Facile Chemical Synthesis and Potential Supercapattery Energy Storage Application of Hydrangea-type Bi$_2$MoO$_6$

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ABSTRACT: Soft chemical synthesis is used to obtain a hydrangea-type bismuth molybdate (Bi$_2$MoO$_6$) supercapattery electrode that demonstrates considerable energy/power density and cycling life. Structure and morphology studies, initially, reveal a phase-pure polycrystalline and hydrangea-type surface appearance for Bi$_2$MoO$_6$, which upon testing in an electrochemical energy storage system displays supercapattery behavior, a combination of a supercapacitor and a battery. From the power law, an applied-potential-dependent charge storage mechanism is established for the Bi$_2$MoO$_6$ electrode material. A Trasatti plot evidences the presence of inner and outer surface charges. The hydrangea-type Bi$_2$MoO$_6$ electrode demonstrates a specific capacitance of 485 F g$^{-1}$ at 5 A g$^{-1}$ and a stability of 82% over 5000 cycles. An assembled symmetric supercapattery with a Bi$_2$MoO$_6$/Bi$_2$MoO$_6$ configuration demonstrates energy and power densities of 45.6 W h kg$^{-1}$ and 989 W kg$^{-1}$, respectively. A demonstration elucidating the lighting up of three light-emitting diodes, connected in series, by the symmetric supercapattery signifies the practical potentiality of the as-synthesized hydrangea-type Bi$_2$MoO$_6$ electrode in energy storage devices.

1. INTRODUCTION

Energy generation, storage, harvesting, and transportation are highly essential to maintain the cost of living in developed as well as in underdeveloped countries as the development of any country is more or less dependent on the availability of resources. In the upcoming years, the demand for energy will rapidly increase globally and become 10-fold higher than the present requirement; as a result there is a need to acquire energy from modern products and services.1 Therefore, the need for enhanced-performance, inexpensive, and pollution-free or ecofriendly energy production systems is increasing day by day. Several efforts are being made to upgrade the performance of energy storage devices, including supercapacitors and batteries.2 After capacitors have found a niche in the industrial, academic, and research market owing to their special electrochemical properties, such as high energy/power density, stability, galvanostatic charging and discharging processes, impedance, etc.3,4 Various materials including carbon,5–8 transition-metal oxides,9–11 and conducting polymers12,13 have been envisaged as electrode materials in supercapacitors. Generally, carbon-based materials demonstrate a high power density and a low energy density but a long cycling life.14 Transition-metal oxides offer a fast and reversible surface redox reaction with higher specific capacitance (SC) and, therefore, are frequently preferred in commercial energy storage products.15 But poor conductivity,16 low stability,17 limited rate capability, etc., are few of their demerits.18 Various strategies such as tuning nanostructures at the nanoscale dimension,19,20 adatom in the host active material matrix to increase electrical conductivity,21 and mixing two or more active materials with a fast redox reaction22–24 were applied successfully in the past to solve these issues to some extent. Improving the redox reactions and electrical conductivity via mixing of two or more metal oxides is a modern approach in metal oxides, which was previously adopted in metal alloys; thereby, considerable research activities are underway in this direction.25–28 Electrode materials of these composites, sometimes called hybrid materials, demonstrate higher electrochemical supercapacitor performance than individual components. In addition, by forming a composite of two metal oxide electrodes of different properties, i.e., a supercapacitor and a battery, a supercapattery can be easily achieved.29–31 Moreover, in addition to supercapattery performance, both conductivity and surface area of the resultant electrode are optimum. Bismuth molybdate (Bi$_2$MoO$_6$)31–33 CoMoO$_4$34 NiMoO$_4$35 etc., are a few of these supercapattery electrode
Scheme 1. Schematic Presenting the Growth of Hydrangea Flower-Type Bi₂MoO₆ (Photograph Courtesy of PVS)

2. RESULTS AND DISCUSSION

2.1. Growth Mechanism. In the wet chemical method, direct formation of hydrangea-type Bi₂MoO₆ onto Ni-foam, with a three-dimensional (3D) metal architecture, depends on the adsorption and ion-by-ion condensation, which is highly suitable and used in the past for producing nanostructures of mixed metal oxides. We proposed a plausible growth mechanism for Bi₂MoO₆ by considering adopted synthetic conditions. Bi₂MoO₆ could be a result of (a) nucleation, (b) aggregation, (c) random arrays, and (d) crystal growth (as illustrated in Scheme 1).

