Graphical Abstract
Synthesis, Crystal Structure and Pseudocapacitor Electrode Properties of γ-Bi$_2$MoO$_6$ Nanoplates

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Abstract

Nanoplate-like bismuth molybdates (γ-Bi$_2$MoO$_6$) is prepared for the first time by urea assisted solution combustion synthesis (SCS) and studied the structural and electrochemical properties to explore the possibility of using as negative electrodes in pseudocapacitors. The formation of single phase γ-Bi$_2$MoO$_6$ and plate like morphology is revealed from XRD Rietveld refinement and FESEM, respectively. The pseudocapacitive behavior of γ-Bi$_2$MoO$_6$ is analyzed by cyclic voltammetry and galvanostatic charge-discharge techniques. The effect of Na based aqueous electrolytes on capacitance of the Aurvillius type structured Bi$_2$MoO$_6$ is investigated. As prepared γ-Bi$_2$MoO$_6$ nanoplates provide the high specific capacitance (519 Fg$^{-1}$) compared with the high-temperature monoclinic phase γ(H) Bi$_2$MoO$_6$ in 1 M NaOH electrolyte. The obtained high specific capacitance of as prepared Bi$_2$MoO$_6$ could be attributed to the decrease in particle size, increase in active sites, and nano plate-like structure of as prepared γ-Bi$_2$MoO$_6$.

Keywords: Combustion synthesis, Bismuth molybdate, Aurvillius structure, Rietveld Refinement, Pseudocapacitor,

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1. Introduction

Electrochemical capacitors (ECs) are considered as an indispensable alternative energy/power sources in recent times since it is widely used in power applications like UPS, cameras, electric vehicles, mobile phones and forklifts and so forth. ECs fill a gap between batteries and conventional capacitors in power and energy density values. It has advantages like high power density, extended cycle life and wide assortment of applications [1-3]. However, the energy density of most of the commercial symmetric supercapacitors based on activated carbon (AC) (about 5 Wh kg$^{-1}$) is lower than in batteries [1]. One of the strategies to improve the energy density is asymmetric fabrication of supercapacitors by using positive and negative electrodes with high working potentials [4].

Recently, metal molybdate (MMoO$_4$ and M$_2$O$_3$.nMoO$_3$, M = metal) based electrodes have received significant interest in Li-ion batteries and supercapacitors due to their stable crystal structure and redox behaviour of metals (Ni, Co and Mn) in aqueous alkali electrolytes [5-15]. Especially, heterostructured MnMoO$_4$/CoMoO$_4$ nanowires showed a SC of 187.1 F g$^{-1}$ and excellent cycling stability [10]. Likewise, CoMoO$_4$/NiMoO$_4$.xH$_2$O bundles delivered a capacitance of 1039 F g$^{-1}$ [11]. It has also demonstrated the suitability of NiMoO$_4$ as a new positive electrode material which provided the SC of 1116 F g$^{-1}$ at 5 mA cm$^{-2}$ [12]. Recently, we have fabricated a full cell based on β-NiMoO$_4$-CoMoO$_4$.xH$_2$O nanocomposite as positive electrode and activated carbon (AC) as negative electrode and the cell delivered a high capacitance (80 F g$^{-1}$) and energy density (28 Wh kg$^{-1}$) and good cycling stability up to 1000 cycles [13]. Liu et. al has fabricated an asymmetric supercapacitor using NiMoO$_4$/AC materials (1.6 V), which delivered a high specific capacitance (SC) of 96.7 F g$^{-1}$ and energy density of 34.4 Wh kg$^{-1}$ [14]. Still the electrochemical performance of metal molybdate based asymmetric capacitor can be increased by finding a suitable negative electrode material.
Bismuth molybdates are the important class of semiconducting materials having the general chemical formula of $\text{Bi}_2\text{O}_3.\text{nMoO}_3$, where $\text{n}=3$, 2, 1. The molybdates are widely used in photocatalytic applications due to its special physicochemical properties [15, 16]. On the other hand, Recently hierarchical structured bismuth molybdate nanowires prepared by facile electrodeposition-heat method has been studied as a negative electrode material for supercapacitors [17]. It delivered a high SC of $1075 \text{ F g}^{-1}$ at $1 \text{ A g}^{-1}$ with good cycling stability up to 1000 cycles in 6 M KOH electrolyte. However they have adopted complicated synthesis procedure and prepared mixture of $\text{Bi}_2\text{MoO}_6$ and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ phases. To the best of our knowledge there is no report on electrochemical properties of single phase $\gamma$-$\text{Bi}_2\text{MoO}_6$ and large scale synthesis of $\gamma$-$\text{Bi}_2\text{MoO}_6$ by combustion synthesis.

In this present work, Aurvillius type structured bismuth molybdate ($\text{Bi}_2\text{MoO}_6$) nanoplates are successfully synthesized by solution combustion synthesis (SCS) technique. The structural, morphological and electrochemical capacitive properties of $\text{Bi}_2\text{MoO}_6$ are characterized. The charge storage mechanisms in Aurvillius type structured $\gamma$-$\text{Bi}_2\text{MoO}_6$ in various electrolytes (1 M NaOH, 1 M $\text{Na}_2\text{SO}_4$, 1 M $\text{NaNO}_3$ and 1 M NaCl) are investigated. The $\gamma$-$\text{Bi}_2\text{MoO}_6$ particles provide high specific capacitance of $519 \text{ F g}^{-1}$ at a scan rate of $2 \text{ mV s}^{-1}$ in 1 M NaOH due to the partial dissolution of $\text{BiO}_2^-$ ionic species, increase in active sites, surface area and decrease in particle size compared to the $\gamma$(H) $\text{Bi}_2\text{MoO}_6$.

