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Ismail Adegbola Akintayo

SRM University-AP

Rasik Manve

SRM University-AP

Jatis Kumar Dash

SRM University-AP

Sabyasachi Mukhopadhyay

sabyasachi.m@srmap.edu.in

SRM University-AP

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CORRELATING CHARGE-STORAGE KINETICS, QUANTUM CAPACITANCE, AND SURFACE CHARGE DENSITY IN $\text{Bi}_2\text{O}_2\text{S}$: AN EXPERIMENTAL-DFT STUDY

*Ismail Adegbola Akintayo, Rasik Manve, Jatis Kumar Dash & Sabyasachi Mukhopadhyay***

Department of Physics, SRM University-AP, Amaravati, Andhra Pradesh 522240, India

*Corresponding authors: jatis.d@srmap.edu.in; sabyasachi.m@srmap.edu.in

ABSTRACT

Understanding charge storage in layered electrode materials requires distinguishing electrochemical kinetics from the intrinsic ability of the electrode to accumulate electronic charge. Here, phase-pure $\text{Bi}_2\text{O}_2\text{S}$ was investigated using electrochemical measurements and density functional theory (DFT) calculations to establish this relationship. Cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy revealed a strongly rate-dependent charge-storage response, with a specific capacitance of 866 F g^{-1} at 1 A g^{-1} . The scan-rate dependence gave an average b-value of ~ 0.61 , while Dunn analysis showed that diffusion-dependent processes dominate the charge-storage response. DFT calculations further demonstrated that surface modification alters the electronic charge-storage ability of $\text{Bi}_2\text{O}_2\text{S}$. The calculated quantum capacitance increased from $493.14 \mu\text{F cm}^{-2}$ for the pristine surface to $638.75 \mu\text{F cm}^{-2}$ following OH adsorption. Surface charge densities of 513.46 and $506.76 \mu\text{C cm}^{-2}$ were obtained for K-top and K-hollow configurations, respectively. Experimental surface charge densities approached the DFT-derived range at higher current densities, whereas larger deviations at lower current densities indicate additional contributions from electrolyte-mediated and Faradaic processes. These results establish an experimental-DFT framework for relating rate-dependent electrochemical charge storage to the intrinsic electronic charge-accumulation behaviour of $\text{Bi}_2\text{O}_2\text{S}$.

Keywords: $\text{Bi}_2\text{O}_2\text{S}$; charge-storage kinetics; quantum capacitance; surface charge density; density functional theory; electrochemical-DFT correlation.

1.0 INTRODUCTION

The increasing demand for sustainable energy-storage devices has intensified research towards electrochemical systems for electric transport, portable electronics, and renewable-energy applications^{1,2}. Supercapacitors serve an intermediate device between conventional dielectric capacitors and batteries because they offer relatively rapid charge-discharge cycling and accumulate charge via interfacial and Faradaic processes³. Electric double-layer capacitors (EDLCs) primarily store charge through the reversible accumulation of electrolyte ions at the electrode/electrolyte interface, whereas battery-type and pseudocapacitive electrodes involve charge transfer associated with redox reactions. Hybrid charge-storage systems can therefore combine these mechanisms, but their electrochemical response depends strongly on the electrode structure, surface chemistry, electrolyte-ion transport, charge-transfer kinetics, and electronic properties of the active material^{4,5}. A major challenge in understanding such electrodes is that the experimentally measured capacitance represents the combined response of several processes rather than a single intrinsic material property. During charging, electrolyte ions migrate towards the electrode surface, while electronic charge is simultaneously accumulated in the electrode and this may be accompanied by surface redox reactions or ion incorporation. The relative contribution of these processes depends on the charging rate and the accessibility of electrochemically active sites. Consequently, a high measured capacitance does not necessarily represent the intrinsic electronic charge-accommodation capability of an electrode. Instead, the experimentally observed response can also depend on accessible surface area, electrolyte penetration, ion transport, electrode architecture, and Faradaic reaction⁶⁻⁸. Distinguishing these contributions is therefore important for establishing a mechanistic description of charge storage.

Quantum capacitance (QC) provides an electronic descriptor for examining this intrinsic response. In a low-dimensional electrode, the total capacitance associated with electronic charge accumulation can be described by the series contribution of the electric double-layer capacitance and QC. It is related to the availability of electronic states around the Fermi level and therefore provides information on the tendency of an electrode to acquire additional electronic charge⁸. Density functional theory (DFT) calculations serve

as complementary tool to electrochemical measurements which is used to examine electronic structure and then allow estimation of quantities such as the density of states, quantum capacitance, and surface charge density (SCD). Interestingly, these calculated quantities should not be directly equated with experimentally measured gravimetric capacitance because the latter additionally contains contributions from electrolyte transport, accessible surface area, ion adsorption, and electrochemical reactions^{9,10}. Establishing the relationship between these electronic descriptors and experimentally accessible charge storage can therefore provide insight into how intrinsic electronic properties contribute to the overall electrochemical response.

Layered bismuth oxychalcogenides, $\text{Bi}_2\text{O}_2\text{X}$ ($\text{X} = \text{S}, \text{Se}, \text{and Te}$), offer a robust material for investigating this relationship owing to their layered crystal structures and composition-dependent electronic properties. $\text{Bi}_2\text{O}_2\text{S}$ consists of alternating cationic $[\text{Bi}_2\text{O}_2]^{2+}$ layer and anionic S^{2-} slabs, giving rise to an anisotropic structure and unique electronic features^{9,11}. In particular, the layered structure of $\text{Bi}_2\text{O}_2\text{S}$ provides surface sites and pathways that can interact with electrolyte species, while its electronic structure can be modified by surface adsorption. These features make $\text{Bi}_2\text{O}_2\text{S}$ relevant for examining the coupling between electrolyte-induced surface processes and electronic charge accumulation.

Despite these features, the charge-storage behaviour of phase-pure $\text{Bi}_2\text{O}_2\text{S}$ has not been sufficiently examined from the perspective of rate-dependent kinetics and its relationship with intrinsic electronic charge accumulation. Conventional electrochemical characterization can establish the dependence of capacitance on scan rate or current density, but it does not by itself distinguish whether the observed changes originate predominantly from ion transport, surface-controlled reactions, or the electronic charge-storage capacity of the electrode. Conversely, DFT calculations provide an electronic description of the electrode surface, but the calculated quantum capacitance and surface charge density represent the intrinsic response of a defined model and do not include all electrolyte-mediated and electrochemical processes present in an experimental electrode. A direct comparison between these two levels of description is therefore necessary to determine under which electrochemical conditions the experimentally accessible charge approaches the intrinsic electronic response of the material.

In the present work, phase-pure $\text{Bi}_2\text{O}_2\text{S}$ was synthesized and investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) to establish its charge-storage kinetics. The scan-rate dependence of the electrochemical response was analysed using the power-law relationship and Dunn's method to distinguish surface-controlled and diffusion-dependent contributions, while EIS was used to examine interfacial charge-transfer and ion-transport characteristics. DFT calculations were subsequently performed for pristine and electrolyte-species-modified $\text{Bi}_2\text{O}_2\text{S}(001)$ surfaces to determine the changes in electronic structure, quantum capacitance, and surface charge density associated with K^+ and OH^- adsorption. The calculated electronic descriptors were then compared with experimentally derived charge-storage characteristics at different current densities. This combined experimental–DFT approach is used to establish how rate-dependent ion transport and Faradaic processes influence the experimentally accessible charge relative to the intrinsic electronic charge-accumulation capacity of $\text{Bi}_2\text{O}_2\text{S}$.

