposited C-dot film is used as the counter electrode. It is prepared from C-dot suspension by using FTO as the working electrode and Pt wire as the counter electrode. A potential of 20 V is applied for 2 min. This results in the formation of dark brown colored C-dot layer over FTO. 1 M $LiClO_4$ in PC gel is employed as the electrolyte for the supercapacitor. Gel electrolyte is prepared by dissolving 12 wt% of PMMA in PC contain 1 M $LiClO_4$, by continuous stirring and heating at 65 °C for 1 h. A transparent homogeneous gel is obtained and further used for the quasi solid state device fabrication.

2.4. Characterizations

X-ray diffraction patterns are recorded using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (1.54 Å). The sample is scanned in the range between 10° and 80°. Raman spectra of the electrodes are recorded with a labRAM HR 800 (HORIBA Jobin Yvon) and laser excitation wavelength is fixed as 488 nm. XPS was acquired using a PHI 5000 Versa Probe II equipped with a monochromatic Al Ka (1486.6 eV), a X-ray source and a hemi-spherical analyzer. Appropriate electrical charge compensation was employed. The field emission scanning electron microscopy (FESEM) investigations are carried out using a Zeiss Ultra Plus scanning electron microscope for surface morphology analysis. Transmission electron microscopy (TEM) are carried out by FEI Tecnai T20 with a FEG source operating at 220 kV. The optical transmission spectra are recorded by using a Perkin Elmer, Lambda-950 UV/vis spectrometer and Shimadzu UV- 3600 Plus UV–vis–NIR spectrophotometer. Steady state photoluminescence are measured using FLS 980 (EDINBURGH Instruments). Suitable filter is used during the measurement and along with background correction. Electrochemical characterization such as cyclic voltammetry (CV), galvanostatic charge discharge characteristics (GCD), and electrochemical impedance spectroscopy (EIS) measurements are performed with a PAR potentiostat/galvanostat (model PARSTAT 2273) at room temperature. Three electrode cells are assembled employing the working electrode, C-dot counter electrode and a reference electrode (Ag/AgCl (3 M KCl)), immersed in 1 M Na_2SO_4 electrolyte. Two electrode cells with working and counter electrode are also assembled using 1 M $LiClO_4$ in PC gel electrolyte. CVs and GCDs are carried out over the potential range from 0 to 1 V for three electrode cell whereas 0–2 V for two electrode cell.

3. Result and discussion

3.1. Structural and morphology analysis

The crystal structure and purity of as prepared samples were analyzed by using X-ray diffraction (XRD). The XRD pattern of pristine V_2O_5 and C-dot@V_2O_5 is presented in Fig. 1a. Pure V_2O_5 matches well with the JCPDS file number 41-1426 and consistent with the orthorhombic structure and which shows sharp diffraction peak, indicating the well crystallized nature. The diffraction peaks at 25.2 (102) and 33.73 (212) corresponds to the tetragonal crystal structure of VO_2 (JCPDS file no 42-0876). Whereas the other diffraction peaks at d = 3.4