2. Experimental

2.1 Material Synthesis

All chemicals were purchased from Aldrich and used as received without further purification. For a typical synthesis of $\text{Bi}_2\text{MoO}_6$, $\text{Bi}_2\text{O}_3$ (2.33 g), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}$ (0.88 g) and $\text{CO(NH}_2)_2$ (0.61 g) were used. Initially, $\text{Bi}_2\text{O}_3$ was dissolved in 5 ml of $\text{HNO}_3$. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}$ and urea were dissolved in 5 ml of $\text{H}_2\text{O}$, separately. The solutions were mixed together to form a homogeneous mixture. An ammonia solution was added to the
above mixture for adjusting pH as 7. Then the solution was placed on hot plate and maintained at the temperature around 200 °C for dehydration. Then the solid precursor was shifted to muffle furnace at 300 °C. After a few minutes, decomposition with gradual release of gases was observed. Finally foamy powder of Bi₂MoO₆ was collected and ground in an agate mortar. The sample Bi₂MoO₆ was calcined at 400 °C and 600 °C for 3h.

2.2 Characterization

Phase formation was identified by Powder X-ray diffractometer 5635 (Siemens, D500 advance) with CuKα radiation. A quantitative two-phase full-profile Rietveld refinement was performed by using WinCSD program package. The Raman spectrum was recorded using LABRAM HR micro Raman spectrophotometer equipped with Ar laser (514.5 nm). To investigate the morphology of the prepared samples, high magnification with a Field Emission Scanning Electron Microscopy (FE-SEM) on a Zeiss Ultra FEG 55 instrument at 20 kV operating voltage. The sample was deposited onto the conductive carbon tapes, which were placed over the top of FE-SEM Cu stubs. The specimen for transmission electron microscopy (TEM) was obtained by drying droplets of the as prepared sample from ethanolic dispersion onto a carbon coated Cu grid (300 mesh). TEM analyses were performed with TECNAI-20 high-resolution transmission electron microscope, using an accelerating voltage of 200 kV.

2.3 Electrode preparation and electrochemical studies

To prepare active electrode material, Bi₂MoO₆ (80 wt %), carbon black (15 wt %) and polyvinilidene fluoride (PVDF) (5 wt %) were suspended in 0.4 ml of N-methyl-2-pyrrolidinone (NMP) to form a slurry. The slurry was coated on a small piece of graphite sheet (area of coating, 1 cm²). The calculated loaded active material was 2 mg. The cyclic voltammetry and galvanostatic charge-discharge studies of the composites were carried out
using VSP, Bio-Logic Science Instruments in 1 M Na₂SO₄, 1 M NaCl, 1 M NaNO₃ and 1 M NaOH electrolytes at room temperature.

3. Results and discussion

3.1 Synthesis of Bismuth molybdate

Solution combustion synthesis (SCS) was adopted for the preparation of bismuth molybdate (Bi₂O₃·nMoO₃, where n=1) was performed by using urea as a fuel. The SCS technique has advantages of short reaction time and high reaction temperature attained by exothermic combustion reactions [18, 19]. Initially, the bismuth oxide precursor was dissolved in nitric acid and converted to bismuth nitrate. The fuel to oxidant ratio was maintained as one to produce ignition of mixed precursors. The combustion of urea facilitates to increase flame temperature by generation of gases. The reaction is,

\[14\text{Bi(NO}_3\text{)}_3 + (\text{NH}_4\text{)}_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O} + 32\text{CO(NH}_2\text{)}_2 \rightarrow 7\text{Bi}_2\text{MoO}_6 + 32\text{CO}_2 + 80\text{H}_2\text{O} + 56\text{N}_2\]

3.2 Structural analysis

The XRD phase analysis of as prepared Bi₂MoO₆ revealed that all diffraction maxima, with an exception of the weak peak at 25.2 deg., assigned to the γ-Bi₂MoO₆ (koechlinite) phase. However, a minor amount of bismuth oxide could not be ruled out, because the positions of all reflections of Bi₂O₃ coincide with the maxima of the main Bi₂MoO₆ phase. In order to make a final conclusion about the presence of the bismuth oxide in the as-prepared Bi₂MoO₆ sample, a quantitative two-phase full-profile Rietveld refinement has been performed by using WinCSD program package [20]. Atomic positions in γ-Bi₂MoO₆ (space group Pca2₁) and in δ-phase of Bi₂O₃ (space group Fm3m) reported in references [21] and [22] were used as a starting models for the refinement. Several our trials of refinement process showed that including of secondary Bi₂O₃ phase into the refinement procedure improve the fit and residuals in comparison with the single-phase mode (Fig. 1). According to the data obtained, the relative amount of γ-Bi₂MoO₆ and δ-Bi₂O₃ phases in the as-prepared
sample is 88 wt.% and 12 wt.%, respectively. During the refinement procedure, the lattice parameters of both phases were refined together with background and peak profile parameters and correction of absorption and instrumental sample shift. Positional and displacement parameters of atoms were refined only for the main \( \gamma \)-Bi\(_2\)MoO\(_6\) phase. At that for the oxygen species a so-called “soft” refinement procedure was used and their displacement parameters were refined in overall mode. For the minority Bi\(_2\)O\(_3\) phase only the lattice parameter was refined, whereas positional and displacement parameters of atoms were fixed according to the data [22]. The refined structural parameters of the \( \gamma \)-Bi\(_2\)MoO\(_6\) phase in urea as-prepared sample, as well as the residuals obtained are given in Table 1.

