Rapid Synthesis of Bismuth Molybdate Nanoplates for Supercapacitor Applications by Microwave Combustion Method

A. Shameem, V. Siva, A. Murugan, Shamima Hussain, S. Asath Bahadur*

Abstract*: Orthorhombic structured bismuth molybdate (Bi_2MoO_6) is obtained by one pot microwave combustion method. The characteristic performance of Bi_2MoO_6 nanocatalyst are described by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) furnished with Energy - dispersive X-ray spectroscopy (EDS) and Fourier change infrared (FT-IR) spectroscopy. The average crystallite size for Bi_2MoO_6 estimated from XRD is about 28.9 nm. The surface morphology from SEM pictures displays nanoplates. The FTIR is utilized to recognize the structural coordination and the presence of functional group. The electrochemical studies are taken to readily comprehend the electrochemical performance of the modified active electrode with notable specific capacitance value are found 234.9 Fg^{-1} at 5 mVs^{-1} and cyclic retention is stable up to 900 cycles (98.7 %). The as-synthesized dynamic material acts as a novel electrode material for supercapacitor.

Keywords: **Bi_2MoO_6, Microwave combustion method, Nanoplates, Electrochemical performance.**

I. INTRODUCTION

Supercapacitors having larger power densities as well as superior cycle stability have drawn significant consideration in course of recent years because of the increased energy anxiety and natural pollutant issues [1]–[4]. Recently, various nanomaterials with large specific surface areas are examined through enhanced charge gathering and ion transportation for electrochemical usage [4]-[8]. Also, the manufacture of fascinating nano-architectures is additionally considered as a powerful technique to uplift the electrochemical behaviours. As of late, the discerning structure of nanosheets [6], [9], [10] nanowire [3], [11] and nanorod [4], [12] has been considered as an incredible accomplishment in electrochemical (EC) research.

Bismuth molybdate (Bi_2MoO_6), an Aurivillius (orthorhombic) type structure is broadly utilized in photocatalytic applications because of their interesting optical and electric behaviours [13]. Also, they are contemplated as an excellent electrode material for supercapacitors. Moreover, it is utilized as an admirable electrode material in supercapacitors, conveys a high specific capacitance with great cyclic stability. This may be because of the fractional dissolution of $(Bi_2O_2)_n^{2+}$ ionic species with incremental active sites. Yet its EC execution is much lower because of their adverse electron transfer. As revealed, Bi_2MoO_6 nanosheets acquiesce a capacitance of 25 F g^{-1} at 5 mVs^{-1} in 1 M NaCl electrolyte [10]. However, their EC properties should be improved practically for applications. As a result, many researchers focused their attention and interest for the development of high performed electrochemical device.

The combustion method facilitated with microwave irradiation, which conspicuously decreases the reaction time, having improved command over dimension and structure of the nanomaterials. This preparation strategy is exceptional as it has numerous favourable circumstances like upgraded response energy, specific materials coupling, quick volumetric warming, high response rate, expanded item yield, most virtue item, and so forth than traditional strategies. Moreover, this technique can suppress the by-products during preparation [2], [4], [5], [14]. They are significant for nanostructured materials development which relies upon the response condition. Only few reports are available on the development of Bi_2MoO_6 nanoplates exhibits for electrochemical applications. Herein the present work, we report a Bi_2MoO_6 nanoplates array on Ni foil, which was effectively achieved by one pot microwave combustion method. The outcomes demonstrate to facilitate the Ni foil-based materials display a prevalent EC behaviour with a high specific capacitance. The nanoplate cluster structures could provide huge surface area and excellent electron transport execution for high rate supercapacitors.

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II. EXPERIMENTAL

A. Material and methods

Bismuth nitrate pentahydrate, Sodium molybdate dehydrate and Urea were bought from Merck, India with AR grade materials. Double distilled (DD) water was utilized all through this investigations. Ethanol was acquired from Sigma Aldrich.

Bi_2MoO_6 nanoplates has been prepared by a simple microwave combustion method as depicted earlier [2], [4], [5]. $Bi(NO_3)_3.5H_2O$, $Na_2MoO_4.2H_2O$ and $CO(NH_2)_2$ (1:1:4 molar ratio) were each dissolved together in 50 mL of DD water under magnetically stirred in ambient condition. Then the solution was moved into a domestic microwave oven IFB-20PG3S. After the reaction, the precipitates were confined and wash down with DD water and ethanol, and dried at oven a night.

