Supplementary Information

Metal-Organic Framework-Derived Ultra-Microporous Bismuth Oxide Synchronizing Energy Density and Stability in Symmetric Supercapacitors

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Physical Characterizations

The X-ray diffraction (XRD) patterns were acquired with a high-resolution RIGAKU (RU-200BH) X-ray diffraction meter, using Cu Kα radiation having of 1.54 Å monochromatic wavelengths as the source. The intensity data was gathered utilizing a step size of 0.001°/s in angle-range of (10°- 80°). N_2 adsorption and desorption measurements were performed at 77 K utilizing a BELSORP-MAX-II analyzer (BEL Japan, Inc.). The Brunauer-Emmett-Teller (BET) method was utilized to ascertain the surface area and pore volume of the synthesized samples, with testing conducted in the relative pressure (P/P_0) range of 0.05 to 1.0. The elemental composition, chemical states, and electronic structure were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI-5000 VersaProbe III spectrometer. The surface morphologies and elemental analysis of samples were analyzed using a scanning electron microscope (SEM) and Energy-dispersive X-ray analysis (EDX), model KYKY-2800B was conducted at an accelerating voltage of 30 kV and a Touch off angle of 30°. The Stellar Net Fourier Transform Infrared (FT-IR) spectrometer (FS5-SC-05) was utilized to analyze the structural bands and molecular structure.

The average crystallite size using x-ray diffraction was calculated using equation 1 below:

$$D = \frac{k\lambda}{\beta.cos\theta} \quad (1)$$ [17]

The % crystallinity of the prepared samples were calculated using the equation as mentioned below:

$$(\%)Crystallinity = \frac{\sum Area\ of\ crystalline\ peaks}{\sum Area\ of\ crystalline\ peaks + Area\ of\ amorphous\ halo} \times 100 \quad (2)$$ [17]

Electrochemical Characterizations

All electrochemical characterizations were done using a Metrohm (PGSTAT-204) potentiostat/galvanostat in a three-electrode setting at ambient temperature. The apparatus included a glassy carbon working electrode functionalized with an active material, an Ag/AgCl reference electrode, and a platinum wire counter electrode, and 1 M KOH as the electrolyte. The electrochemical measurements were carried out in 1 M KOH aqueous electrolyte. Alkaline electrolytes are particularly suitable for Bi_2O_3-based electrodes due to the reversible redox activity of Bi species in OH^--rich environments. KOH provides high ionic conductivity and fast OH^- ion transport, which enhance charge-transfer kinetics and reduce internal resistance.

Additionally, 1 M concentration ensures a balance between ionic conductivity and electrochemical stability. Based on preliminary optimization experiments, 1 M KOH was selected as the optimal electrolyte for the present study. To assess both the electrochemical behaviors and capacitive response, cyclic voltammetry (CV) was performed at a meaningful potential range at different scan rates. Galvanostatic charge-discharge (GCD) tests at various current density parameters were conducted in order to find the specific capacitance, rate capability, and cycling stability. The electrochemical impedance spectroscopy (EIS) was conducted within the frequency band (specify range, say 100 kHz to 0.01 Hz) at open circuit potential using an AC amplitude.

Ink Preparation Procedure

For electrochemical measurements, a slurry (ink) was prepared by mixing 0.016 g of the synthesized active material with Nafion binder solution (5 wt%) and ethanol in an 8:1:1 mass ratio (active material : Nafion solid content : solvent). The mixture was ultrasonicated to obtain a homogeneous and stable dispersion. A controlled aliquot of the prepared ink was drop-cast onto a pre-treated glassy carbon working electrode and dried at 80 °C to ensure uniform adhesion and solvent evaporation. The mass loading of the active material on the working electrode was determined using a high-precision microbalance. The active material loading (approximately 0.2 mg per electrode) was calculated from the difference between the mass of the coated electrode and that of the bare glassy carbon electrode. Electrochemical measurements were carried out in 1 M KOH aqueous electrolyte (pH ≈ 14 at room temperature).

The electrochemical properties, including specific capacitance were calculated from GCD curves using the equations below:

$$Cs = \frac{I}{m} \times \frac{dt}{dv}$$

(3)[18]

The co-relation factor R^2 extrapolated from peak current were calculated using the following equation:

$$R^2 = 1 - \frac{\sum (yi - y'i)^2}{\sum (yi - y^-)^2}$$

(4)[18]

The diffusion co-efficient was calculated from EIS spectra using the equation below:

$$D = 0.5 \times (R \times T)^2 (A \times n^2 \times F^2 \times C \times \sigma)^2$$

(5)[19]

The energy and power densities, were derived from galvanostatic charge-discharge (GCD) curves of the synthesized samples using the following equations.