Thermal treatment of the Bi\(_2\)MoO\(_6\) sample at 400 °C for 3 hours practically does not change the phase composition of the specimen: according to the results of two-phase Rietveld refinement, the sample consists of 90 wt. % \( \gamma \)-Bi\(_2\)MoO\(_6\) and 10 wt.% of Bi\(_2\)O\(_3\). However, some narrowing of the diffraction maxima of the main \( \gamma \)-Bi\(_2\)MoO\(_6\) phase is observed, which may indicate the increase of the average particle size after the heat treatment. The increasing particle size in the 400 °C annealed sample is confirmed by FESEM data (see section 3.3).

Quite different phase behaviour is observed in the Bi\(_2\)MoO\(_6\) sample after heat treatment at 600 °C for 3 h. Examination of the XRD pattern show that high-temperature monoclinic modification of bismuth molybdate - \( \gamma(H) \)Bi\(_2\)MoO\(_6\) according to the notations of [23, 24] – is the predominant phase in this sample (Fig. 2). Besides, the residual reflections of room-temperature \( \gamma \)-Bi\(_2\)MoO\(_6\) phase are presented at the XRD pattern. It is evident, that the high-temperature \( \gamma(H) \)Bi\(_2\)MoO\(_6\) phase is formed due to irreversible structural phase transition which occurs in Bi\(_2\)MoO\(_6\) above 600 °C [24-26]. Relative amount of both Bi\(_2\)MoO\(_6\) phases has been established by simultaneous two-phase full-profile Rietveld technique. According to the results obtained, the sample annealed at 600 °C consists of 89 wt. % of high-temperature
γ(H)Bi₂MoO₆ phase and 11 wt.% of residual γ-Bi₂MoO₆ (Fig. 2). During the refinement procedure, the lattice parameters of both modifications of Bi₂MoO₆ were refined together with background and peak profile parameters and correction of absorption and instrumental sample shift. The atomic positions in γ(H)Bi₂MoO₆ and γ-Bi₂MoO₆, obtained from neutron powder diffraction experiments in Refs. [24 and 21], were fixed at all stages of the refinement procedure.

Table 2 summarizes the refined lattice parameters of the crystalline phases detected in all three samples investigated. For a comparison, the literature data for the corresponding phases are presented as well. Figure 3 represents the crystal structures of both modifications of Bi₂MoO₆ in projection on xy-planes. Structure of γ-Bi₂MoO₆ is plotted by using of Rietveld refined structural parameters presented in Table 1, whereas for the representation of high-temperature γ(H)-Bi₂MoO₆ structure the atomic position reported in [24] were used.

Similar to the relative tungsten compound Bi₂WO₆, γ-structure of the bismuth molybdate with the layered Aurivillius type of structure is usually represented as perovskite-like slabs of (MoO₄)²⁻, which are sandwiched between fluorite-like (Bi₂O₂)²⁺ layers, as shown in the left panel of figure 3. The (MoO₄)²⁻ slabs are formed by deformed MoO₆ octahedra sharing four corners with the neighbouring MoO₆ octahedra in the same plane perpendicular to the b axis [21, 28]. In the (Bi₂O₂)²⁺ layers the Bi³⁺ ions have a pyramidal coordination and sterochemically active lone pair of electrons, which are directed into the sandwiched (MoO₄)²⁻ slabs in an asymmetric manner. It may be a reason for the distortion and tilting of MoO₆ octahedra observed in γ-Bi₂MoO₆ structure [21, 27].

In contrast to the room-temperature γ-structure, the high-temperature polymorph of Bi₂MoO₆ is characterized by tetrahedral coordination of Mo ions and is closely related to the α- and β-molydates Bi₂Mo₃O₁₂ and Bi₂Mo₂O₉ with fluorite-related structures [31]. The γ(H)-Bi₂MoO₆ structure (Fig. 3, right panel) is characterized with an original organization of
Bi$^{3+}$ and O$^{2-}$ species making columns and ribbons linked to MoO$_4$ tetrahedra as demonstrated by Buttrey et al. [24] on the basis of structural determination by neutron powder diffraction technique.