B. Characterization and working electrode preparation

The crystal structure of Bi_2MoO_6 was confirmed by Bruker D8 advance ECO XRD systems possesses SSD160 1D Detector XRD. The morphology and elemental confirmation can be investigated utilizing scanning electron microscope: ZEISS EVO 18 Research attached with EDS . The Fourier transform infrared spectra of the powders have been occupied with the scope of 4000–400 cm^{-1} by Shimadzu (IR Tracer-100) spectrophotometer by KBr pellet procedure. The household IFB-20PG3S microwave have been utilized for the preparation having 1000 W with vitality 2.45 GHz.

Moreover, the electrochemical measurements of electrodes made utilizing as-prepared Bi_2MoO_6 were measured with help of cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) systems by the assistance of electrochemical workstation (Model-CHI 6008E, USA). EC execution of an active altered electrode is performed within 3 M KOH electrolyte. The three-electrode cell setup made up of altered Bi_2MoO_6 as a working terminal, Pt electrode as a counter terminal and Ag/AgCl electrode as a reference terminal. The combination of Bi_2MoO_6: acetylene black (85:15) with suitable amount of Nafion (binder) was utilized to form slurry and after that spread on Nickel foil (1 × 1 cm^2).

III. RESULT AND DISCUSSION

A. XRD analysis

Figure1 illustrates a XRD pattern of Bi_2MoO_6 at diffraction peaks between 2θ = 10 - 80°. The diffraction peaks have been recorded to be orthorhombic system with koechlinite phase, relating to JCPDS Card no.:76-2388. The sample has a high level of crystallinity which is clarified by sharp and strong peaks. It is exposed that all the diffraction peaks are promptly recorded to end-centred lattice bismuth molybdenum oxide, with lattice constants: a=5.50 Å, b=16.24 Å, and c=5.49 Å. The prepared Bi_2MoO_6 are orthorhombic crystal structure and Cmca(64) space group. The average crystallite size of Bi_2MoO_6 was determined by well-known Scherrer equation,

$$D = \frac{k\lambda}{\beta COS\theta} \text{ nm} \qquad (1)$$

The average crystallite size was observed around 28.9 nm.

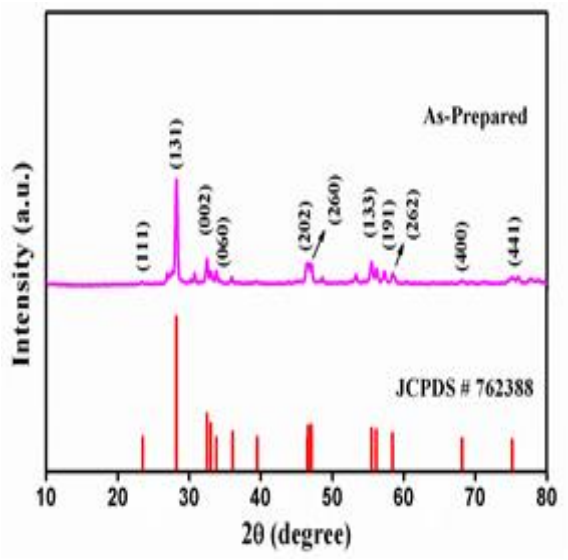

Fig. 1. Powder XRD plots of Bi_2MoO_6 nanoparticles with JCPDS number

B. FT-IR

Figure 2 represents the FT-IR spectrum of the Bi_2MoO_6. A small band is credited at 2320 cm^{-1} might be a result of CO_2 or nitrile group. The significant peaks at 400–910 cm^{-1} have been generally associated to Bi-O, Mo-O extending and Mo-O-Mo connected stretching modes [15]. A peaks around 845 cm^{-1} distributed as asymmetric and a blind peak at 797 cm^{-1} as symmetric stretching modes of Mo-O_6 identifying with the vibrations of O atoms. A peak at 720 cm^{-1} is credited as an asymmetric stretching of Mo-O_6 including vibrations of the central O atom. A peak near 567 cm^{-1} convey as a bending vibration of Mo-O_6. Besides, a peak attributed at 456 cm^{-1}, which is allocated for stretching and bending vibrations of Bi-O_6, asserting the structure of the crystal [16].

