Organic–Inorganic Complexation Chemistry-Mediated Synthesis of Bismuth–Manganese Bimetallic Oxide for Energy Storage Application

Nishu Devi, Sarit K. Ghosh, Venkata K. Perla, and Kaushik Mallick*

ABSTRACT: An organic–inorganic complexation method was applied for the synthesis of bismuth–manganese bimetallic oxide (BMO) nanoparticles where highly dispersed oxide particles were stabilized in an organic matrix (hexamethylenediamine). The as-synthesized hybrid material was subjected to microscopic, optical, and structural studies to gain comprehensive insights into the system. In the X-ray diffraction pattern, the majority of the diffracted peaks are matched to the orthorhombic phase of the Bi₃Mn₂O₇ structure. To extract the electrochemical property, the hybrid system was applied as an anode material and investigated for supercapacitive performance under alkaline conditions. The specific capacitance obtained was 612 F g⁻¹ at the current density of 1 A g⁻¹, and under the same current density, the energy density and power density achieved were 137.78 W h kg⁻¹ and 0.90 kW kg⁻¹, respectively.

1. INTRODUCTION

Technology development for energy storage devices has recently attracted remarkable attention due to growing demands and public consciousness on environmental pollution. Among various energy storage devices, electrochemical supercapacitors have been considered as one of the candidates that can provide a higher power density and longer cycle life compared to batteries and a higher energy density than conventional capacitors. Various carbon-based materials, conjugated polymers, and transition metal oxides have been widely investigated as electrode materials for electrochemical supercapacitor application. Among the various oxide materials, mono- and bimetallic transition metal oxides of Co, Cu, Ni, Mn, Ti, V, Ni–Co, and Ni–Mn have been investigated very often due to their multiple oxidation states for a redox reaction.

Among the transition metal oxides, manganese oxide is regarded as a promising candidate for supercapacitor electrode due to its high specific capacitance, environment amiability, natural abundance, and low cost. Apart from these, manganese oxide also exists with a range of stable oxide forms and is associated with a variety of crystal structures, defects, and morphologies, which make manganese oxide more distinctive than other transition metal oxides. These versatile parameters play a crucial role in the electrochemical properties when manganese oxides are applied as electrode materials. Manganese-based bimetallic oxides have been considered as a promising candidate for supercapacitor application due to their outstanding reversible capacities. CoMn₂O₄–graphene nanoribbon reported high energy density and power density with excellent cycling stability (96% retention of the initial specific capacitance after 1500 cycles). A facile co-precipitation route was reported for the preparation of porous CoMn₂O₄ microspheres as a supercapacitor electrode, which exhibited a high specific capacitance value of 788 F g⁻¹ at the current density of 1 A g⁻¹. The core–shell arrangement of MnCo₂O₄ and MnO₂-based nanowire on nickel foam exhibited enhanced specific capacitance (858 F g⁻¹ at 1 A g⁻¹), high energy density, and long-life cycling stability, where the electrode architecture received advantages of the synergistic effects from both MnCo₂O₄ and MnO₂. The nanorods of MnWO₄ with the diameter of 5 nm and length of about 50 nm exhibited good electrochemical performance with the specific capacitance value of 219 F g⁻¹ at a current density of 0.4 A g⁻¹. The energy and power densities of the MnWO₄-based device were reported to be 16 W h kg⁻¹ and 319 W kg⁻¹, respectively, at 0.8 A g⁻¹, and it also exhibited good cycle-life stability. Very few reports are available in the literature on the combination of transition and post-transition bimetallic oxides.
as electrode materials for supercapacitor applications. A low-temperature solid-state chemical route has been reported to synthesize a Bi2O3-MnO2 nanocomposite with a specific capacitance of 161 F g\(^{-1}\) at the current density of 1 A g\(^{-1}\) and the device demonstrated 95% of stability retention for 10,000 charge-discharge cycles at the current density of 5 A g\(^{-1}\). Effects of temperature on electrochemical properties of bismuth oxide-manganese oxide-based pseudocapacitor exhibited a prominent role of temperature on the capacitor performance. The device showed maximum energy and power density values of 9.5 Wh kg\(^{-1}\) and 102.6 W kg\(^{-1}\) at 60 °C, respectively, which are approximately twice the values for the device at 0 °C. The highest performance of the device with the specific capacitance value of 150.2 F g\(^{-1}\) was obtained at 60 °C, whereas at 0 and 30 °C, the specific capacitance values of 76.4 and 136.4 F g\(^{-1}\) were achieved, respectively. A hydrothermal approach was implemented to fabricate manganese oxide-bismuth carbonate and manganese oxide-bismuth oxide composite systems, where the materials showed specific capacitance values of 196 and 139.4 F g\(^{-1}\), respectively. In our previous communications, we have reported the role of bismuth-based oxide, sulfide, and fluoride as active electrode materials for electrochemical supercapacitor application. In this report, a one-pot synthesis route for the preparation of organic molecule (hexamethylenediamine, HMDA)-stabilized bismuth-manganese bimetallic oxide nanoparticles has been described. In this synthesis method, HMDA played a dual role; initially, it was used as a complexation agent for bismuth(III) and at the end of the synthesis, HMDA acted as a stabilizer for the bismuth-manganese bimetallic oxide nanoparticles. The organic-inorganic composite system was used as an electrode material for supercapacitor application. The supercapacitive performance of the composite system was investigated in terms of specific capacitance and energy and power densities.