According to the literature data, a transition between $\gamma$-Bi$_2$MoO$_6$ and $\gamma$(H)-Bi$_2$MoO$_6$ structures passes through a formation of intermediate $\gamma$(I)-Bi$_2$MoO$_6$ phase, which exist in a narrow temperature range between a reversible phase transition at 567–604 °C and an irreversible, reconstructive phase transformation at 604–670 °C into a fluorite-related $\gamma$(H)-Bi$_2$MoO$_6$ structure [26,30,31]. There is still a discussion in the literature on the structure of intermediate Bi$_2$MoO$_6$ phase. Sankar et al. [30] suggested that this phase has the same symmetry as the low temperature $\gamma$-Bi$_2$MoO$_6$ but with more distorted MoO$_6$ octahedra. Buttrey et al. [31] concluded that the distinction between the $\gamma$(L)- and $\gamma$(I)-forms is primarily due to the presence or absence, respectively, of incommensurate in-plane modulations. However, in the recent studies of polymorphism in Bi$_2$MoO$_6$ and Bi$_2$WO$_6$ structures it was suggested that the orthorhombic intermediate phase of Bi$_2$MoO$_6$ is nonpolar (point group $mmm$) [26]. In the last studies was also suggested that Bi$_2$MoO$_6$ might exhibit one more phase transition at 310 °C into a polar Aurivillius type phase with orthorhombic symmetry (point group $2mm$) [26].

The high temperature $\gamma$(H) phase modification of as prepared Bi$_2$MoO$_6$ at a calcinations temperature of 600 °C is further evidenced from Raman spectrum. Fig. 4 shows the Raman spectrum of 600 °C calcined Bi$_2$MoO$_6$. The observed peaks at 901, 884, 867, 827, 793 and 774 cm$^{-1}$ are assigned to stretching modes of Mo-O bond [32, 33]. The strong intense peak at 901 cm$^{-1}$ is due to the antisymmetric stretching of Mo-O mode which is characteristic of MoO$_4$ tetrahedra [34]. Peaks due to bending modes of MoO$_6$ octahedral unit and stretching, bending modes of Bi-O is obtained in the spectral region of 270-320 cm$^{-1}$ [32-34]. The $\gamma$(L) phase of Bi$_2$MoO$_6$ has a more regular MoO$_6$ octahedron with bands in the spectral
region of 730-540 cm\(^{-1}\) [32]. The absence of Mo-O stretching bands of MoO\(_6\) octahedra in the spectral region 730-540 cm\(^{-1}\) and the presence of characteristic peak of MoO\(_4\) tetrahedra are indicating the \(\gamma(H)\) Bi\(_2\)MoO\(_6\) structure with slightly distorted and isolated MoO\(_4\) tetrahedra [32].

3.3 Morphological Analysis

The morphology of as-prepared and calcined Bi\(_2\)MoO\(_6\) samples was analyzed by FESEM and are shown in Figure 5. It can be clearly seen from the Figure 5 (a,b) that the nano plate-like structure of as-prepared Bi\(_2\)MoO\(_6\) particles. The sizes of the nanoplates are in nanometer range (25-180 nm) and thickness of the nanoplates is around 8 nm. The FESEM image of 400 °C calcined Bi\(_2\)MoO\(_6\) (Fig. 5 (c,d)) shows increase in particle size (90-200 nm), which is due to the agglomeration and coalescence of nanoplates. The size (300-500 nm) and shape of the 600 °C calcined Bi\(_2\)MoO\(_6\) sample completely changed from as prepared sample owing to the phase transition of Bi\(_2\)MoO\(_6\) (\(\gamma\) to high temperature \(\gamma(H)\) phase) and coalescence of grains. The increase in calcinations temperature will increase the diffusion rate. The rise in diffusion rate will speed up coalescence process of neighboring grains which produces increase in particle size and larger structures of the calcined samples [35]. The TEM image of Bi\(_2\)MoO\(_6\) particles showed nanoplate-like morphology of as prepared Bi\(_2\)MoO\(_6\) particles and substantiate the FESEM results (Fig. 6 a, b). When comparing the morphology of three different crystal phases of bismuth molybdates, nano plate-like structure of the as prepared Bi\(_2\)MoO\(_6\) particles are more suitable for charge storage by the increase in active sites of the material. It is believed that nano plate-like structures could improve electrochemical performance due to the increase in surface area and active sites of the electrode material and a decrease in diffusion distance of electrolyte [36, 37]. The N\(_2\) adsorption-desorption isotherms, pore size distributions (BJH-plot) of as prepared Bi\(_2\)MoO\(_6\) nanoplates is shown in Figure 7. The calculated specific surface area (\(S_{BET}\)) is 8.8 m\(^2\) g\(^{-1}\) for nanoplate-like Bi\(_2\)MoO\(_6\). Further,
the presence of mesopores and macropores on the surface of the particle is evidenced from the BJH curve (inset Fig. 7). The observed pores may facilitate to improve the electrode/electrolyte contact area, which enhances the more number of ions to lodge in the electrode material.

3.4 Electrochemical Analysis

The electrochemical behavior of the bismuth molybdates were investigated using three-electrode cells with 1 M NaOH as an electrolyte, in which Pt wire and Hg/HgO were used as the counter and reference electrode, respectively. The cyclic voltammetry (CV) curves of as-prepared and calcined bismuth molybdates recorded at various scan rates of 2 – 50 mV s⁻¹ and are presented in Figure 8 (a-c). A well-defined redox peaks was observed for the bismuth molybdate samples. The observed redox reactions is attributed to the reversible reaction of bismuth(III) to Bi metal, which indicates pseudocapacitance [38, 39]. The redox reactions in bismuth molybdates is similar to bismuth oxide and redox properties of bismuth oxide in hydroxide group containing electrolyte (KOH, NaOH) was well described in various works [38-41]. The reports pointed out that the reduction of bismuth oxide is due to the partial dissolution of the oxide to BiO₂⁻ ionic species in hydroxide group containing electrolyte. The reduction process of BiO₂⁻ ionic species to Bi metal is given by the following reactions,

\[
\text{BiO}_2^- + e^- \rightarrow \text{BiO}_2^{2-} \quad (1)
\]

\[
2\text{H}_2\text{O} + 3\text{BiO}_2^{2-} \xrightarrow{\text{disproportionation}} 2\text{BiO}_2^- + 4\text{OH}^- + \text{Bi}^0 \quad (2)
\]

\[
\text{Bi}^0 \rightarrow \text{Bi} \quad (3)
\]

