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Supporting information

Engineering Cationic Vacancies on Sphere-like Zinc Cobaltite Microstructures *via* Self-Assembly of Silkworm-like Interconnected Nanoparticles for Battery-type Supercapacitors

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1. Materials

The Nickle foam (NF, 1.6 mm thickness) used in this experiment was purchased from MTI Corporation, USA, Zinc (II) nitrate trihydrate [$Zn(NO_3)_2 \cdot 3H_2O$], and Cobalt (II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$], Urea [CH_4N_2O], potassium hydroxide [KOH] as obtained from Sigma-Aldrich. Hydrochloric acid [HCl] and Dimethylformamide [DMF, C_3H_7NO] were received from Dae-Jung Chemical & Metals Co., LTD. The deionized water (DIW) was made in our lab.

2. Material characterization

The crystal structures of the produced V_{Zn}-ZCO sample were inspected using an X-ray diffractometer (XRD; PANalytical X'Pert Pro) with a Cu-Kα radiation source is 1.54 A°. Fourier transforms infrared (FTIR) spectra were recorded on a spectrophotometer (model 5300, Jasco, USA) to obtain the bonding information. Thermogravimetric analysis (TGA) of the sample was recorded on a thermal analyzer (SDT-Q 600, TA Instruments USA). Field emission SEM (FESEM; S-4800, Hitachi, Japan) was used to examine the morphologies of the sample, and an X-ray column linked to the FESEM apparatus was used to assess the sample elemental composition. Images were captured using a field-emission electron gun in the Schottky mode while being operated at 200 kV for high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F20 S-Twin, USA). A small number of the sample were mixed in ethanol, sonicated for 10 min, dropped onto a commercially available C-coated Cu grid, and dried for 10 min under visible light for the HRTEM imaging. A monochromatic Al Kα X-ray photoelectron spectrometer (XPS, K-alpha, Thermo Scientific, USA) was used to measure the chemical composition and oxidation states of the V_{Zn}-ZCO sample. The commercial program Avantage was used to record and process the data (version 5.932, Thermo Scientific, USA). Using a surface analyzer (3-Flex, Micrometrics, USA) N_2 adsorption-desorption curves were recorded.

3. Electrode preparation

The active electrode material was drop-cast using commercial Ni foam as a current collector. The working electrode was washed with a 1 M HCl solution, DI water, and ethanol for 10 min each under ultrasonication to remove the surface oxide layer, and it was then dried at 80 °C for three

hours before being drop-cast into the Ni foam (2.5 x 1 cm^2). The subsequent step involved dispersing the 80:10:10 weight ratio mixture of V_{Zn}-ZCO sample (active material), PVDF (binder), and carbon black (conductive material) in 0.5 mL of an NMP solution. Over a working area of 1.5 x 1 cm^2, the slurry was drop-cast over the cleaned Ni foam, where it was then dried for 9 hours at 80 °C. Finally, a thin film of V_{Zn}-ZCO -coated Ni foam working electrode was formed by applying a pressure of 10 MPa.

4. Electrochemical measurements

At room temperature, the electrochemical measurements were carried out utilizing a three-electrode setup and a computerized electrochemical workstation (BioLogic, EC Lab software version V11.36). In this experiment, aqueous 3 M KOH was employed as the active electrolyte, and the reference, counter, and working electrodes were Ag/AgCl, a Pt wire, and coated Ni foam, respectively. Galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) curves, as well as electrochemical impedance spectroscopy (EIS), were used to assess the electrochemical performance of the V_{Zn}-ZCO electrode.