2.0 EXPERIMENTAL METHODS

2.1 Synthesis and Characterization of $\text{Bi}_2\text{O}_2\text{S}$

2.1.1 Chemicals and Reagents

Bismuth nitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], thiourea ($\text{CH}_4\text{N}_2\text{S}$), disodium ethylenediaminetetraacetic acid (Na_2EDTA), sodium hydroxide (NaOH), potassium hydroxide (KOH), N-methyl-2-pyrrolidone (NMP), conductive carbon black, poly(vinylidene fluoride) (PVDF), ethanol, nickel foam, hydrazine hydrate (HH), and deionized (DI) water were used as received without any further purification.

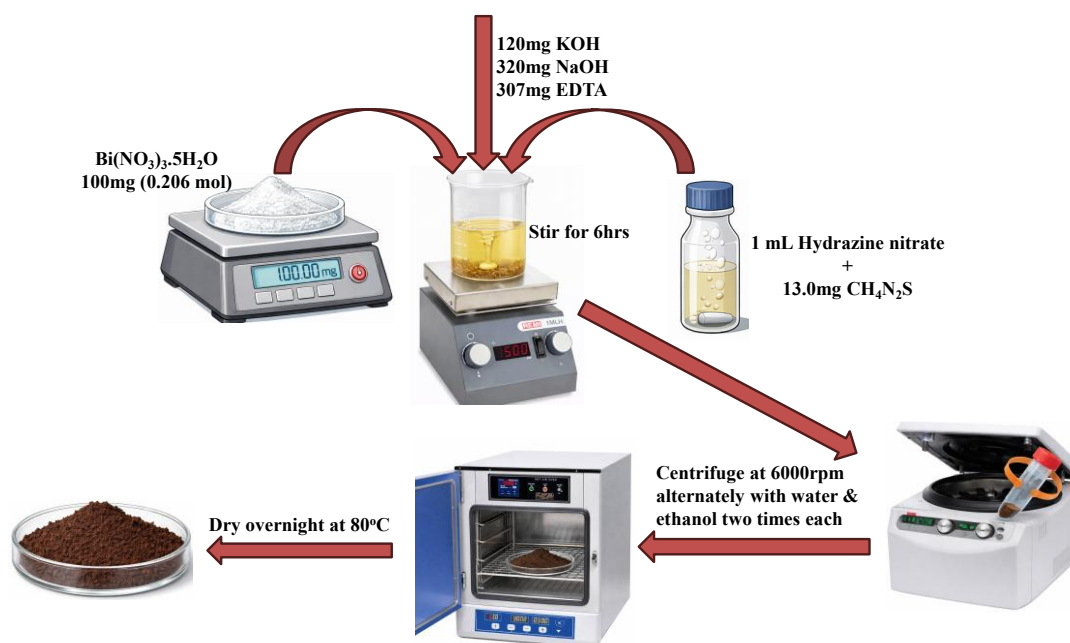
2.1.2 Synthesis of $\text{Bi}_2\text{O}_2\text{S}$

$\text{Bi}_2\text{O}_2\text{S}$ nanosheet was synthesized through a facile wet-chemical precipitation method. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (100 mg) was dissolved in DI water under magnetic stirring for 30 min. In a separate vial, hydrazine hydrate (1 mL) and thiourea (13.0 mg) were mixed and sonicated for 30 min. The resulting solution was added gradually to the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution under continuous stirring. An alkaline solution containing EDTA (307 mg), KOH (120 mg), and NaOH (320 mg) were then added sequentially with stirring. The reaction mixture was stirred for 6 h and left overnight. The precipitate was collected by centrifugation at 6000 rpm,

washed twice each with DI water and ethanol, and dried at 60 °C overnight. The resulting Bi₂O₂S powder was used for further characterization and electrode fabrication.

2.1.3 Characterization

The crystal structure was analysed by X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer operated at 45 kV and 30 mA over a 2 θ range of 5-120°. Surface morphology and microstructure were examined using a JEOL IT800HL field-emission scanning electron microscope (FESEM) at accelerating voltages of 0.1-30 kV. Energy-dispersive X-ray spectroscopy (EDX) was used for elemental analysis and mapping. Fourier-transform infrared (FTIR) spectra were recorded using a Shimadzu IRTracer-100 over 400-4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition and chemical states. N₂ adsorption-desorption measurements were performed at 77 K using an Anton Paar Autosorb 6300 PFE analyser. The Brunauer-Emmett-Teller (BET) surface area and pore-size distribution were determined from the adsorption-desorption isotherms.



2.1.4 Electrode Fabrication and Electrochemical Characterization

2.1.4.1 Electrode Fabrication

Nickel foam (2 x 1 cm²) was used as the current collector. The substrates were ultrasonically cleaned in 2.5 M HCl for 10 min, rinsed with deionized (DI) water, sonicated in ethanol for 10 min, and dried at 60 °C overnight. The electrode slurry was prepared by mixing Bi₂O₂S, conductive carbon, and poly(vinylidene fluoride) (PVDF) in *N*-methyl-2-pyrrolidone (NMP) at a 7:2:1 weight ratio. The slurry was coated onto a 1 x 1 cm² area of the pretreated nickel foam and dried. The active-material loading was determined from the mass difference before and after coating and was maintained at approximately 2 mg per electrode.

2.1.4.2 Electrochemical Characterization

Electrochemical measurements were performed at room temperature using a BioLogic SP-150 potentiostat in a three-electrode configuration with 2 M KOH aqueous electrolyte. Bi₂O₂S-coated nickel foam, platinum foil, and Ag/AgCl served as the working, counter, and reference electrodes, respectively. Cyclic voltammetry (CV) was performed at different scan rates within a potential window selected to avoid electrolyte decomposition. The specific capacitance (C_p) was calculated from the integrated CV area using eqn. (1):

$$C_p = \frac{\int I dV}{2mv\Delta V} \quad [1]$$

Where C_p is measured in $F g^{-1}$, v is scan rate in mVs^{-1} , ΔV is the potential window, and m is mass of active material deposited on the electrode in g. Galvanostatic charge-discharge (GCD) tests were performed at different current densities to evaluate gravimetric C_p , coulombic efficiency, and cycling stability using eqn. 2.

$$C_p = \frac{I_d \Delta t}{\Delta V} \quad [2]$$

where I_d is the current density, Δt (s) is the discharge time, m (g) is the active-material mass, and ΔV is discharge potential window excluding IR drop. Electrochemical impedance spectroscopy (EIS) was

conducted from 100 kHz to 0.01 Hz to evaluate the interfacial and charge-transfer characteristics of the electrode.