The oxidation peaks due to the reaction of Bi metal to Bi (III) is observed in the CV curves corresponding to the above reduction reactions. The small oxidation peak in the curve is due
to the small amount of absorbed BiO$_2^-$ ionic species located near electrode/electrolyte interface. Compared to the absorbed BiO$_2^-$ ionic species, the majority of the dissolved BiO$_2^-$ ions produce more peak current by the increase in concentration of BiO$_2^-$ ions. The peak current value and covered current area of the CV curves of the as prepared Bi$_2$MoO$_6$ is relatively higher than the calcined samples. The specific capacitance calculated for the samples are presented in Figure 8 (d), the higher capacitance of 519 Fg$^{-1}$ is delivered by as prepared sample compared to calcined samples. This is not only attributed to decrease in particle size of as prepared Bi$_2$MoO$_6$, the nanoplate-like structure of the material, which enhances the ionic transport and diffusion of electrolytes to improve the active sites [36, 37]. The reproducibility of redox peaks in the given scan rates are due to the rapid electronic and ionic transport [11, 12]. Hence, the as prepared Bi$_2$MoO$_6$ was identified as the optimized electrode based on their better electrochemical performances.

**Effect of anions on the electrochemical capacitance of Bi$_2$MoO$_6$**

In order to understand the charge storage properties of electrode, the electrochemical behavior of the Bi$_2$MoO$_6$ is investigated in various Na based electrolytes including 1M Na$_2$SO$_4$, 1M NaCl and 1M NaNO$_3$. Figure 9 (a-d) shows the CV curves of the optimized Bi$_2$MoO$_6$ in different electrolytes. It shows that the charge storage mechanism of Bi$_2$MoO$_6$ is different in different electrolytes. The observed rectangular form of the CV curve (Fig. 9 (a)) in 1 M Na$_2$SO$_4$ indicates that the electrode stores the charges based on adsorption/desorption of electrolyte ions at the electrode/electrolyte interfaces. In other words, the charge storage in this electrolyte is due to the formation of electrical double layer (EDL) instead of fast surface redox reactions (pseudocapacitance). On the other hand, the prominent redox peaks are obtained in 1 M NaCl and 1 M NaNO$_3$ electrolytes, which confirm the pseudocapacitive behavior of the Bi$_2$MoO$_6$ (Fig 9 b,c). The redox peaks in 1 M NaCl is attributed to Na$^+$ ion intercalation/deintercalation in the electrode matrix. However the material in this electrolyte
exhibits low current compared to 1 M NaNO$_3$ and 1 M NaOH. The observed high peak current in 1 M NaNO$_3$ and 1 M NaOH electrolyte is due to the partial dissolution of the oxide into BiO$_2^-$ ionic species and the reversible reaction of Bi(III) to Bi metal [38, 39].

Fig. 9d shows the comparison of the specific capacitance at 5 mV s$^{-1}$ in all the electrolytes. The obtained specific capacitance of 43, 25, 494 and 519 F g$^{-1}$ is corresponding to 1 M Na$_2$SO$_4$, 1 M NaCl, 1 M NaNO$_3$ and 1 M NaOH electrolyte respectively. The observed difference in specific capacitance can be explained based on the variation of anionic size and pH of the electrolyte. The ionic radius of SO$_4^{2-}$, Cl$^-$, NO$_3^-$ and OH$^-$ ions are 258 pm, 190 pm, 179 pm and 133 pm, respectively [42-44]. It can be seen that the lower anionic radii of OH$^-$ (133 pm) gives the higher specific capacitance of 519 F g$^{-1}$ and vice versa. It reveals that the anionic size is played an important role to achieve the high specific capacitance of the electrode. Similarly, when increasing the anionic size of the ions, the electrode resistance is also increases, i.e., the slope (R=V/I) of the discharge current in CV curve is high at the reverse switching potential [45]. According to the Pour-baix diagram of Bi, the Bi$^{3+}$ ions involves in redox reactions in alkali aqueous (1 M NaOH) electrolyte. On the other hand this reaction is not possible in neutral aqueous electrolytes like NaCl and Na$_2$SO$_4$. The observed redox peaks of Bi$_2$MoO$_6$ in NaOH electrolyte is mainly due to the redox reactions (eqns. 1-3). Hence, the Bi$_2$MoO$_6$ is exhibits higher specific capacitance in 1 M NaOH electrolyte compared to other electrolytes. It is due to the smaller anion (OH$^-$) size and the redox reaction of Bi metal to Bi (III) [38, 39, 42, 43]. Overall, the electrochemical performance of bismuth molybdates is appreciable in 1 M NaOH solution and identified as the optimized electrolyte.