2. RESULTS AND DISCUSSION

The formation mechanism of the organic matrix (hexamethylenediamine)-stabilized bismuth-manganese bimetallic oxide (BMO) nanoparticles is described as follows. During the reaction between hexamethylenediamine (HMDA) and bismuth nitrate, the organic molecule acts as a ligand that coordinated with bismuth nitrate through the lone pair of nitrogen and forms the Bi(III)-HMDA complex. After the reaction between hexamethylenediamine (HMDA) and bismuth nitrate, the organic molecule acts as a ligand that coordinated with bismuth nitrate through the lone pair of nitrogen and forms the Bi(III)-HMDA complex. After the reaction between hexamethylenediamine (HMDA) and bismuth nitrate, the organic molecule acts as a ligand that coordinated with bismuth nitrate through the lone pair of nitrogen and forms the Bi(III)-HMDA complex.

The X-ray diffraction pattern of the synthesized material is shown in Figure 1A. The majority of the diffracted peaks are matched to the orthorhombic phase of the Bi2MnO5 structure (ICDD: 04-017-8615, red bar) with lattice constant values of \(a = 5.51\) Å, \(b = 16.80\) Å, and \(c = 5.45\) Å. A few additional peaks positioned at 26.01, 26.61, 33.31, 33.60, and 41.02° are also observed, which corresponds to the metastable orthorhombic phase of the Bi3Mn2O7 structure (ICDD: 04-021-5355, green symbol), which ultimately produced the stable form of bismuth-manganese bimetallic oxide (BMO) nanoparticles. The transmission electron microscopy (TEM) image of Bi(III)-HMDA complex with a SAED image (inset). (B) TEM image of HMDA-stabilized BMO nanoparticles with different magnifications. (D) High-magnification TEM image of the nanoparticles with the indexed SAED image (inset).
The surface electronic states and chemical compositions of the product were obtained from X-ray photoelectron spectroscopy (XPS) analysis; Figure 3. The binding energy values, obtained from the XPS analysis, were estimated by referencing the C 1s line at 284.45 eV of the survey spectrum, Figure 3a, generated from the HMDA matrix. The high-resolution XPS spectra of Mn 2p, Bi 4f, 4d, and O 1s are displayed in Figure 3b–f. Figure 3b shows the spin–orbital doublet of Mn 2p (j = 3/2, 1/2) centered at 641.7 (Mn 2p3/2) and 652.64 eV (Mn 2p1/2) with a peak separation of 10.94 eV, indicating the existence of the Mn4+ oxidation state.32,33 Again, the deconvolution of the spectrum, Figure 3c, within the range from 636 to 644 eV, indicates the coexistence of Mn3+ and Mn4+ valence state at 640.15 and 641.93 eV, generated from 4d3/2, respectively;35 Figure 3e. Further, in the O 1s spectrum, lattice oxygen and surface-adsorbed oxygen, respectively.36,37

Figure 4. Fourier transform-infrared (FTIR) spectra of (a) HMDA, (b) Bi-HMDA complex, and (c) HMDA-stabilized BMO.