2.2 Modelling and Computational Details

First-principles calculations were performed using the Vienna *Ab initio* Simulation Package (VASP)¹². The projector augmented-wave (PAW) method was used to describe the ionic cores and valence electrons, with the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) for exchange-correlation effects¹³. Long-range van der Waals interactions were included using the Grimme DFT-D3 correction. The HSE06 hybrid functional¹⁴ was used to obtain the bandgap of bulk $\text{Bi}_2\text{O}_2\text{S}$. A plane-wave cutoff energy of 520 eV was used for the bulk and slab calculations shown in **Fig. 2**. Atomic positions were relaxed until the total-energy change was below 1×10^{-6} eV and the residual force on each atom was below $0.01 \text{ eV } \text{\AA}^{-1}$. Brillouin-zone sampling employed Monkhorst-Pack meshes of $7 \times 7 \times 1$ for structural relaxation after convergence tests and $15 \times 15 \times 1$ for density-of-states calculations.

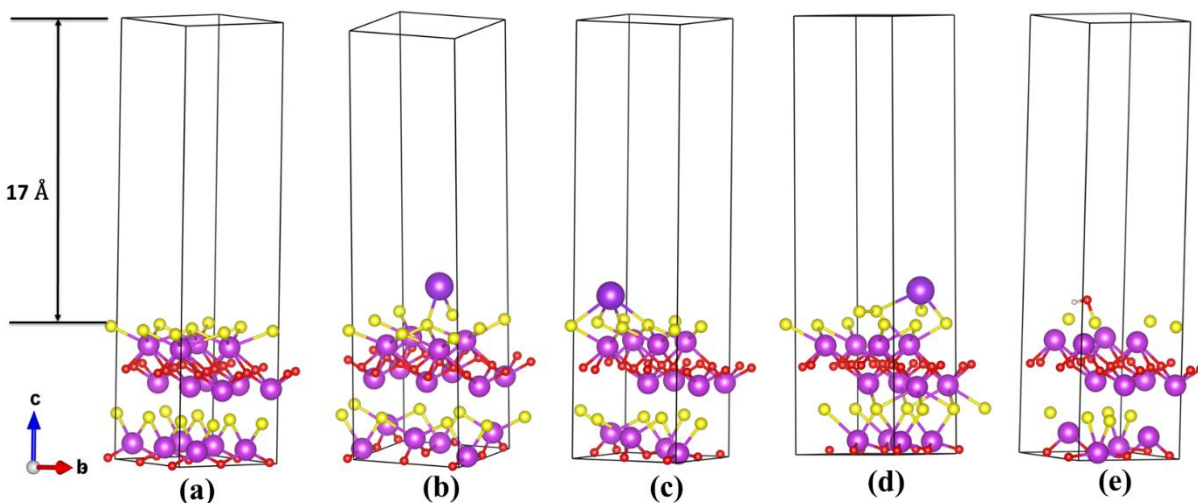


Fig. 2: Optimized atomic configurations of the $\text{Bi}_2\text{O}_2\text{S}$ (001) slab: (a) pristine surface, (b) K adsorption at the top site, (c) K adsorption at the hollow site, (d) K adsorption at the bridge site, and (e) OH^- adsorption on the $\text{Bi}_2\text{O}_2\text{S}$ (001) surface.

A finite $\text{Bi}_2\text{O}_2\text{S}(001)$ slab was used to model the electrode/electrolyte interface. K^+ adsorption was considered at top, hollow, and bridge sites, while OH^- adsorption was also examined on the $\text{Bi}_2\text{O}_2\text{S}(001)$ surface. A vacuum layer of approximately $17 \text{ \AA}$ was introduced along the out-of-plane direction to minimize

interactions between periodic slabs. The relaxed structures were used to calculate the electronic structure, QC (C_Q), and surface charge density (SCD). (C_Q) was calculated from the differential relation

$$C_Q = \frac{dQ}{d\Phi} = e^2 DOS(-Ve) \quad [3]$$

V is the voltage window, Q denotes the change in accumulated charge Q, and $d\Phi$ represents the change in local potential Φ . The excess charge ΔQ is given by the eqn. 4¹⁵

$$\Delta Q = \int_{-\infty}^{+\infty} DOS(E)[F(E) - F(E - e\Phi)]dE \quad [4]$$

where e is the elementary charge, $F(E)$ is the Fermi-Dirac distribution, and (E) is the energy relative to the Fermi level. (C_Q) was then evaluated using

$$C_Q = e^2 \int_{-\infty}^{+\infty} DOS(E)F_T(E - e\Phi)dE \quad [5]$$

$$F_T(E) = \frac{1}{4k_B T} \text{sech}^2\left(\frac{E}{2k_B T}\right) \quad [6]$$

where the thermal broadening function was evaluated at T = 300 K and k_B is the Boltzmann constant. The surface charge density (σ) over the potential range was obtained by integrating the quantum capacitance:

$$\sigma(\Phi) = \int_0^\Phi C_Q d\Phi \quad [7]$$

3.0 RESULT AND DISCUSSION

3.1 Structural, Morphological and Surface Characterization

The XRD pattern of the synthesized $\text{Bi}_2\text{O}_2\text{S}$ is shown in **Fig. 3(a)** and was used to investigate its crystal structure and phase composition. The diffraction peaks located at approximately 24.6° , 29.3° , 32.9° , 44.9° , 47.3° , 58.1° , 68.8° , and 78.5° are indexed to the (110), (040), (101), (141), (002), (132), (212), and (172) planes of orthorhombic $\text{Bi}_2\text{O}_2\text{S}$ (space group $Pnmm$, JCPDS No. 34-1493). No additional reflections associated with Bi_2S_3 , Bi_2O_3 , or other bismuth sulphide impurities are observed¹⁶⁻¹⁸, confirming the phase formation of $\text{Bi}_2\text{O}_2\text{S}$. The strongest reflection occurs at approximately 32.9° , corresponding to (101) plane, indicates preferential crystallographic orientation. This feature is consistent with anisotropic growth

observed in layered bismuth oxychalcogenides $[\text{Bi}_2\text{O}_2\text{X}]$, arising from their alternating $[\text{Bi}_2\text{O}_2]^{2+}$ and X^{2-} layers^{17,19,20}. Using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad [8]$$

where K is shape factor (0.94), λ is the Cu $K\alpha$ wavelength (1.5406 Å), β is full width at half maximum (FWHM), and θ is Bragg diffraction angle. Crystallite sizes estimated using eqn. 8 are summarized in **Fig. S2(a)** and **Table S2**, the values range from 5.66 and 12.39 nm, with an average value of 9.76 ± 2.16 nm, confirming the nanocrystalline nature of the synthesized $\text{Bi}_2\text{O}_2\text{S}$.

The Raman spectrum in **Fig. 2b** exhibits prominent bands near 155 and 960 cm^{-1} and a weaker feature around 300 cm^{-1} . The band near 155 cm^{-1} is assigned to an A_{1g} vibrational mode, while the feature around 300 cm^{-1} is associated with a B_{1g} mode. The higher-frequency band near 960 cm^{-1} is attributed to Bi-S stretching vibration. The observed Raman features are consistent with the vibrational characteristics reported for $\text{Bi}_2\text{O}_2\text{S}$ ^{19,21}.