Galvanostatic charge-discharge measurements were also carried out for as-prepared and calcined bismuth molybdate samples which are given in Figure 10 (a-c). The nonlinear form of the curves substantiates the pseudocapacitance behavior of the material. The
capacitance value of the samples was calculated from the charge-discharge curves of as-prepared Bi₂MoO₆ by using the relation [13], \( C = \frac{I}{m \left( \frac{\Delta V}{dt} \right)} \) where, \( I \) is the current density, \( \Delta V \) is the average slope of the discharge curve and \( m \) is mass of the active electrode material. The specific capacitance calculated for Bi₂MoO₆ is 252 F g⁻¹ at a current density of 2 mA cm⁻² which is higher than 400 °C (153 F g⁻¹) and 600 °C (141 F g⁻¹) calcined samples. The available redox reaction active sites (\( z \)) per mole of the samples are calculated using the relation [43], \( z = \frac{C \Delta V}{M} \), where \( C \), \( \Delta V \), \( M \) and \( F \) represents to capacitance, potential window, molecular weight of Bi₂MoO₆ (609.91 g mol⁻¹) and Faradic constant (96,487 C mol⁻¹), respectively. The number of active sites (\( z \)) calculated at a current density of 2 mA cm⁻² to be high (1.59) for as prepared Bi₂MoO₆ compared to 400 (0.97) and 600 °C (0.89) calcined samples. The increase in capacitance value of the as-prepared Bi₂MoO₆ relative to other two samples is due to (1) less particle size (2) nanoplate-like structure of as prepared Bi₂MoO₆ (3) increase in active sites (\( z \)) and surface area of the sample relative to other two samples which enhance the active sites for ionic diffusion and facilitate electronic and ionic transport [42, 43]. The specific capacitance calculated from charge-discharge curves of Bi₂MoO₆ samples at various current densities are presented in Figure 9 (d). The capacitance value calculated for Bi₂MoO₆ is 342, 252, 206, 186, 169 and 139 F g⁻¹ at a current density of 1, 2, 3, 4, 5 and 10 mA cm⁻², respectively. The observed capacitance value of Bi₂MoO₆ (252 F g⁻¹) is higher than the previously reported negative electrodes including Bi₂O₃ (98 F g⁻¹), BiFeO₃ (81 F g⁻¹), and Ti₂FeRuO₂ (110 F g⁻¹) in 1 M NaOH electrolyte [40, 46, 47]. However, it is lower than the reported thin films of Bi₂MoO₆ and Bi₂Mo₃O₁₂ mixture, which was delivered a high SC of 1075 F g⁻¹ at 1 A g⁻¹. It is well documented that the thin film electrodes always give higher specific capacitance than its bulk electrodes due to its excellent electrical contact to the
substrate, *i.e.*, the current collector and the thin film is more favourable for fast electron transfer and electrolyte diffusion [48,49].

In order to well substantiate the above results, the Nyquist plot of Bi$_2$MoO$_6$ nanoplates in various aqueous electrolytes recorded in open circuit potential (OCP) at a frequency range of 1 MHz to 10 mHz is shown in Figure 11 (a). In general, the Nyquist plot is consists of three different regions like (i) low frequency (capacitive region), (ii) mid frequency region (charge transfer resistance), and (iii) high frequency region (equivalent serial resistance). It is well known that the equivalent series resistance includes the solution resistance, intrinsic resistance of electrode and interface contact resistance of electrode and active material. It was observed from the intercept of the real axis of the impedance in the high frequency region [50]. The equivalent series resistance observed for 1 M NaOH is ($R_{ESR}$=1.4 ohm) low compared to other three electrolytes (inset of Fig 11 (a)) due to the lower anionic size (133 pm). The observed low $R_{ESR}$ value is due to the effect of anion size in the electrolyte. It is well documented that OH$^-$ ions having high ionic conductivity or smaller ionic size in aqueous medium than NO$_3^-$ (179 pm), Cl$^-$ (190 pm), SO$_4^{2-}$ (258 pm) ions. Hence, OH$^-$ ions leads to improve the specific capacitance of the Bi$_2$MoO$_6$ nanoplate electrode. Similarly, the observed low frequency tails also infers the pseudocapacitive property of the material. Long-term cycling stability of the sample was tested up to 500 charge-discharge cycles at a current density of 10 mA cm$^{-2}$ which is shown in Figure 11 (b). Initially, the capacitance of the material was decaying up to 30 cycles. After that the capacitance was more stable up to 200 cycles. Finally, more than 100% of the initial capacitance was retained by Bi$_2$MoO$_6$ nanoplates. The electrochemical performances of Bi$_2$MoO$_6$ nanoplates indicate the suitability of the material as a potential negative electrode material for supercapacitors.

4. Conclusions
In this study, γ-phase of Bismuth molybdate was successfully synthesized by solution combustion synthesis (SCS) technique. From the XRD Rietveld refinement, the formation of high-temperature monoclinic modification of Bi$_2$MoO$_6$ was identified for 600 °C calcined sample. Nanoplate-like morphology of the as prepared Bi$_2$MoO$_6$ was characterized by FESEM and TEM. The effect of calcinations temperatures on capacitance of the materials was tested with various Na based electrolytes. As prepared Bi$_2$MoO$_6$ exhibited enhanced electrochemical capacitive performance of high specific capacitance (519 F g$^{-1}$) and good cycling stability in 1 M NaOH compared to other two samples due to the increase in active sites, surface area and the nanoplate-like structure of the γ-Bi$_2$MoO$_6$. The Bi$_2$MoO$_6$ nano plates are found to be a suitable negative electrode for supercapacitors.