Moreover, a plausible reaction mechanism could be as follows: the Bi³⁺ ions might be attracted toward the triethanolamine (TEA) molecule to form an unstable intermediate complex Bi[N(CH₂−CH₂−OH)] (eq 2). Then, NaOH solution was added into it to increase the pH to −10.53 (eq 3). MoO₄²⁻, obtained from the Na₂MoO₄·2H₂O precursor solution, according to eq 4, was dissolved in deionized water and slowly added to the Bi[N(CH₂−CH₂−OH)] solution, so as to obtain a transparent and clear solution. This solution was kept at 353 K for 3 h. Moreover, Bi[N(CH₂−CH₂−OH)] could lose its stability by activating the bismuth sites, and a π-allyl group could coordinate to a molybdenum ion, which is bridged by an oxygen atom forming a Bi=O−Mo bond through MoO₄²⁻. At the same time, the reaction was allowed to proceed in the same container by attaching OH⁻ to Bi³⁺ to form a stable Bi₂MoO₆(OH)₂ (eq 5) compound. Under heating conditions, Bi₂MoO₆(OH)₂ gradually converted into Bi₂MoO₆ (eq 6). Moreover, during the transformation process, an anisotropic growth of Bi₂MoO₆ could interconnect the molecules with each other. Finally, when Bi₂MoO₆(OH)₂ was completely transformed into Bi₂MoO₆, a kinetically stable Bi₂MoO₆ framework was obtained.

\[
\begin{align*}
\text{Bi(NO₃)₃}·5\text{H₂O} & \rightarrow \text{Bi}^{³⁺} + 3\text{NO}_3⁻ + 5\text{H}^+ + 3\text{OH}^- \\
\text{Bi}^{³⁺} + 3\text{N}⁻(\text{CH}_₂−\text{CH}_₂−\text{OH})_₃ & \rightarrow \text{Bi}[\text{N}⁻(\text{CH}_₂−\text{CH}_₂−\text{OH})_₃]₃ \\
\text{NaOH} & \rightarrow \text{Na}^+ + \text{OH}^- \\
\text{Na}_₂\text{MoO}_₄·2\text{H₂O} & \rightarrow 2\text{Na}^+ + \text{MoO}_₄²⁻ \\
2\text{Bi}[\text{N}⁻(\text{CH}_₂−\text{CH}_₂−\text{OH})_₃]₃ + \text{MoO}_₄²⁻ & \rightarrow (\text{OH})₂\text{Bi}⁻\text{O}−\text{Mo(O}_₂⁻−\text{O}−\text{Bi(OH)}₂ \\
(\text{OH})₂\text{Bi}⁻\text{O}−\text{Mo(O}_₂⁻−\text{O}−\text{Bi(OH)}₂ & \rightarrow \text{O} = \text{Bi}−\text{O} \\
& \rightarrow \text{Mo(O}_₂⁻−\text{O}−\text{Bi} = \text{O} + 2\text{H}_₂\text{O}
\end{align*}
\]
TEM, (h) high-magnification TEM, (b) high-magnification HR-TEM images, and (i) SAED pattern of Bi$_2$MoO$_6$.

Figure 1. (a–c) FE-SEM images at different magnifications showing hydrangea flowers, (d–f) elemental mappings of Bi, Mo, and O, (g) TEM, (h) high-magnification HR-TEM images, and (i) SAED pattern of Bi$_2$MoO$_6$.