samples are due to the N–H bending vibration of primary amines. Another vibrational band at 1560 cm−1 responsible for N–H bending is only visible in HMDA, whereas for (b) and (c), the absence of such a band indicates the restriction of the bending vibration due to the complexation and functionalization phenomenon. The CH2 scissor-vibration at 1493 cm−1 is also only visible for HMDA. Two prominent bands with the peak position at 1332 and 1388 cm−1 in HMDA are due to CH2-deformation and C–H bending vibration, respectively. For Bi-HMDA complex and HMDA-stabilized BMO, due to the effect of overlapping and broadening, the above vibrational bands are observed at 1388 cm−1. For the aliphatic amines, the C–N stretching vibration is observed with medium or weak intensity within the region of 1250–1020 cm−1. For the samples, HMDA and HMDA-stabilized BMO, such vibrational bands are observed, whereas the absence of C–N stretching vibration is noticed in the Bi-HMDA complex. The N–H stretching vibration was observed for three samples within the range of 3400–3250 cm−1 with different intensities and width. The C–H stretching was observed for HMDA at 2934 and 2857 cm−1 and for HMDA-stabilized BMO at 2982 and 2904 cm−1 with varying intensities, whereas for Bi-HMDA complex, such a kind of vibrational band was absent. The overlapping, shifting, broadening, intensification, disappearance, and reappearance of the vibrational bands for the three samples indicate Bi-HMDA complexation and BMO-HMDA functionalization phenomenon.

The electrical transport property of the device (Au∥BMO∥Au) was measured by applying a voltage sweep from +5 to −5 V and vice versa. Figure 5 represents the current–voltage graph in a semilog pattern. At the low-voltage region (from 0.0 to 0.6 V), the charge transfer mechanism was followed by thermionic emission, ln (I) vs V0.5, where few electrons were generated at the interface between the electrode and the active material; Figure 5, inset. A barrier height was obtained with the value of 0.76 eV calculated from the thermionic emission fitting parameters. At a higher-voltage range (from 0.6 to 5 V), the carriers exited from their localized
states, nanoparticles acted as traps, and passed through the higher density of states where the electron migration mechanism was followed by Poole–Frenkel (PF) emission, \(\ln(I/V)\ vs\ V^{0.5}\).

In general, electrochemical capacitors are evaluated using electrochemical impedance spectroscopy to quantify the resistance and capacitance in the system. The Nyquist plot of the BMO-modified electrode exhibited (Figure 6) the characteristics of a capacitive process of the material, which consists of a broad semicircular-like feature toward the higher-frequency side. In the lower-frequency region, the Warburg diffusion coefficient \((W_{dl})\) is predominant, which indicates the contribution of free charge carriers. The spectrum was recorded within the frequency range from 7 MHz to 10 MHz in KOH solution (0.1 mol·dm\(^{-3}\)) as an electrolyte. The overall spectrum was fitted according to the model shown in Figure 6 (inset), which consists of internal resistance \((R_0)\) in series with a parallel \(R_1\|Q_1\) circuit, where the \(R_1\|Q_1\) element corresponds to the BMO. Low internal resistance \((R_0 = 15.8 \Omega)\) indicates the structural homogeneity of the nanoparticles, whereas higher charge transfer resistance \((R_1 = 790 \Omega)\) corroborates with a higher charge storage capacity of the system. The fitting parameters, such as constant phase element, \(Q_1 = 12.5 \times 10^{-6}\ F_s^{n-1}\), and exponent parameter, \(n \sim 0.91\), indicate the pseudocapacitive nature of the active material. In the Nyquist plot, a bigger semicircular characteristic toward the lower-frequency region, instead of a straight line, with a higher diffusion impedance \((W_{imp} \sim 120 \Omega)\) indicates an access restriction of the ion species toward the interior of the electrode material. For the HMDA-stabilized bimetallic particles, the organic molecule creates a barrier for the ion species to access the active material (Bi–Mn-oxide).

To investigate the electrochemical performance of the bismuth–manganese oxide-based working electrode, a cyclic voltammetry study was performed within the potential range from 0 to \(-0.9\) V under different scan rates (within 10–100 mV·s\(^{-1}\)); Figure 7A. With the increase of the scan rate, an increase of current density value and shifting of peak potential was noticed. The oxidation peak shifts toward the positive potential direction and the reduction peak shifts toward the negative potential direction, which represents the increase of internal diffusion resistance. The specific capacitance of the material was calculated by galvanostatic charge–discharge cycles under different current densities; Figure 7B. A sudden voltage drop was observed during the discharge cycles for all applied current densities, but the magnitude of voltage drop was decreased with decreasing current density. At the current density 50 A·g\(^{-1}\), the potential dropped to \(-0.75\) V, whereas at 1.0 A·g\(^{-1}\), the voltage drop value was \(-0.55\) V. At a lower current density, ions are exposed to the surface for an extended period of time, which facilitates the ion penetration mechanism and results in the decrease of the voltage drop value. Multiple steps were observed during the discharge phases when the cycles were performed under low current densities. For lower current densities, two transitions during the discharge cycle are due to the change in the valence state from Bi(III) to Bi(0). The nonlinear behavior of the charging–discharging curves indicate a pseudocapacitive behavior of the electrode material. During the charging and discharging processes, the following reversible redox reactions can be proposed, originating from the bismuth–manganese-based bimetallic oxide (Bi\(_3\)Mn\(_2\)O\(_7\)) system.