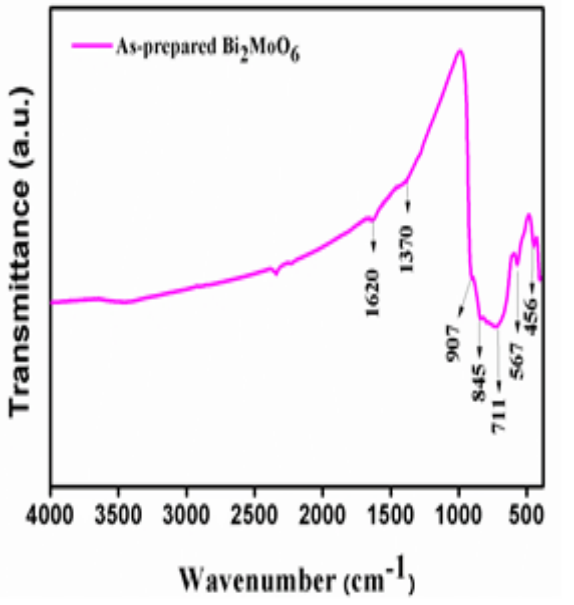

Fig. 2. FT-IR spectrum of Bi_2MoO_6 nanoplates.

C. SEM with EDS

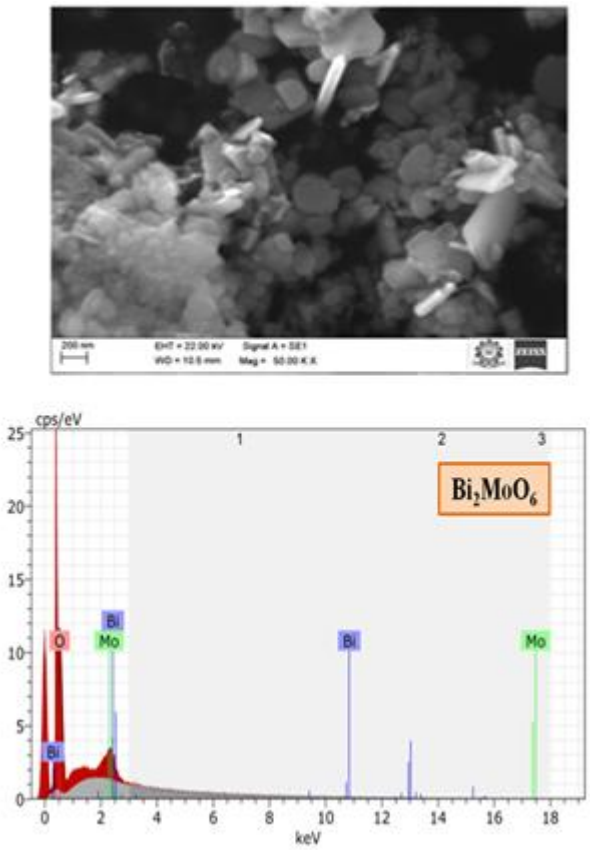

Fig. 3. (a) SEM picture and (b) EDS spectrum of Bi_2MoO_6 nanoplates

The preliminary seed crystallographic stage is a fundamental factor responsible for the shape affirmation of the crystals. At the point when the crystalline stage is settled, the ascribed cell structures of the seeds solidly impact further development [17]. The Bi_2MoO_6 involves turning $(Bi_2O_2)_n^{2+}$ stratum, perovskite-like $(MoO_4)_n^{2-}$stratum, and octahedral Mo chains assure in the intense intrinsic anisotropic improvement in various molybdates [18]. The surface morphology of Bi_2MoO_6 was confirmed using SEM and ascribed in figure 3 (a) which affirms that the as-prepared nanomaterials having the uniform size nanoplates like structures.

A fine homogeneity was seen for Bi_2MoO_6 by EDS relating with XRD pattern. It is worth seen that the occurrence of Bi, Mo, C and O by EDS analysis and is shown in figure 3(b). The C presence is because of the carbon tape utilized in EDS analysis. The component offers further bits of knowledge for the basic preparation and dispersion inside the Bi-Mo-O nanomaterials. Bi, Mo, and O in Bi_2MoO_6 are very much disseminated, representing that they can be portrayed as Bi-Mo-O combinations.

