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Facile synthesis of V^{4+}-doped and graphene-decorated V_2O_5/biomass carbon nanocomposite using graphene quantum dot for supercapacitors with wide voltage window and high energy density

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1. Experimental

1.1. Materials and reagents

Citric acid (CA), serine (Ser), histidine (His) and boric acid (H_3BO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). NH_4VO_3 was purchased from Aladdin. Silver nanowires (Ag NW) in isopropanol (5 mg mL^{-1}) was purchased from Jiangsu XFNANO Materials Tech Co., Ltd. B/GQD was prepared according to reported in the literature. The solid electrolyte (PVA/Li_2SO_4) was prepared by adding 2.0 g polyvinyl alcohol (PVA) and 10 mL of 3 mol L^{-1} Li_2SO_4 solution in 20 mL ultrapure water and then heated at 75℃ with stirring until a clear homogeneous solution was formed. Rambutan was purchased from Hainan Province and then rambutan peel was collected, followed by washing in distilled water and freeze-dried for use.

1.2. Material characterization

The morphology and structure of as-synthesized materials was characterized by scanning electron microscope (SEM, JEOL, S-4800) and transmission electron microscope (TEM, JEOL, Jem-2100). The crystal structure and chemical composition of as-synthesized materials was studied by X-ray diffraction (XRD, Bruker D8 ADVANCE, Cu Kα radiation, λ = 0.15406 nm). The valence states of as-synthesized materials were characterized by X-ray photoelectron spectroscopy (XPS, Kratos, Axis supra) with mono chromated Al KR radiation. The band gap of as-synthesized materials was evaluated by obtaining UV-visible diffuse reflectance spectra by UV-visible spectrophotometer (UV-vis, Shimadzu, UV-3600 Plus). The oxygen vacancies of as-synthesized materials were characterized by the electron paramagnetic resonance spectra (EPR, Bruker EMX PLUS, X-band≈9.8 GHz). The morphology of rambutan peel was characterized by ultra-depth three-dimensional microscope (Keyence, VHX-1000C).

1.3 S/H-GQD-B synthesis

S/H-GQD-B was synthesized using one reported procedure.[1] In a typical synthesis, 0.1 mole of citric acid, 0.1 mole of histidine, 0.02 mole of serine and 0.02 mole of H_3BO_3 were mixed in in 50 mL deionized water. The solution was heated at 90^{o}C under stirring until all free water molecules were removed from the system. Followed by thermal treatment at 180^{o}C for 3 h. The formed S/H-GQD-B crude product was dispersed in ultrapure water to form 100 mg mL^{-1} S/H-GQD-B solution. Adjusted its acidity to pH 7.0 by dropping 1 mol L^{-1} NaOH solution, dialyzed in dialysis bag with molecular weight cut-off of 3000 Da and freeze-dried. The resultant S/H-GQD-B solid was stored in dark at 4^{o}C before use.

1.4 Electrochemical measurements

The three-electrode testing system and flexible symmetrical supercapacitor were employed for

evaluating electrochemical performance of V_2O_5-S/H-GQD-B/BC. The three-electrode testing system consists of titanium sheet working electrode (1cm×1cm) bearing V_2O_5-S/H-GQD-B/BC, platinum foil counter electrode (1cm×1cm), saturated calomel reference electrode and 1.0 mol L^{-1} Li_2SO_4 electrolyte. To prepare working electrode, V_2O_5-S/H-GQD-B/BC (90 wt.%), carbon black (5 wt.%) and polyvinylidene difluoride (PVDF)(5 wt.%) were dispersed in N-methyl-2-pyrrolidinone and homogenized on one ball mill for 24 h to form stable paste. The paste containing 1-5 mg of active mass was coated on the titanium sheet surface, dried for 24 h and pressed under 5 MPa in sequence.

Cyclic voltammogram (CV), chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge curves were carried out on CHI 660D electrochemical workstation. For EIS measurements the potential amplitude of ±5 mV and frequency of 0.01-10^5 Hz were adopted. The specific capacitance of single electrode in three-electrode testing system (C_g) were calculated by according to the equation (1).[2] In the equation, C_g, I, m, ΔV and t presents the gravimetric capacitance (F g^{-1}), current (A), the active mass (g), potential range (V) and discharging time (s), respectively.

$$C_g = \frac{It}{m\Delta V} \qquad (1)$$

The specific capacitance (C_{g2}), energy density and power density of symmetric supercapacitor can be calculated by according to the equations (2, 3 and 4).[2] The C_{g2} presents the gravimetric capacitance (F g^{-1}) of a single electrode. E_g (W h g^{-1}) and P_g (W g^{-1}) present the gravimetric energy density and gravimetric power density basing on the total active material in the cell, respectively. I, ΔV and t present the current (A), the active mass of active material in single electrode (g), potential range and discharging time (s).

$$C_{g2} = \frac{2It}{m\Delta V} \qquad (2)$$

$$E_g = \frac{C_{g2}\Delta V^2}{8 \times 3.6} \quad (3)$$

$$P_g = \frac{E_{g2} \times 3600}{t_{discharge}} \quad (4)$$

References

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