percolation and mass transport. The high-magnification image (Figure 1c) suggests the development of a hydrangea-type architecture composed of dozens of curved two-dimensional (2D) nanopetals of ~70 (±05) nm thickness. The air gap between the petals was 580 (±20) nm. These open and free interspaced gaps between the petals of the hydrangea-type architecture of Bi$_2$MoO$_6$ would be an excellent morphology for electrochemical energy storage device applications.43 The surface composition of Bi$_2$MoO$_6$ obtained from FE-energy-dispersive X-ray spectroscopy measurements is shown in Figure 1d–f. A uniform distribution of Bi, Mo, and O on the hydrangea Bi$_2$MoO$_6$ surface is confirmed. The spectrum showed peaks of Bi and Mo at 2.5 eV and of oxygen at 0.5 eV, suggesting the presence of these elements in the sample product, i.e., Bi$_2$MoO$_6$. The elemental mapping of Bi$_2$MoO$_6$ as shown in Figure S3, clearly corroborates a ratio of 24:13:63 atom % for Bi, Mo, and O, providing the quantitative signature of Bi$_2$MoO$_6$. The high-resolution transmission electron microscopy (HR-TEM) image (Figure 1g) highlights the group of petals belonging to hydrangea with fine edges and the (Figure 1g, inset). The obtained lattice interplanar distance of 0.32 nm in the HR-TEM image corresponds to the (134) crystallographic plane of Bi$_2$MoO$_6$ (Figure 1h). The selected area electron diffraction (SAED) pattern, shown in Figure 1i, suggests the existence of a polycrystalline crystal structure due to the formation of highly concentrated circular rings, rather than spots and a foggy cloud, for Bi$_2$MoO$_6$. The X-ray diffraction (XRD) pattern was used to confirm the phase purity of Bi$_2$MoO$_6$. In Figure 2a, the XRD pattern of Bi$_2$MoO$_6$ is presented, where the obtained sharp and well-defined diffraction peaks were in accordance to JCPDS card no. 00-022-0112, revealing the formation of phase-pure orthorhombic Bi$_2$MoO$_6$. The diffraction peaks of Bi$_2$MoO$_6$ appearing at 2θ = 15.90, 27.33, 31.56, 32.63, 45.41, 53.77, and 57.22°, as shown in Figure 2a, were assigned to the (220), (134), (414), (522), (074), (922), and (816) crystal planes, respectively. The peak positions and respective planes were well indexed, and there were no additional peaks detected from impurities.

Figure 2. (a, b) XRD and full-range X-ray photoelectron spectroscopy (XPS) survey spectra of the Bi$_2$MoO$_6$ electrode. Enlarged XPS spectra of (c) Bi 4f, (d) Mo 3d, and (e) O 1s. (f) Nitrogen adsorption–desorption isotherms of the Bi$_2$MoO$_6$ electrode (inset shows the Barrett-Joyner-Halenda (BJH) pore-size distribution plot).

The XPS survey spectrum (see Figure 2b) clearly demonstrates the existence of Bi, Mo, and O elements in Bi$_2$MoO$_6$. Figure 2c–e shows the magnified XPS scans of Bi 4f, Mo 3d, and O 1s. In the Bi 4f spectrum (see Figure 2c), two XPS peaks at ~158.4 and 163.8 eV were identified, assigned to Bi$^{3+}$ 4f$_{7/2}$ and Bi$^{3+}$ 4f$_{5/2}$, respectively.43 In the Mo 3d pattern (Figure 2d), the binding energies at 231.5 and 234.7 eV were assigned to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ of Mo$^{6+}$, respectively. In Figure 2e, the peaks at 529.2 and 530.3 eV were due to Bi–O (lattice O) and Mo–O, respectively. To characterize the porous nature of Bi$_2$MoO$_6$, the nitrogen adsorption/desorption isotherm was measured and is shown in Figure 2f. The as-prepared Bi$_2$MoO$_6$ exhibited a specific surface area of 47.11 m$^2$. In the isotherms, the hysteresis loops matched those of mesoporous, as the average pore diameter was 13.04 nm, which, eventually, would play a significant role in the electrochemical charge/mass transport processes by promoting the penetration of electrolyte ions deep into an electrode material in addition to the near surface with extensive surface redox reactions. Therefore, the as-prepared mesoporous and high surface area hydrangea-type Bi$_2$MoO$_6$ electrode on Ni-foam would demonstrate a better electrochemical performance than the planar and rigid architectures.47

2.3. Electrochemical Analyses. The electrochemical performance of the as-prepared hydrangea-type Bi$_2$MoO$_6$ electrode was measured in a 1 M KOH solution as the electrolyte. The SC values were measured from the cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) curves. Figure 3a presents the comparative cyclic voltammetry (CV) curves of blank Ni-foam and Bi$_2$MoO$_6$ electrodes at a fixed scan rate of 100 mV s$^{-1}$. The CV curves recorded at different scan rates ranging from 5 to 100 mV s$^{-1}$ and in the voltage window of −1.0–0.0 V (Figure 3b) show the redox peaks attributed to the Faradaic reactions from Bi(III) to Bi metal of Bi$_2$MoO$_6$.46 The Faradaic redox reaction of Bi$_2$MoO$_6$ in 1 M KOH electrolyte is similar to that of Bi$_2$O$_3$. The quasi-reversible Faradaic reactions were evidenced by the presence of redox peaks in the CV curve (i.e., Bi$^{3+}$ to Bi$^{0}$). For Bi$_2$MoO$_6$, a single reduction peak (R1) with high current intensity could be due to the reduction of Bi$^{3+}$ to Bi$^{0}$ (~0.82 V), and, on the other hand, the two anodic peaks (O1 and O2) found at ~0.48 and ~0.30 V accounted for the oxidation of Bi$^{0}$ to Bi metal and the oxidation of Bi metal to Bi$^{3+}$, respectively.
The possible oxidation and reduction processes taking place during the redox reaction could be as follows:

\[
\begin{align*}
\text{Bi}_2\text{MoO}_6 + 2\text{OH}^- &\leftrightarrow 2\text{BiO}_2^2- + \text{H}_2\text{MoO}_4 \\
\text{BiO}_2^2- + e^- &\leftrightarrow \text{BiO}_2^{2-} \\
3\text{BiO}_2^{2-} + 2\text{H}_2\text{O} &\leftrightarrow 2\text{BiO}_2^- + 4\text{OH}^- + \text{Bi}^{(O)} \\
\text{Bi}^{(O)} &\rightarrow \text{Bi(metal)}
\end{align*}
\]

Oxidation peaks at “O1” and “O2” were attributed to the presence of a minor amount of Bi metal situated at the Bi metal/electrolyte interface, and the oxidation peak O2 along with the voltage plateau indicated the oxidation of Bi metal to Bi(III) as follows:

\[
\text{Bi(metal)} \rightarrow \text{Bi}^3+ + e^-
\]

The above equations support the occurrence of the quasi-Faradaic signature, where with an increase in scan rate the oxidation peak potential shifts to a more positive direction and the reduction peak potential to the negative direction. Well-defined redox peaks in the CV profile are obtained only for Bi₂O₃, as it was found earlier that the molybdenum (Mo) element in Bi₂MoO₆ cannot participate in redox reactions. The molybdenum redox species could lead to the improvement of the SC values by increasing the electrical conductivity. In addition to this, the anodic/cathodic peak current position of each CV curve was increased with increasing scan rate from 5 to 100 mV s⁻¹, suggesting the existence of sufficient not only electronic but also ionic transport in the case of the Bi₂MoO₆ electrode (see Figure 3b). Interestingly, the anodic/cathodic peak shifted in both potential regions (i.e., negative and positive), with increasing scan rate due to the occurrence of a charge diffusion polarization effect. As a result of the quasi-reversibility of the material, the oxidation/reduction peaks were shifted to the positive and negative potential sides with increasing scan rate from 5 to 100 mV s⁻¹, which could be due to (a) high Ohmic resistance, (b) slow electron transfer kinetics, and (c) low ionic diffusivity of the battery-type materials. However, the redox peaks were clearly visible even at 100 mV s⁻¹, indicating fast charge transfer, i.e., capacitive-type behavior in Bi₂MoO₆.

SC, one of the important electrochemical parameters, decreased with respect to the scan rate, which could be due to the low movement and delayed interaction time of the electrolyte ions within the electrode material. The maximum SC of 495 F g⁻¹ was obtained at 5 mV s⁻¹. The total SC is the algebraic sum of the SC contributions from the inner and outer surface charges. Therefore, the SC contributions were determined using Trasatti plots, where the Y-intercept of the linear fit between the SC and the square root of the scan rate (υ₁/₂) at υ = 0 (Figure S4a) gives the total SC, i.e., 523 F g⁻¹ in the present case. At a lower scan rate, electrolyte ions have unlimited access to the electrode surface; therefore, a large amount of charge can be stored on both the inner and outer sides of the electrode. Likewise, the Y-intercept of the linear fit between the SC and υ₁/₂ at υ = ∞ (Figure S4b) provides the SC contribution from the outer surface, i.e., 124 F g⁻¹ in the present case. A prolonged time, due to a low scan rate, allows the electrolyte ions to access majority of electrode material for excess redox reactions. Hence, the obtained SC is that contributed by only the inner surface. Furthermore, the SC contribution from the inner surface was 399 F g⁻¹. The Bi₂MoO₆ electrode stored a large amount of charge on the electrode material and high surface area, responsible for excessive reactions. A power law was used to systematically differentiate the relative contributions from either capacitive or battery-type mechanisms to the total charge stored in the electrodes. The scan rate-dependent peak current can be defined as follows:

\[
i = aυ^b
\]

where l is the current (A), υ is the scan rate (V s⁻¹), and a and b are adjustable parameters. The value of b was derived from the slope of the linear fit of log(υ) against log(υ) at a fixed potential (V). If the value of b is smaller than 0.5, the current obeys a diffusion-controlled battery-type mechanism; however, if it is above/close to 1, the material follows a capacitive mechanism. Figure 3c shows a plot of log(υ) and log(υ) at different potentials, i.e., -0.4888, -0.4000, -0.2912, and -0.1815 V. At the initial oxidation potential of -0.4888 V, b was 0.93, suggesting the dominance of a capacitive mechanism in Bi₂MoO₆. At the peak potential of 0.4000 V, b was 0.58, indicating the existence of a battery-type charge storage mechanism. Subsequently, values of b were 0.65 and 0.71 at the end of the oxidation potential range, i.e., 0.2912 and 0.1815 V, representing the involvement of a mixed charge storage mechanism. Hence, the Bi₂MoO₆ electrode material could store a charge through both mechanisms. The amount of charge stored by the battery/capacitive mechanism in the redox peak regions was measured through a power law equation as...
Pseudocapacitive Electrode Materials

Material due to the hydrangea-type architecture of Bi$_2$MoO$_6$. Ions could penetrate more deeply into the Bi$_2$MoO$_6$ electrode electrochemical reversibility with fast charge transfer kinetics. The SCs of the supercapattery Bi$_2$MoO$_6$ electrode, illustrating excellent potential-dependent/independent regions. The SCs of the Bi$_2$MoO$_6$ electrode at applied current densities are shown in Figure 3e. It could be due to the easy and rapid penetration between these petals and the mesoporous character of the hydrangea-type Bi$_2$MoO$_6$ electrode material due to the hydrangea-type architecture of Bi$_2$MoO$_6$. At a high scan rate, the capacitive current increased. This measurement supported the conclusion that the Bi$_2$MoO$_6$ electrode could have contributions from both battery/capacitive-controlled intercalation mechanisms, suggesting a supercapattery behavior. To avail more information on the capacitance properties of the Bi$_2$MoO$_6$ electrode, galvanostatic charge/discharge measurement was carried out. To evaluate the SC of the Bi$_2$MoO$_6$ electrode, GCD measurements were attempted, where the SC value decreased from 485 to 65 F g$^{-1}$ (Figure 3e). It could be due to the easy and rapid penetration of electrolyte ions into the Bi$_2$MoO$_6$ electrode and the accessibility of its whole area by electrolyte ions. The GCD curves showed two regions: a steep voltage drop region, attributed to the internal resistance, and a prolonged plateau of voltage, due to the involvement of a quasi-Faradaic process in the supercapattery Bi$_2$MoO$_6$ electrode, illustrating excellent electrochemical reversibility with fast charge transfer kinetics. The Bi$_2$MoO$_6$ electrode could store charge using the capacitive/battery-type mechanism in the respective potential-dependent/independent regions. The SCs of the Bi$_2$MoO$_6$ electrode at applied current densities are shown in Figure S5. The SC values were decreased with an increase in current density because of the slowed migration of electrolyte ions and charge transfer during the electrochemical reaction. The EIS (Figure 3f) plot was more vertical in the high-frequency and low-frequency ranges, suggesting the presence of capacitive- and battery-type contributions. In short, from the Nyquist plot, the supercapattery nature of Bi$_2$MoO$_6$ is corroborated. The 0.67 Ω semi-circular diameter in the higher frequency region, which is a charge-transfer resistance, was considerably smaller, revealing the existence of fast transfer of electrolyte ions across the electrolyte/electrode interface. The lower value of around 0.52 Ω of series resistance of the Bi$_2$MoO$_6$ electrode confirmed a good ionic response. The electrochemical reaction on the Bi$_2$MoO$_6$ electrode surface, i.e., a hydrangea-like architecture with arbitrary petals of high surface area, could enhance the conductive corridors by providing shorter diffusion routes. Such electrochemical performance of the Bi$_2$MoO$_6$ electrode was facilitated by many interconnecting ultrathin porous petals by affording more active sites for efficient electrolyte ion transport on the active material surfaces. Moreover, the open and free interspaces between these petals and the mesoporous character of the hydrangea-type Bi$_2$MoO$_6$ electrode could serve as ion reservoir channels, responsible for shortening the ion diffusion length from the external electrolyte to the interior surfaces, thus, potentially, improving the intercalation/de-intercalation rate of ions and, thereby, increasing the utilization of active materials. The long-term cycle stability of electrode materials is another key factor from the point of view of practical applications. The long-term cycle stability of the as-prepared Bi$_2$MoO$_6$ electrode material was evaluated by repeating charge–discharge tests at 5 A g$^{-1}$, 5000 times. As shown in Figure 3g, it can be seen that the SCs of the Bi$_2$MoO$_6$ electrode material dramatically decreased to 82% from 1 to 5000 cycles, revealing its negligible degradation.