D. Electrochemical Properties

a. Cyclic Voltammetry analysis

Figure 4 (a) shows CV curves of modified Bi_2MoO_6 electrodes attained on different scan rates (5-75 mVs^{-1}) in the potential scope of -1.0 to 0 V. From the CV analysis, it represents pseudocapacitive behavior. The capacitance characteristics that the electrode is managed by Faradaic, crediting a reversible redox reaction. To procure information about the capacitive properties, specific capacitance (C_{sp}) estimations of the bismuth molybdate nanoplates are determined utilizing

$$C_{sp} = \int Idv \; / \; sm \Delta V \qquad (1)$$

Where, ∫Idv - area of the CV curve (A), s-scan rate (Vs^{-1}), ΔV-potential window (V) and m-mass of the material (g). The C_{sp} values are intended for various scan rates and were plotted in figure 4 (b). The CV curve display two oxidation peaks because of the event, reversible faradaic practice of bismuth (Bi^{3+} to Bi^0) by electrolytic ion diffusion process [19]. The calculated C_{sp} values are 234.9, 227.14, 200.2, 190.96 and 144.06 Fg^{-1} at different scan rate from 5 to 75 mVs^{-1} respectively. In addition, a positive shift of oxidation peaks and negative shift of reduction peaks are noticed, signifying the reversible faradaic redox response of active electrode is improved with increase in scan rate [19].

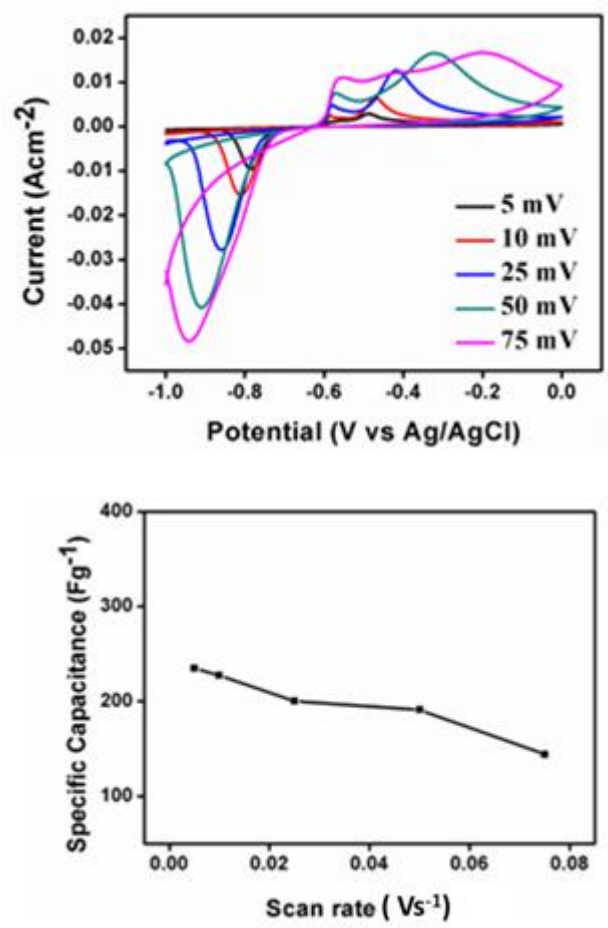

Fig. 4. (a) CV curves of Bi_2MoO_6 nanomaterials The CV measurements of prepared sample at a scanning rate of 5 - 75 mV s^{-1} in 3M KOH electrolyte and (b) C_{sp} of the samples versus scan rate.

b. Chronopotentiometry

Figure 5 (a) signifies the GCD estimation connected with various current densities (1 to 7 mA cm^{-2}) contained by potential -1 to 0 V. At all current densities perception indicates symmetric potential versus time curves.

It recommends prevalent charge-discharge columbic competence with lesser polarization of active materials in the pseudocapacitive profile [20]. The C_{sp} value is much higher than previous report [21]. The cyclic execution is another critical authenticity for supercapacitors in suitable exercise. The elongated cyclic execution of the electrode was evaluated through a constant GCD release system to 1500 cycles at a current density of 3 A g^{-1} is represented in figure 5 (b). The capacitance retention almost remains constant up to 900 cycles (98.7%) and behaves little drop to 92.3% after 1500 cycles. It might be because of the better contact between the sample and electrolyte. Impressing, the cyclic stability remains stable than the previously reported [21]. These results keep the insight for high performed supercapacitors.