The FESEM images (**Fig. 2c, d**) show the morphology of the synthesized $\text{Bi}_2\text{O}_2\text{S}$. The lower-magnification image (**Fig. 2d**) shows densely packed nanosheet agglomerates, whereas the higher-magnification image (**Fig. 2c**) shows thin, interconnected sheets with an irregular platelet-like morphology. Interparticle voids are visible between the sheets, giving the material a three-dimensional porous appearance. The EDX spectrum (**Fig. 2e**) shows signals corresponding to Bi, O, and S, with no additional elemental peaks. The measured elemental ratios are close to the expected stoichiometric composition, while the small deviations may be attributed to the inherent limitations of EDX quantification, particularly for light elements²². Elemental maps of Bi, O, and S are shown in **Fig. S3(a-d)**. The three elements are distributed relatively uniformly across the examined region, with no obvious elemental segregation.

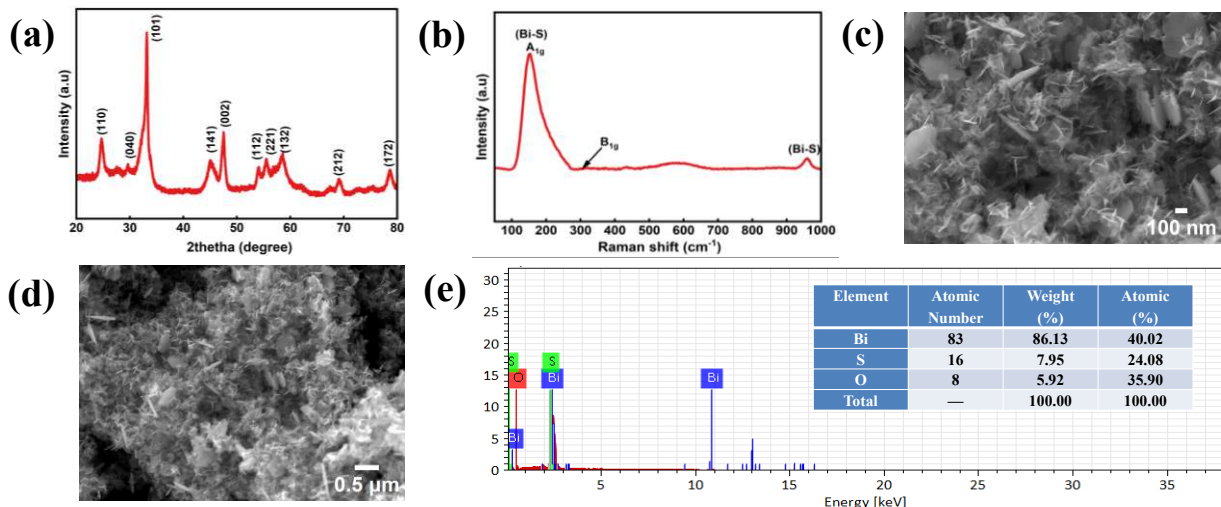


Fig. 3: (a) XRD pattern of orthorhombic $\text{Bi}_2\text{O}_2\text{S}$ (b) Raman spectrum of synthesized $\text{Bi}_2\text{O}_2\text{S}$ NS recorded using a 735 nm excitation laser (c, d) FESEM images at different magnifications showing the hierarchical nanosheet morphology of $\text{Bi}_2\text{O}_2\text{S}$ (e) EDX spectrum with quantitative elemental analysis of Bi, O and S

The FTIR spectrum of $\text{Bi}_2\text{O}_2\text{S}$ is displayed in **Fig. 4a**. The broad band at $3200\text{--}3400\text{ cm}^{-1}$ is assigned to O-H stretching from surface hydroxyl groups and adsorbed water. The weak band near 2900 cm^{-1} is related to C-H stretching, and the band at 1627 cm^{-1} corresponds to H-O-H bending of adsorbed water. The bands between 1000 and 1400 cm^{-1} are associated with C-O-containing groups. The bands near 930 and $460\text{--}600\text{ cm}^{-1}$ are assigned to Bi-O and Bi-S vibrations, respectively, consistent with $\text{Bi}_2\text{O}_2\text{S}$ formation^{9,23}.

The N_2 adsorption-desorption isotherm of $\text{Bi}_2\text{O}_2\text{S}$ (**Fig. 4b**) shows a type-IV isotherm with an H3 hysteresis loop, indicating a mesoporous structure associated with stacked nanosheets. The increase in N_2 uptake above $P/P_0 = 0.90$ is related to capillary condensation in the mesopores and interparticle voids. The BET surface area, pore volume and average pore diameter are $48.91\text{ m}^2\text{ g}^{-1}$, $0.2399\text{ cm}^3\text{ g}^{-1}$ and 24.0 nm , respectively. The BJH pore-size distribution (**Fig. 4c**) shows pores mainly in the $5\text{--}50\text{ nm}$ range, with a maximum around 24 nm . These features indicate that the material has a mesoporous structure with accessible surface area for electrolyte ions. The BET fitting data are given in **Fig. S3(a)**.

The XPS survey spectrum (**Fig. S3(f)**) shows Bi, O, S and C. The Bi 4f spectrum (**Fig. 4d**) consists of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks at 159.2 and 164.6 eV , respectively, with a separation of 5.4 eV , showing with the presence of Bi^{3+} oxidation state in the material and no other states like Bi^0 , Bi^{5+} . The S 2p spectrum (**Fig.**

4e) shows S 2p_{3/2} and S 2p_{1/2} peaks at 161.4 and 162.6 eV, respectively, which are assigned to S²⁻ species bonded with Bi^{20,24}. The O 1s spectrum (**Fig. 4f**) contains peaks at 530.1, 531.9 and 533.6 eV, corresponding to lattice oxygen, oxygen-deficient/vacancy-related species and adsorbed oxygen/water, respectively²⁴⁻²⁷.