References

Figure Captions

Figure 1 Graphical results of two-phase Rietveld refinement showing coexistence of $\gamma$-Bi$_2$MoO$_6$ (blue) and $\delta$-Bi$_2$O$_3$ (red) phases in the urea as-prepared sample. Experimental XRD pattern is shown in comparison with the calculated patterns. The difference between measured and calculated profiles is shown as a curve below the diagrams. Short vertical bars indicate the positions of diffraction maxima of $\gamma$-Bi$_2$MoO$_6$ and $\delta$-Bi$_2$O$_3$ (upper and lower rows, respectively). (Inset) Graphical results of full-profile Rietveld refinement of Bi$_2$MoO$_6$ urea as-prepared sample in single phase mode.

Figure 2 Graphical results of Rietveld refinement showing coexistence of $\gamma$-(H)Bi$_2$MoO$_6$ (blue) and $\gamma$-Bi$_2$MoO$_6$ (red) phases in the sample annealed at 600 °C for 3 h. Short vertical bars indicate the positions of diffraction maxima of $\gamma$-(H)Bi$_2$MoO$_6$ and $\gamma$-Bi$_2$MoO$_6$ (upper and lower rows, respectively).

Figure 3 Crystal structures of room and high-temperature modifications of Bi$_2$MoO$_6$ (left and right panels, respectively). Coordination polyhedra of Mo (MoO$_6$ octahedra and MoO$_4$ tetrahedra) and the shortest Bi-O bonds (up to 2.57 Å and 2.46 Å, respectively) are shown.

Figure 4 Raman Spectrum of Bi$_2$MoO$_6$ sample calcined at 600 °C 3h.

Figure 5 FESEM images of (a,b) as-prepared, (c,d) 400 and (e,f) 600 °C for 3h calcined Bi$_2$MoO$_6$ samples with two different magnifications.
Figure 6 (a) TEM and (b) HRTEM images of as-prepared Bi$_2$MoO$_6$.

Figure 7 N$_2$ adsorption-desorption isotherms and (inset) pore-size distributions of as-prepared Bi$_2$MoO$_6$.

Figure 8 CV curves of (a) as-prepared, (b) 400 and (c) 600 °C calcined Bismuth molybdates and (d) Specific capacitance of Bi$_2$MoO$_6$ samples at various scan rates.

Figure 9 CV curves of as-prepared Bi$_2$MoO$_6$ in various electrolytes (a) 1 M Na$_2$SO$_4$, (b) 1 M NaCl and (c) 1 M NaNO$_3$. (d) SC vs. electrolyte for Bi$_2$MoO$_6$ at 2 mV s$^{-1}$ scan rate.

Figure 10 Galvanostatic charge-discharge curves of (a) as-prepared, (b) 400 and (c) 600 °C calcined Bismuth molybdates and (d) Specific capacitance of Bi$_2$MoO$_6$ samples at various current densities.

Figure 11 (a) Nyquist plot of the Bi$_2$MoO$_6$ nanoparticles in various electrolytes (Inset shows the enlarged Nyquist plot at the high frequency region). (b) Capacitance retention versus cycle number of the Bi$_2$MoO$_6$ nanoparticles.
Figure 1
Figure 2
Figure 3
Figure 4

![Graph showing Raman Shift (cm⁻¹) vs Intensity](image-url)
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9

(a) and (b) show cyclic voltammograms with different scan rates. (a) has scan rates of 5, 10, 20, and 50 mV s\(^{-1}\) and (b) has scan rates of 5, 10, 20, and 30 mV s\(^{-1}\). (c) illustrates the faradaic current response with scan rates of 5, 10, and 20 mV s\(^{-1}\). (d) presents the specific capacitance for solutions of 1 M Na\(_2\)SO\(_4\), 1 M NaCl, 1 M NaNO\(_3\), and 1 M NaOH.
Figure 10
Figure 11

(a) Nyquist plots for different electrolytes: 1 M NaOH, 1 M Na$_2$SO$_4$, 1 M NaCl, 1 M NaNO$_3$. The plots show the relationship between impedance ($Z'$ and $Z''$) and frequency.

(b) Specific capacitance ($F_{g^{-1}}$) as a function of cycle number, indicating the stability and charge retention over multiple cycles.
Table 1. Crystallographic data for γ-Bi$_2$MoO$_6$ (space group $Pca_2_1$, $Z = 4$, $a = 5.493(2)$ Å, $b = 16.214(2)$ Å, $c = 5.498(2)$ Å; $R_I = 0.059$, $R_p = 0.172$)