Fig. 5. (a) GCD curves at various current densities and (b) Cycling performance of the Bi_2MoO_6 nanoplates at 3 A g^{-1}.

c. Electrochemical impedance spectroscopy

So as to expose the cause for the electrochemical properties of electrodes, EIS are described as well Nyquist plots are exposed in figure 6. The curve exhibits two segments: two semicircles within a low-frequency region and a high-frequency region. Semicircle occurrence in low frequency may be the result of diffusion and accumulation of ions in electrode-electrolyte interface region. The sample

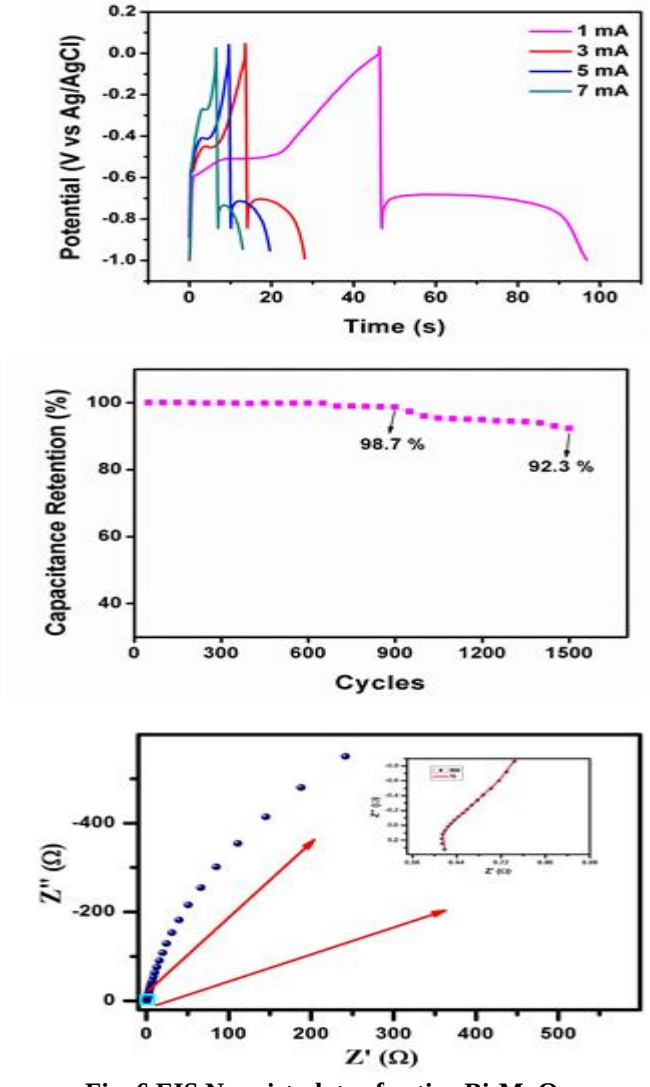

Fig. 6 EIS Nyquist plots of active Bi_2MoO_6.

resistance (R_s) due to its static charge carrier is measured to be 0.60Ω at lower frequency. Charge-transfer resistance (R_{ct}) is measured within the region of semicircle in the frequency region and found to be 0.05Ω. [22], [23].

IV. CONCLUSION

The nanostructured Bi_2MoO_6 nanoplates were effectively prepared by one pot microwave assisted combustion method. XRD pattern exposed orthorhombic koechlinite Bi_2MoO_6 system with an average crystallite size of 28.9 nm. SEM pictures were delineates nanoplates morphology and the presence of appropriate components was in EDS. FT-IR spectrum were utilized for the recognition of structural coordination. XRD, EDS and FT-IR authenticate the prepared Bi_2MoO_6 is impurity free sample. The electrochemical performance was studied and approves the faradaic pseudocapacitive profile. An upgraded C_{sp} sophisticated with 92.3 % retentivity after 1500 cycles. The engineered system bears a fruitful technique to make improved nanostructures for the utilization in supercapacitors.

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