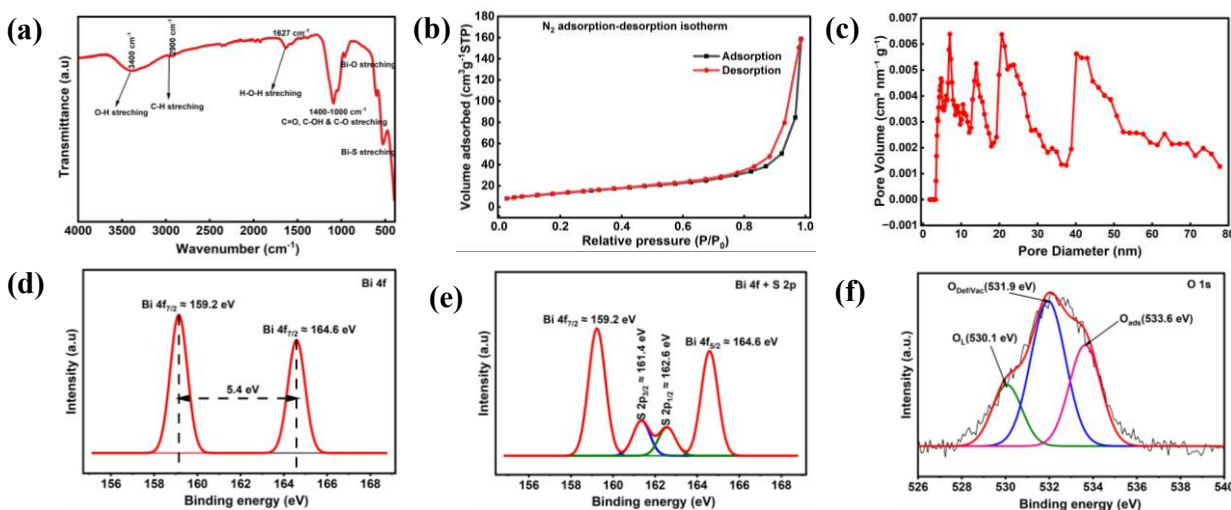


Fig. 4: (a) FTIR spectrum showing the characteristic Bi-O and Bi-S vibrations (b) N₂ adsorption-desorption isotherm (c) Pore-size distribution obtained from BJH method for Bi₂O₂S (d) XPS deconvoluted Bi 4f and S 2p spectra, (e) Bi 4f spin-orbit splitting, (f) O 1s peak fitting.

3.2 Electrochemical charge-storage behaviour

3.2.1 CV response and rate-dependent kinetics

The electrochemical response of Bi₂O₂S was evaluated by cyclic voltammetry (CV) at scan rates of 10-100 mV s⁻¹ within 0-0.6 V (vs Ag/AgCl), as shown in **Fig. 5a**. The CV curves retain their overall shape with increasing scan rate, although a slight shift in the redox peaks is observed because of electrode polarization. The presence of distinct anodic and cathodic peaks indicates that charge storage is mainly associated with reversible Faradaic reactions. In alkaline electrolyte, these reactions involve Bi redox sites and OH⁻ ions, with ion transport through the layered structure contributing to the overall response. Similar behaviour has been reported for Bi₂O₂Se and Bi₂O₃ electrodes in alkaline electrolytes^{9,28}. The scan-rate dependence of the

peak current was evaluated using $i = av^b$, where (i) is the peak current, (v) is the scan rate, and (b) is the kinetic parameter. A (b) value of 0.5 indicates diffusion-controlled behaviour, whereas a value of 1 indicates surface-controlled kinetics. The average (b) value of approximately 0.61 (**Fig. 5b**) indicates a mixed charge-storage mechanism, with a substantial diffusion contribution. The specific capacitance decreases from approximately 420 F g⁻¹ at 10 mV s⁻¹ to 150 F g⁻¹ at 100 mV s⁻¹ (**Fig. S4(c)**), corresponding to about 36% retention. The decrease at higher scan rates is associated with restricted ion transport and incomplete utilization of electroactive sites. The observed capacitance is within the range reported for related bismuth-based electrodes^{29,30}.

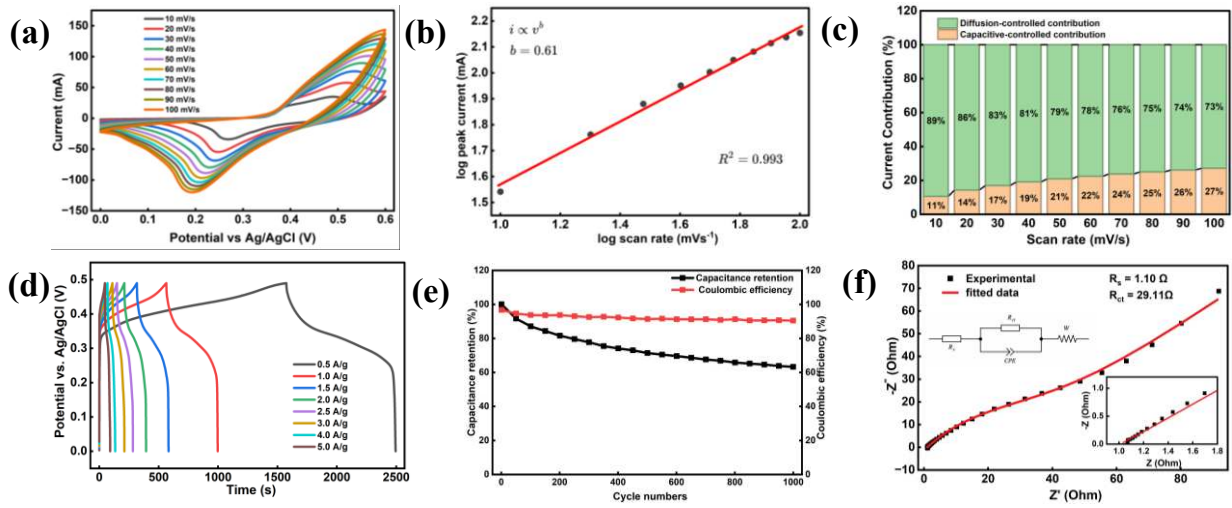


Fig. 5: (a) Cyclic voltammetry curves of Bi₂O₂S electrode at various scan rates, (b) log (i) vs log(v) plot for determination of b-value, and (c) capacitive and diffusion-controlled contributions (d) GCD curves at current densities 0.5-5 A g⁻¹ (e) cycling stability and coulombic efficiency over 1000 cycles (d) Nyquist plot of the Bi₂O₂S electrode with the fitted equivalent circuit (R_s - R_{ct} -CPE- W) inset with high-frequency region.

3.2.2 Capacitive and diffusion-controlled contributions

The contributions from surface-controlled and diffusion-controlled processes were further quantified using

$$i_p = k_1 v + k_2 v^{1/2} \quad [8]$$

and

$$i_p / v^{1/2} = k_1 v^{1/2} + k_2 \quad [9]$$

where k_1 and k_2 are constants, i_p is the peak current determined by the sum of capacitive-controlled ($k_1 v$) and diffusion-controlled ($k_2 v^{1/2}$). The values of k_1 and k_2 are evaluated from a linear fitting of $i_p/v^{1/2}$ versus $v^{1/2}$. As shown in **Fig. 5(c)**, the diffusion-controlled contribution is dominant over the scan-rate range investigated. At 10 mV s⁻¹, diffusion-controlled and surface-controlled processes account for 89% and 11% of the total response, respectively. With increasing scan rate, the surface-controlled contribution increases to 27% at 100 mV s⁻¹, while the diffusion-controlled contribution decreases to 73%. Thus, charge storage in Bi₂O₂S is dominated by diffusion-assisted Faradaic processes, with a smaller surface-controlled contribution that becomes more pronounced at higher scan rates. This trend is consistent with the (b) value obtained from the scan-rate analysis in **Fig. 5(b)**

3.2.3 GCD performance and rate capability

The charge-storage behaviour was further examined by galvanostatic charge-discharge (GCD) measurements at current densities of 0.5-5.0 A g⁻¹ (**Fig. 5d**). The profiles show distinct charge and discharge plateaus, consistent with Faradaic charge storage. The specific capacitance decreases from approximately 920 F g⁻¹ at 0.5 A g⁻¹ to 470 F g⁻¹ at 5.0 A g⁻¹, corresponding to 51% retention (**Fig. S4(d)**). The decrease with increasing current density results from the shorter time available for ion transport and redox reactions within the electrode. The cycling stability was evaluated at 5 A g⁻¹ for 1000 cycles (**Fig. 5e**). The electrode retains approximately 63% of its initial capacitance, while the coulombic efficiency remains between 91 and 94%. The capacitance loss may arise from gradual changes in the electrode structure and loss of electroactive sites during repeated ion insertion and extraction. The cycling result indicates that further improvement in long-term stability is required for practical application.