Table 1. Literature Review of Reported Synthesis Methods and Obtained Electrochemical Performance of Bi$_2$MoO$_6$ as Pseudocapacitive Electrode Materials

| working electrode | synthesis method | morphology          | potential window/(electrolyte) | specific capacitance (SC) | stability (cycle) | references |
|-------------------|-----------------|---------------------|-------------------------------|---------------------------|------------------|------------|
| Bi$_2$MoO$_6$     | combustion      | nanoplates          | $-1.0$ to $0.0$ V              | 342 F g$^{-1}$ (1 mA cm$^{-2}$) | 100% (500)       | 29         |
|                   | hydrothermal    | nansheet array      | $1$ M NaOH                    | 37.3 F g$^{-1}$ (2 A cm$^{-2}$) | 89% (1000)       | 32         |
| Bi$_2$MoO$_6$     | reflux          | hierarchical nanotubes | $-0.4$ to $-0.1$ V            | 171.3 F g$^{-1}$ (0.585 A cm$^{-2}$) | 92.4% (1000)     | 33         |
| Bi$_2$MoO$_6$     | solvothermal    | nanopetals          | $-0.2$ to $0.6$ V 6 M KOH     | 322.85 F g$^{-1}$ (1 A cm$^{-2}$) | 42% (10 000)     | 40         |
| Bi$_2$MoO$_6$     | hydrothermal    | flow-like           | $0.0$ to $0.6$ V 6 M KOH      | 182 F g$^{-1}$ (1 A cm$^{-2}$) | 80% (3000)       | 41         |
| Bi$_2$MoO$_6$     | sonochemical    | aggregated irregular shaped | $-1.3$ to $0.0$ V 1 M NaOH    | 193 F g$^{-1}$ (2 A cm$^{-2}$) | 91% (1000)       | 42         |
| Bi$_2$MoO$_6$     | wet chemical    | hydrangea flowers   | $-1.0$ to $0.0$ V 1 M KOH     | 485 F g$^{-1}$ (5 A cm$^{-2}$) | 82% (5000)       | present work |

$$i_p = s_1 \theta + s_2 \theta^{1/2}$$

(16)

It can be changed to

$$i_p/\theta^{1/2} = s_1\theta^{1/2} + s_2$$

(17)

where $i_p$ is the peak current, and $s_1 \theta$ and $s_2 \theta^{1/2}$ are the current contributions from the capacitive and intercalation mechanisms. We obtained a linear plot for the Bi$_2$MoO$_6$ electrode in between $i_p/\theta^{1/2}$ vs $\theta^{1/2}$ at 0.2912 V (Figure S4c), whose slope and intercept were $s_1$ and $s_2$, respectively. The capacitive/intercalation current calculated using the above equations is summarized in Figure 3d, where, at a lower scan rate, the diffusion-controlled current was higher because the electrolyte ions could penetrate more deeply into the Bi$_2$MoO$_6$ electrode material due to the hydrangea-type architecture of Bi$_2$MoO$_6$. The EIS (Figure 3f) plot was more vertical in the high-frequency and low-frequency ranges, suggesting the presence of capacitive- and battery-type contributions. In short, from the Nyquist plot, the supercapattery nature of Bi$_2$MoO$_6$ is corroborated. The 0.67 Ω semi-circular diameter in the higher frequency region, which is a charge-transfer resistance, was considerably smaller, revealing the existence of fast transfer of electrolyte ions across the electrolyte/electrode interface. The lower value of around 0.52 Ω of series resistance of the Bi$_2$MoO$_6$ electrode confirmed a good ionic response. The electrochemical reaction on the Bi$_2$MoO$_6$ electrode surface, i.e., a hydrangea-like architecture with arbitrary petals of high surface area, could enhance the conductive corridors by providing shorter diffusion routes. Such electrochemical performance of the Bi$_2$MoO$_6$ electrode was facilitated by many interconnecting ultrathin porous petals by affording more active sites for efficient electrolyte ion transport on the active material surfaces. Moreover, the open and free interspaces between these petals and the mesoporous character of the hydrangea-type Bi$_2$MoO$_6$ electrode could serve as ion reservoir channels, responsible for shortening the ion diffusion length from the external electrolyte to the interior surfaces, thus, potentially, improving the intercalation/de-intercalation rate of ions and, thereby, increasing the utilization of active materials. The long-term cycle stability of electrode materials is another key factor from the point of view of practical applications. The long-term cycle stability of the as-prepared Bi$_2$MoO$_6$ electrode material was evaluated by repeating charge–discharge tests at 5 A g$^{-1}$, 5000 times. As shown in Figure 3g, it can be seen that the SCs of the Bi$_2$MoO$_6$ electrode material dramatically decreased to 82% from 1 to 5000 cycles, revealing its negligible degradation.
electrode materials, obtained using different synthesis methods in different morphologies, given in Table 1 confirm the higher/comparable performance of the present Bi$_2$MoO$_6$ electrode over others.