<table>
<thead>
<tr>
<th>Atoms, sites</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$B_{iso/eq}$ Å$^2$</th>
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</thead>
<tbody>
<tr>
<td>Bi1, 4$^e$</td>
<td>0.5176(7)</td>
<td>0.4216(2)</td>
<td>0.9548(15)</td>
<td>0.53(8)</td>
</tr>
<tr>
<td>Bi2, 4$^e$</td>
<td>0.4789(8)</td>
<td>0.0797(2)</td>
<td>0.9834(15)</td>
<td>0.63(8)</td>
</tr>
<tr>
<td>Mo, 4$^e$</td>
<td>-0.030(2)</td>
<td>0.2392(4)</td>
<td>0.0000*</td>
<td>0.64(10)</td>
</tr>
<tr>
<td>O1, 4$^e$</td>
<td>0.045(12)</td>
<td>0.143(3)</td>
<td>0.078(9)</td>
<td>0.477</td>
</tr>
<tr>
<td>O2, 4$^e$</td>
<td>0.272(15)</td>
<td>-0.007(5)</td>
<td>0.296(12)</td>
<td>0.477</td>
</tr>
<tr>
<td>O3, 4$^e$</td>
<td>0.225(20)</td>
<td>0.505(5)</td>
<td>0.233(18)</td>
<td>0.477</td>
</tr>
<tr>
<td>O4, 4$^e$</td>
<td>0.682(10)</td>
<td>0.234(3)</td>
<td>0.236(13)</td>
<td>0.477</td>
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<tr>
<td>O5, 4$^e$</td>
<td>0.216(7)</td>
<td>0.263(4)</td>
<td>0.354(10)</td>
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<tr>
<td>O6, 4$^e$</td>
<td>0.560(12)</td>
<td>0.356(3)</td>
<td>0.581(9)</td>
<td>0.477</td>
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</tbody>
</table>

* $z$-coordinate of Mo atoms was fixed at 0.
Table 2. Lattice parameters and cell volumes of the $\gamma$-Bi$_2$MoO$_6$, $\gamma$(H)-Bi$_2$MoO$_6$ and $\delta$-Bi$_2$O$_3$ phases in the samples analysed in comparison with the literature data for the corresponding phases.

<table>
<thead>
<tr>
<th>Sample, references</th>
<th>Phase</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$\beta$, °</th>
<th>$V$, Å$^3$</th>
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<tbody>
<tr>
<td>as-prepared</td>
<td>$\gamma$-Bi$_2$MoO$_6$</td>
<td>5.493(2)</td>
<td>16.214(2)</td>
<td>5.498(2)</td>
<td>489.7(4)</td>
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<tr>
<td></td>
<td>$\delta$-Bi$_2$O$_3$</td>
<td>5.492(3)</td>
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<td></td>
<td>165.7(3)</td>
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<tr>
<td>400 °C</td>
<td>$\gamma$-Bi$_2$MoO$_6$</td>
<td>5.497(2)</td>
<td>16.220(2)</td>
<td>5.504(2)</td>
<td>490.8(4)</td>
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<tr>
<td></td>
<td>$\delta$-Bi$_2$O$_3$</td>
<td>5.501(2)</td>
<td></td>
<td></td>
<td>166.5(2)</td>
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<tr>
<td>600 °C</td>
<td>$\gamma$-Bi$_2$MoO$_6$</td>
<td>5.487(2)</td>
<td>16.212(5)</td>
<td>5.514(2)</td>
<td>490.5(5)</td>
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<td></td>
<td>$\gamma$(H)-Bi$_2$MoO$_6$</td>
<td>17.2706(9)</td>
<td>22.443(1)</td>
<td>5.5891(4)</td>
<td>90.481(4)</td>
<td>2166.3(4)</td>
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<td>[27]</td>
<td>$\gamma$-Bi$_2$MoO$_6$</td>
<td>5.4896(3)</td>
<td>16.2266(7)</td>
<td>5.5131(3)</td>
<td>491.0(2)</td>
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<tr>
<td>[28]</td>
<td>$\gamma$-Bi$_2$MoO$_6$</td>
<td>5.487(2)</td>
<td>16.226(6)</td>
<td>5.506(2)</td>
<td>490.2(5)</td>
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<td>[24]</td>
<td>$\gamma$(H)-Bi$_2$MoO$_6$</td>
<td>17.2627(1)</td>
<td>22.4296(2)</td>
<td>5.58489(5)</td>
<td>90.4974(6)</td>
<td>2162.35(4)</td>
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<tr>
<td>[25]</td>
<td>$\gamma$(H)-Bi$_2$MoO$_6$</td>
<td>17.27(2)</td>
<td>22.37(2)</td>
<td>5.593(6)</td>
<td>90.49(7)</td>
<td>2161(7)</td>
</tr>
<tr>
<td>[22]</td>
<td>$\delta$-Bi$_2$O$_3$*</td>
<td>5.478</td>
<td></td>
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<td>164.4</td>
</tr>
<tr>
<td>[29]</td>
<td>$\delta$-Bi$_2$O$_3$*</td>
<td>5.531(1)</td>
<td></td>
<td></td>
<td></td>
<td>169.2(1)</td>
</tr>
</tbody>
</table>

* Normally, this high-temperature polytype is unstable at room temperature, but can be stabilised by cation dopants [22] or due to nanoscale grain sizes [29].
Research Highlights

- The crystal structure of Aurvillius $\gamma$-Bi$_2$MoO$_6$ and $\gamma$(H)Bi$_2$MoO$_6$ was elucidated using Rietveld analysis.
- Nanoplate-like $\gamma$-Bi$_2$MoO$_6$ were prepared by solution combustion method.
- As prepared $\gamma$-Bi$_2$MoO$_6$ nanoplates provide high specific capacitance (519 F g$^{-1}$) than the $\gamma$(H)Bi$_2$MoO$_6$ in 1 M NaOH electrolyte.