3.2.4 EIS and ion-transport characteristics

Electrochemical impedance spectroscopy (EIS) was used to examine the interfacial and ion-transport characteristics of the Bi₂O₂S electrode. The Nyquist plot and equivalent-circuit fitting are shown in **Fig. 5(f)**. The circuit consists of solution resistance (R_s), charge-transfer resistance (R_{ct}), a constant phase element (CPE), and Warburg diffusion impedance (Z_W). The high-frequency intercept gives an (R_s of 1.01

Ω , while the semicircle corresponds to an R_{ct} of approximately 29.11 Ω . The CPE parameters ($Q = 0.0196$ $F.s^{\alpha-1}$, $\alpha = 0.649$) indicate non-ideal capacitive behaviour, consistent with surface heterogeneity arising from nanosheet stacking and the distribution of electroactive sites^{31,32}. The inclined low-frequency region indicates ion diffusion within the electrode. The Warburg impedance is given by

$$Z_w = \sigma \omega^{-0.5} (1 - j) \quad [10]$$

where σ Warburg coefficient, ω is the angular frequency, and j is the imaginary unit. Accordingly, the real component of the impedance can be expressed as:

$$Z_{rel} = R_s + R_{ct} + \sigma \omega^{-0.5} \quad [11]$$

where R_s and R_{ct} denote the solution resistance and charge-transfer resistance, respectively. The calculated Warburg coefficient is 15.77 $\Omega s^{-1/2}$, indicating a measurable contribution to the overall impedance response. This agrees with the CV analysis, which showed that diffusion-controlled processes account for 73-89% of the total charge storage contribution. The EIS results therefore support the mixed surface-controlled and diffusion-assisted charge-storage mechanism identified from the scan-rate analysis.

3.3 Electronic Structure and Electrolyte-Induced Surface Modification

3.3.1 Electronic Structure of Adsorbed Bi₂O₂S

First-principles calculations were performed to study the electronic structure of Bi₂O₂S using the PBE, HSE06, and HSE06+SOC approaches. The calculated band structures and projected density of states (PDOS) are presented in **Fig. S11**. The corresponding band gaps are 0.83, 1.54, and 1.36 eV for PBE, HSE06, and HSE06+SOC, respectively, compared with the experimentally determined optical band gap of 1.10 eV (**Fig. S3(g)**). The PDOS shows that the valence-band maximum is dominated primarily by S 3p states, with a smaller contribution from O 2p states, whereas the conduction-band minimum is mainly associated with Bi 6p states. These results establish the electronic states that contribute to the near-Fermi-level response of Bi₂O₂S and provide a reference for evaluating changes induced by electrolyte-species adsorption.

3.3.2 K^+ and OH^- Adsorption on $Bi_2O_2S(001)$

To examine the electrode-electrolyte interface, a $Bi_2O_2S(001)$ slab was constructed as a representative surface model. The (001) surface was selected based on its reported stability, while K^+ and OH^- were considered as representative electrolyte species used in electrochemical measurements. The adsorption configurations and corresponding adsorption energies are summarized in **Table S12** and **Fig. S9**. All investigated configurations exhibit negative adsorption energies, indicating favourable interactions between the electrolyte species and the $Bi_2O_2S(001)$ surface. OH^- shows strongest interaction with the surface, with an adsorption energy of -9.90 eV, which is associated with interaction between OH^- and surface Bi sites. The adsorption results were subsequently used to examine the changes in the electronic structure and charge-storage-related properties of the surface. The different K^+ adsorption geometries also produce distinct adsorption energies, illustrating that the local adsorption environment influences the interaction between the electrolyte species and the surface. The adsorption results were subsequently used to examine the changes in the electronic structure and charge-storage-related properties of the surface.

3.3.3 Adsorption-Induced Electronic-State Modification

The effect of electrolyte-species adsorption on the electronic structure of $Bi_2O_2S(001)$ was examined using spin-polarized total and projected density of states (TDOS/PDOS), as shown in **Fig. 6(a-f)**. The corresponding spin-resolved TDOS profiles are provided in **Fig. S13**. The approximately symmetric spin-up and spin-down distributions indicate negligible net magnetization for the investigated configurations. The pristine Bi_2O_2S slab retains its semiconducting character, with the valence-band region dominated by S 3p states with contributions from O 2p orbitals, while the conduction-band region is primarily associated with Bi 6p states. Adsorption of K^+ and OH^- introduces changes in the electronic states near the Fermi level and modifies the contributions of Bi 6p, S 3p, and O 2p orbitals. Among the K^+ configurations, the bridge site produces the most pronounced modification of the electronic states, whereas OH^- adsorption results in a stronger perturbation of the near-Fermi-level region. These adsorption-induced changes indicate that electrolyte species modify the local electronic environment of the Bi_2O_2S surface. The increased density of states near E_F after ion adsorption indicates a greater availability of electronic states for charge

accumulation. This change in the electronic structure is relevant to the quantum-capacitance response of the electrode and provides an electronic basis for the charge-storage behaviour observed experimentally.

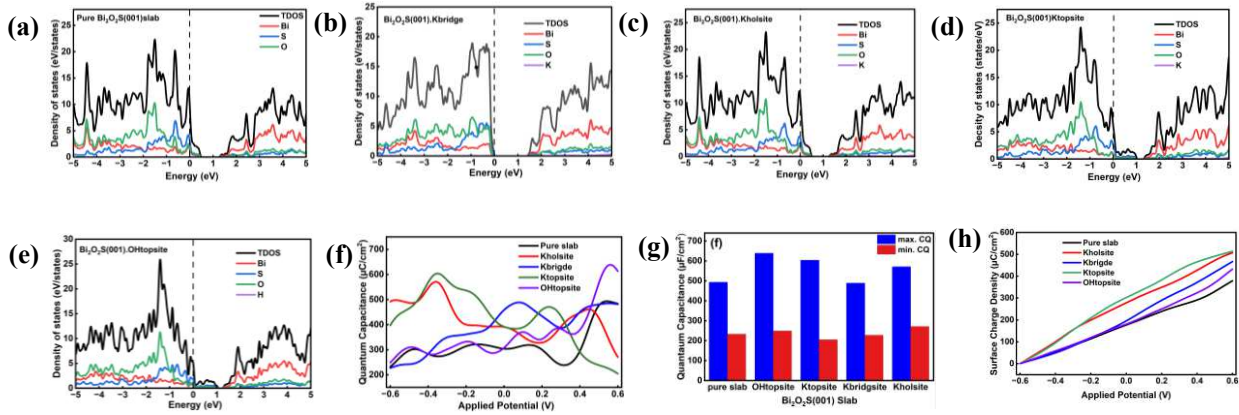


Fig. 6: PDOS of (a) pristine slab (b) K-bridge (c) K-hollow (d) K-top site and (e) OH-top adsorption configurations (f) C_Q vs applied potential for all slabs (g) comparison of the maximum and minimum C_Q values.