2.4. Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ Symmetric Supercapattery Device Performance. Based on the above discussions, the Bi$_2$MoO$_6$ electrode showed a lengthened potential window from 0.0 to 1.5 V, and so a symmetrical supercapattery device was assembled to test its commercial benefits. The overall process of device fabrication is elaborated in Figure 4. For a symmetric supercapattery cell, Bi$_2$MoO$_6$ electrodes of the same quality (including Ni$^2+$F and mass of Bi$_2$MoO$_6$) were used as negative and positive electrodes in the presence of a polypropylene separator in a plastic cylindrical tube (Figure 4a,b). To design a portable symmetric Bi$_2$MoO$_6$ electrode device, two Bi$_2$MoO$_6$ electrodes were round-folded in the form of a sandwich-type structure using a flexible polypropylene separator. The separator paper was placed between these two electrodes so as to avoid grounded connection of the portable device. Furthermore, these sandwiched Bi$_2$MoO$_6$ electrodes were inserted into a plastic cylindrical tube vertically, as shown in Figure 4d, into which a 1 M KOH electrolyte was poured and the wire contacts were drawn carefully from each electrode via the seal of the plastic tube (see Figure 4d,e). Finally, Figure 4f demonstrates that the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ cell is ready for electrical operation process. All electrochemical tests (CV, GCD profiling, and cycling stability) of the Bi$_2$MoO$_6$ symmetrical supercapattery device were performed and reported. The CV and charge–discharge curves of the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical supercapattery device at different scan rates are shown in Figure 5a,b, respectively.

The Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical supercapattery device showed decrement in the SC values from 40.5 to 25 F g$^{-1}$ as the current densities increased from 1 to 5 F g$^{-1}$ (Figure 5c).

The Ragone plot of the symmetric supercapattery device at different current densities is given in Figure 5d, where the above results were based on the mass of the two active electrodes. It can be understood that the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical supercapattery device exhibited a remarkable energy density/power density (45.6 W h kg$^{-1}$/989 W kg$^{-1}$), which is greater than those of symmetrical cells reported previously for CS@Bi$_2$MoO$_6$//CS@Bi$_2$MoO$_6$ (10.8 W h kg$^{-1}$/410 W kg$^{-1}$), RuO$_2$/graphene//RuO$_2$/graphene (11 W h kg$^{-1}$/76 W kg$^{-1}$), Ni@FeCo$_2$O$_4$@MnO$_2$//Ni@FeCo$_2$O$_4$@MnO$_2$ (22.2 W h kg$^{-1}$/978.3 kW kg$^{-1}$), and GR/BiVO$_4$/GR/BiVO$_4$ (45.69 W h kg$^{-1}$/800 kW kg$^{-1}$) devices. The energy density/power density value (45.6 W h kg$^{-1}$/989 W kg$^{-1}$) obtained in the present work was appealing. Electrochemical charge storage mechanisms of the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetric supercapattery are displayed briefly as a schematic in Figure 5e.

In addition, to check the practical feasibility of the as-developed Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical supercapattery device, three cells were connected in series and charged through an external power source (at 4.5 V voltage) for 5 min and finally discharged through three differently colored LEDs, where the LEDs with considerable light intensities were illuminated for ∼18 min without any fluctuation, demonstrating the promising future of the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical cell device (Figure 6a–i).