Energy Density (E_d) = E = ½ × Cs × V^2 (6)[20]

Power Density = E_d × 3600/Δt (7)[21]

Supercapacitor device Fabrication

A symmetric supercapacitor was built with MOF-derived Bi_2O_3 as an active material of the positive and negative electrode. The electrodes to be used in the working solution were prepared by applying a uniform layer of a mass mixture of MOF-derived Bi_2O_3, carbon black, and PVDF binder on copper tape sources in a mass ratio of (8:1:1). The electrodes were 1 cm^2 in geometric area. Active material loading on the positive electrode was 2.216 mg and 2.213 mg on the negative electrode, respectively, which validates almost similar mass loading. Charge balance with a symmetric supercapacitor gives:

$$q^+ = q^- \quad (8)$$

$$m^+ Cs^+ \Delta V = m^- Cs^- \Delta V \quad (9)$$

The mass loading (m) should be done equally because all the electrode materials were loaded with the same kind of material and they are operated in the same potential window. The two electrodes have a minimal deviation of less than 0.2% and this confirms that the mass matches and the devices are well fabricated. The overall active weight of the assembled apparatus was thus 4.429mg. Between the electrodes, a porous filter paper separator that was soaked in 1 M KOH electrolyte was used followed by placing the cell together and sealing it as illustrated in (Fig. 10a) in main manuscript. Two-electrode experiments were carried out on a potential range of 0-0.6 V using 1 M aqueous KOH and electrochemical. The charge storage behavior, electrochemical kinetics and cycling stability of the symmetric device were analyzed using cycle voltammetry (CV), galvanostatic charge/ discharge (GCD), and electrochemical impedance spectroscopy (EIS).

Supporting Figures

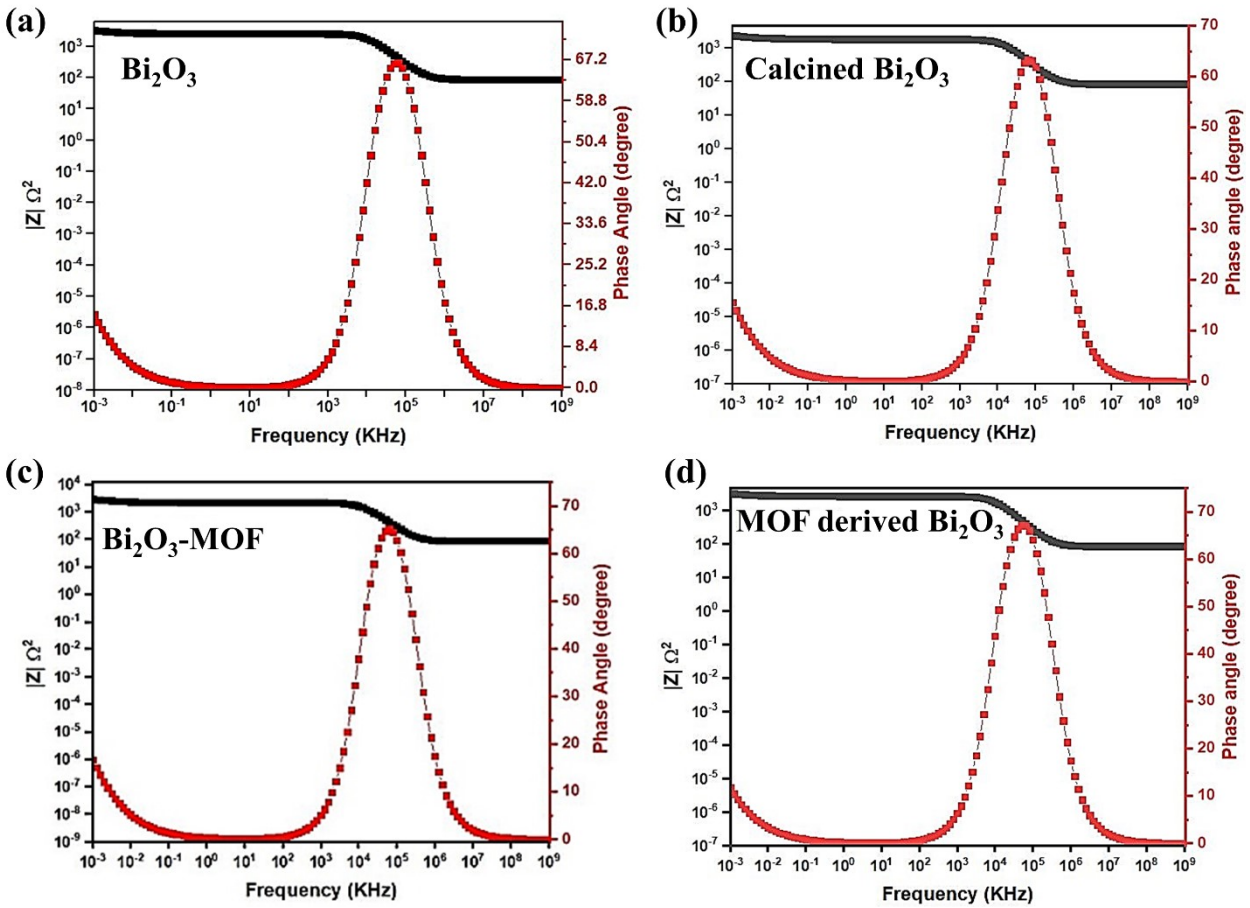

Fig. S1 Electrochemical Bode Plots of (a) Bi_2O_3, (b) Calcined Bi_2O_3, (c) Bi_2O_3-MOF, (d) MOF derived Bi_2O_3.