3.4 Quantum Capacitance and Surface Charge Density

Quantum capacitance (C_Q) reflects the electronic response of an electrode and is determined by the density of states (DOS) near the Fermi level. It becomes important in low-dimensional and semiconducting materials, where the electronic and electrostatic capacitances can be comparable. The calculated C_Q values over the potential range of -0.60 to $+0.60$ V are shown in **Fig. S14**, with their corresponding plots in **Fig. 6(g)**. Pristine Bi₂O₂S(001) slab shows C_Q values of 232.80 – $493.14 \mu F cm^{-2}$. Ion adsorption changes the potential dependence of C_Q , with the magnitude varying among adsorption configurations. The maximum C_Q values for K-top, K-hollow and K-bridge are 603.83 , 570.82 and $488.67 \mu F cm^{-2}$, respectively. The K-bridge configuration gives a C_Q value close to that of the pristine surface despite its stronger K⁺ adsorption, indicating that adsorption energy alone does not determine the quantum-capacitance response. Instead, C_Q depends on the distribution of electronic states near the Fermi level. The OH-adsorbed surface gives the highest C_Q , reaching $638.75 \mu F cm^{-2}$, with a minimum value of $248.77 \mu F cm^{-2}$. This increase is associated with the modified Bi 6p and O 2p states near the Fermi level. Similar adsorption-induced changes in C_Q

have been reported for low-dimensional electrode materials like transition-metal dichalcogenides and MXenes^{33,34}.

The surface charge density (SCD) was calculated to examine the potential-dependent charge accumulation at the Bi₂O₂S(001) surface. The complete SCD-potential plots are provided in **Fig. S15**, and the corresponding maximum values are compared in **Fig. 6(h)**. The pristine surface reaches a maximum SCD of 378.92 $\mu C cm^{-2}$. K adsorption increases the maximum SCD to 513.46, 506.76 and 466.85 $\mu C cm^{-2}$ for the K-top, K-hollow and K-bridge configurations, corresponding to increases of 35.5%, 33.7% and 23.2%, respectively. OH-adsorption gives a maximum SCD of 431.98 $\mu C cm^{-2}$, an increase of 14.0%. The different trends in C_Q and SCD are noteworthy. OH-adsorption produces the highest C_Q , whereas K-top and K-hollow show higher SCD values. This difference arises from the quantities represented by the two descriptors: C_Q describes the differential electronic response to potential, whereas SCD represents the accumulated surface charge over the potential range. Thus, the C_Q and SCD results provide complementary descriptions of the electronic response of the Bi₂O₂S surface to electrolyte-ion adsorption.

3.5 Linking Electronic Descriptors with Experimental Charge Storage

The calculated C_Q and SCD were compared with the experimental specific capacitance (C_p) from CV and CGD measurements. This comparison was used to investigate the relationship between electronic response of Bi₂O₂S and its measured charge storage behaviour.

3.5.1 C_Q vs. CV-derived C_p

C_Q is converted from areal capacitance ($\mu F cm^{-2}$) to gravimetric capacitance (C_g) in $F g^{-1}$ using experimentally determined BET specific surface area ($SSA = 48.911 m^2 g^{-1}$) with relation³⁵

$$C_g^{DFT} (F g^{-1}) = C_Q (\mu F cm^{-2}) \times S_{BET} \times 10^{-2} \quad [12]$$

The spin-up and spin-down DOS are nearly identical for the relaxed structures. Therefore, the total C_Q was obtained by summing up both spin-channel contributions. C_g^{DFT} is corresponding BET-normalized

gravimetric capacitance. The resulting maximum and minimum C_Q values and their corresponding C_g^{DFT} values are listed in **Table S12**.

The pristine surface has a maximum C_Q of $986.274 \mu\text{Fcm}^{-2}$, corresponding to a BET-normalized C_g^{DFT} of 482.40 F g^{-1} . Among the modified surfaces, OH-top gives the highest maximum C_Q and corresponding C_g^{DFT} , with values of $1277.508 \mu\text{Fcm}^{-2}$ and 624.85 F g^{-1} , respectively. The maximum C_g^{DFT} values for K-top, K-hollow, and K-bridge are 590.69 , 558.39 , and 478.03 F g^{-1} , respectively. The K-bridge value is close to that of the pristine surface, showing that this adsorption configuration produces a comparatively small change in the calculated electronic charge-accumulation response. The CV-derived capacitance decreases from 424.94 F g^{-1} at mVs^{-1} to 146.79 F g^{-1} at 100 mVs^{-1} (**Fig. 7(a)**), demonstrating the reduced utilization of electrochemically accessible charge-storage sites as the scan rate increases. As shown in **Fig. 7(b)**, the maximum BET-normalized C_g^{DFT} of the pristine surface (482.40 F g^{-1}) is close to the CV-derived capacitance at the lowest scan rate. at 100 mVs^{-1} , showing the reduction of the utilization of electrochemically accessible sites at higher scan rates. The calculated value for the pristine surface (482.40 F g^{-1}) is reasonably close to the experimental value at the lowest scan rate, although the BET-converted DFT values provide a qualitative basis for comparison with the experimental capacitance; however, the calculated values generally exceed the experimental measurements because the DFT model represents an idealized crystalline surface, whereas the experimental electrode is affected by defects, aggregation, incomplete electrolyte accessibility, and ion/electronic transport limitations^{35,36}.