Figure 6a presents an assembly of the three Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical supercapattery devices in series with a panel of three differently colored (green, yellow, and red) LEDs. Figure 6b highlights an actual image at the initial glowing time of less than 1 min, Figure 6c–f display images with nearly 5 min time intervals that remained almost the same up to ∼17 min, then the green LED was turned off (Figure 6g). After a few seconds, the yellow LED went off (see Figure...
and lastly, the red LED stopped glowing after 30 s (see Figure 6i), suggesting the importance of the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical device with moderate energy/power density in developing supercapattery devices. The stability of the Bi$_2$MoO$_6$//Bi$_2$MoO$_6$ symmetrical supercapattery device was tested using GCD operations, and the results are displayed in Figure 5f. Over about 5000 cycles at a current density of 1 A g$^{-1}$, the SC based on the total mass of the two electrodes was about 31.6 F g$^{-1}$, which corresponds to 78% of its initial capacitance (40.5 F g$^{-1}$), evidencing the moderate chemical stability and mechanical robustness of the as-fabricated hydrangea-type Bi$_2$MoO$_6$ symmetric supercapattery device before its commercial use.

3. CONCLUSIONS

In summary, hydrangea-type Bi$_2$MoO$_6$ with upright standing narrow petals (separated by a considerable number of crevices) of high surface area was successfully synthesized by a simple and inexpensive wet chemical method. These special properties of Bi$_2$MoO$_6$ would lead to a smaller ion diffusion length and an easy electrolyte ion transfer for better electrode surface utilization and performance. In the electrochemical studies, the hydrangea-type Bi$_2$MoO$_6$ electrode exhibited an SC of 485 F g$^{-1}$ at 5 A g$^{-1}$ and supercapattery character. A symmetric supercapattery device assembly of Bi$_2$MoO$_6$ delivered an energy density of 45.6 W h kg$^{-1}$ at a power density of 989 W kg$^{-1}$. Finally, the symmetric supercapattery device successfully illuminated three differently colored LEDs with their maximum intensity. With this motivation, future work to synthesize and design other binary metal oxides/sulfides/selenides, etc., in 2D and 3D morphologies for various applications, such as in gas sensors, solar cells, electrocatalysts for water splitting, etc., is underway.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Bismuth(III) nitrate pentahydrate [Bi-(NO$_3$)$_3$·5H$_2$O], sodium molybdate dehydrate (Na$_2$MoO$_4$·2H$_2$O), sodium hydroxide (NaOH), and triethanolamine (TEA) were obtained from Sigma-Aldrich. Concentrated nitric acid (HNO$_3$) was obtained from Junsei Chemical. All chemicals were of analytical grade and were used without any further purification.

4.2. Bi$_2$MoO$_6$ Synthesis. The synthesis of Bi$_2$MoO$_6$ via a wet chemical method was considered. Briefly, a solution of 0.1 M Bi(NO$_3$)$_3$·5H$_2$O dissolved in 5 mL of HNO$_3$ and 4 mL of triethanolamine (TEA) was prepared in 50 mL of deionized water. A 0.1 M NaOH solution was mixed with constant stirring by maintaining a speed of 150 rpm so as to form a clear transparent solution (∼10.5 pH). Finally, 0.2 M Na$_2$MoO$_4$·2H$_2$O was dissolved in 50 mL of deionized water. A clear solution was formed and the Na$_2$MoO$_4$ solution was added into the above mixed solution. The whole solution mixture was stirred for 1 h and then well-cleaned pieces of Ni-foam (3 × 3 cm$^2$) were inserted vertically into the solution, and the reaction was allowed to run at 353 K for 3 h. At the end of the reaction time, whitish Bi$_2$MoO$_6$ directly deposited on the Ni-foam,
which was washed with deionized water several times, dried, and air-annealed at 427 K for 2 h for removing any residual hydroxide species. The formation of Bi$_2$MoO$_6$ was evidenced as the white product was changed to a biscotti-type product (synthesis process is given in Figure S1 of the Supporting Information). Further, various characterization tools and electrochemical analyses were employed for physical and electrochemical measurements, as discussed earlier.$^5$,$^4$3

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00522.

Electrochemical energy storage performance formulae; actual photographs of the experimental setup; FE-SEM; EDX; Trasatti plots; and variation of the SC by GCD curves (PDF)

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**Notes**

The authors declare no competing financial interest.

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