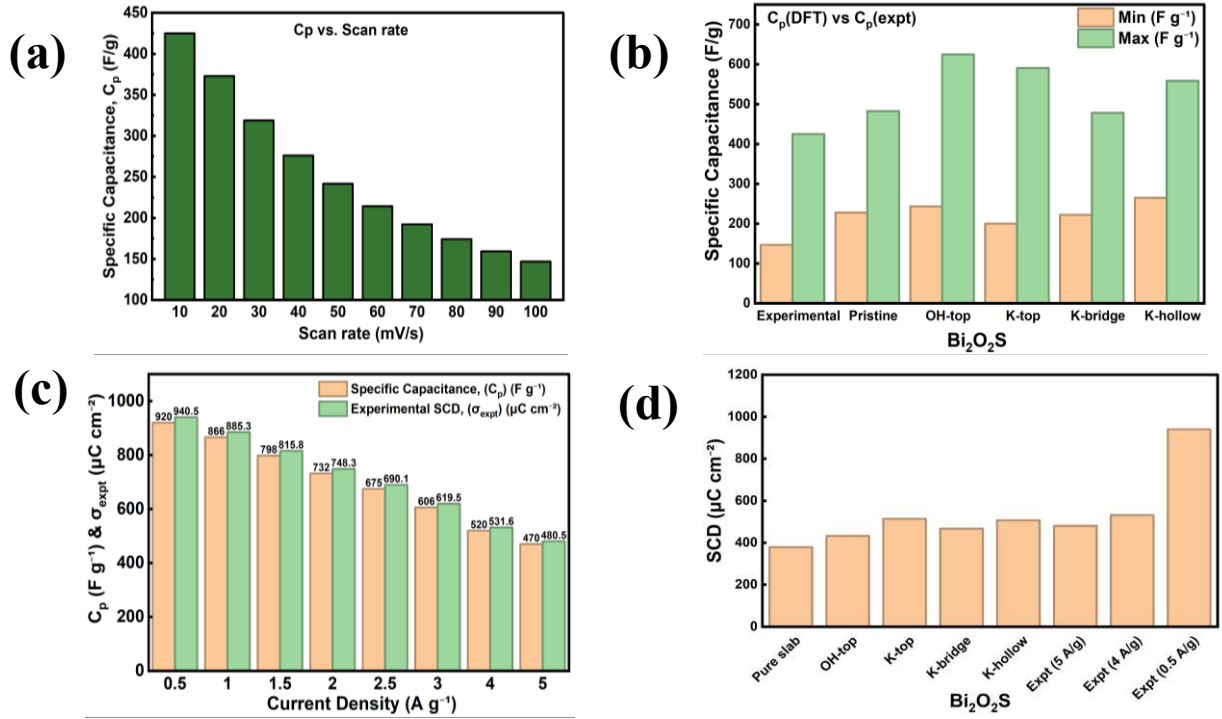


Fig. 7: (a) C_p obtained from CV at different scan rates (b) Comparison of the estimated C_g with experimental C_p (c) C_p and its corresponding σ_{exp} vs. current densities (d) DFT-predicted SCD and experimentally derived SCD from GCD measurements.

3.5.2 SCD and GCD-Derived Charge Storage

The experimental SCD was calculated from the GCD-derived specific capacitance using

$$\sigma_{exp} = \frac{C_{GCD} \Delta V}{S_{BET}} \times 10^2 \quad [13]$$

where C_{GCD} is the specific capacitance obtained from GCD in $F g^{-1}$, ΔV is the discharge potential window in V, S_{BET} is the BET specific surface area in $m^2 g^{-1}$, and σ_{exp} is expressed in $\mu C cm^{-2}$. For $\Delta V = 0.50 V$ and $S_{BET} = 48.911 m^2 g^{-1}$, eq. (13) becomes

$$\sigma_{exp} \approx 1.0223 C_{GCD} \quad [14]$$

The values of σ_{exp} are summarized in **Table S13**, while the comparison between calculated experimental SCD values with the DFT-derived values is presented in **Fig. 7(c-d)**. The DFT studies give maximum SCD values of 378.92, 431.98, 513.46, 466.8, and 506.76 $\mu C cm^{-2}$ for pristine, OH-top, K-top, K-bridge and K-

hollow slabs, respectively. K-adsorption substantially enhances SCD with K-top slab exhibit highest value. A notable correspondence is observed between estimated and experimental SCDs at moderate and high current densities. At 5 A g^{-1} , the experimental SCD of 480.5 falls within the DFT range of 466.8-513.5, while at 4 A g^{-1} , the experimental value of $531.6 \mu\text{C cm}^{-2}$ is close to the calculated range of 506.8-513.5 $\mu\text{C cm}^{-2}$. At 0.5 A g^{-1} , however, the experimental SCD increases to $940.5 \mu\text{C cm}^{-2}$, substantially exceeding the DFT range. This difference reflects the additional contributions of EDL charging, Faradaic reactions, ion adsorption, and diffusion that are not fully represented by the intrinsic electronic charge accumulation obtained from DFT. The longer charging time at low current density also promotes greater electrolyte penetration and active-site utilization. The experimental-to-DFT SCD ratio further supports this trend (**Table 1**). The ratio remains close to unity at $4\text{-}5 \text{ A g}^{-1}$ (1.04-1.05 and 0.94-1.03, respectively), whereas it increases to 1.83-2.48 at 0.5 A g^{-1} . Thus, the close agreement at higher current densities indicates a agreement between the DFT-derived electronic charge-accumulation capacity and experimentally accessible SCD, while the larger deviation at low current density indicates increasing contributions from additional electrochemical processes.

Table 1: Comparison of experimental and DFT-derived SCD

Experimental condition	Experimental SCD ($\mu\text{C cm}^{-2}$)	DFT SCD ($\mu\text{C cm}^{-2}$)	$\sigma_{\text{exp}}/\sigma_{\text{DFT}}$
5 A g^{-1}	480.5	466.8-513.5	0.94-1.03
4 A g^{-1}	531.6	506.8-513.5	1.04-1.05
0.5 A g^{-1}	940.5	378.9-513.5	1.83-2.48

CONCLUSIONS

Phase-pure crystalline $\text{Bi}_2\text{O}_2\text{S}$ was synthesized and investigated by combining electrochemical measurements with DFT calculations. The electrode delivered a specific capacitance of 866 F g^{-1} at 1 A g^{-1} . Rate-dependent analysis gave an average b-value of ~ 0.61 , indicating mixed surface-controlled and diffusion-dependent charge-storage kinetics. Dunn analysis showed that the diffusion-dependent contribution increased from approximately 73 to 89%, while the surface-controlled contribution decreased

from 27 to 11% across the investigated scan rates. Thus, diffusion-dependent processes constitute a major part of the electrochemical response of $\text{Bi}_2\text{O}_2\text{S}$. DFT calculations showed that K^+ and OH^- adsorption modifies the electronic structure of $\text{Bi}_2\text{O}_2\text{S}$ by introducing additional states near the Fermi level and increasing the calculated quantum capacitance and surface charge density. The calculated electronic descriptors showed closer correspondence with the experimental response at higher current densities, whereas the larger deviations at lower current densities indicate additional contributions from electrolyte transport, surface reactions, and Faradaic processes. EIS analysis further showed that charge-transfer resistance and ion diffusion contribute to the overall electrochemical response. After 1000 charge-discharge cycles, the electrode retained 63.3% of its initial capacitance. Summarily, the charge-storage behaviour of $\text{Bi}_2\text{O}_2\text{S}$ arises from the combined effects of diffusion-dependent and surface-controlled processes, electrolyte-ion adsorption, and the resulting changes in the electronic structure. The correlation between the DFT-derived electronic descriptors and experimental electrochemical response establishes a direct framework for examining how the electronic properties of $\text{Bi}_2\text{O}_2\text{S}$ relate to its charge-storage kinetics.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

Raw data supporting the findings of this study are available from the corresponding authors upon reasonable request.

AUTHOR CONTRIBUTIONS

Ismail Adegbola Akintayo: Conceptualization, Methodology, Investigation, Material synthesis, Electrochemical measurements, Formal analysis, Data curation, Visualization, Writing - original draft, Writing - review & editing.

Rasik Manve: FTIR & XRD analysis, BET analysis, Formal analysis, Writing - review & editing.

Jatis Kumar Dash and Sabyasachi Mukhopadhyay: Conceptualization, Methodology, Supervision, Project administration, Writing -review & editing.

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