\[
\text{Bi}_3\text{Mn}_2\text{O}_7 + \text{K}^+ + e^- \leftrightarrow (\text{MnOO}^+\text{K}^+) + (\text{K}_2\text{Bi}_2\text{O}_5)
\]

The charge storage of the material under an alkaline condition (1 mol·dm\(^{-3}\) of KOH) undergoes a reaction that involves a change in the valence state, instead of the conventional intercalation–deintercalation mechanism, during the repeatable cycles.

The specific capacitance as a function of the current density is exhibited graphically in Figure 8A. The BMO-modified electrode showed specific capacitances of 612 and 86 F·g\(^{-1}\) at the current densities of 1 and 50 A·g\(^{-1}\), respectively. The decrease of specific capacitance with the increase of current density suggested that the inner active sites of the material were inaccessible at higher current densities. In general, a multicomponent system is advantageous as it improves the electrochemical performance owing to the synergistic effect between different metallic cations. The coexistence of Bi and Mn ions provides richer redox reactions for the electrochemical process, which contributes to higher electrochemical activity. The incorporation of a second metallic component creates additional density of states and facilitates a field-induced band bending effect, which reduces the gap between...
the power density and energy density achieved were 4.5 kW\textpermg and 0.9 kW\textpermk, respectively.

3. CONCLUSIONS

A single-pot, two-step wet chemical synthesis route for the synthesis of hexamethylenediamine-stabilized bismuth–manganese bimetallic oxide (BMO) nanoparticles has been described in this report using an organic–inorganic complexation chemistry approach. According to the X-ray diffraction pattern, the majority of the diffracted peaks are matched to the orthorhombic phase of the Bi$_3$Mn$_2$O$_7$ structure, whereas a few peaks also corroborate with off-stoichiometric orthorhombic BiMnO$_3$. The BMO-modified electrode exhibited a specific capacitance value of 612 F\textpermk at the current density of 1 A\textpermg. The power density and energy density of 0.9 kW\textpermk and 137.78 Wh\textpermg were achieved, respectively, at the current density of 1 A\textpermg. The moderately high specific capacitance and energy and power density values with excellent stability indicate that the BMO-modified electrode could be a promising material for supercapacitor application.

4. EXPERIMENTAL SECTION

4.1. Materials. In this work, all of the materials and chemicals were used as received (without further purification).

4.2. Synthesis. Hexamethylenediamine-stabilized bismuth–manganese bimetallic oxide nanoparticles were synthesized using a wet chemical approach. In a typical synthesis method, 5 mL of bismuth nitrate (0.1 mol dm$^{-3}$) was added to 5 mL of methanolic solution of hexamethylenediamine (0.1 mol dm$^{-3}$) under continuous stirring. Milky white precipitation was formed. To this precipitated solution, 5 mL of potassium permanganate (0.1 mol dm$^{-3}$) was added dropwise and a change of color from milky white to cream-white of the precipitation was noticed. At the end of the addition, the entire reaction mixture was kept for 4 h at rest and later centrifuged. The solid mass was dried at 60 °C under vacuum. The dried material was subjected to optical, microscopic, structural, and electrical characterization. To determine the internal resistance and charge transfer properties of the synthesized material, the electrochemical impedance spectroscopy needs to be checked before use for long-term applications. In this study, the cyclic stability of the BMO-modified electrode was performed for 2200 cycles (Figure 8C). For the current density of 20 A\textpermg, at the beginning of the cycle, the specific capacitance value was 195 F\textpermg and at the end of 2200 cycles, a negligible loss in capacitance value (187 F\textpermg) was observed. In a similar way, at the current density of 5 A\textpermg, the capacitance value changed from 440 at the beginning of the cycle to 425 F\textpermg at the end of the cycle. The decrease in specific capacitance value during the cycling process was probably due to the removal of the active material from the electrode surface through the dissolution and/or detachment process.

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copy study was performed. The synthesized material was applied as an active component for supercapacitor application by extracting the specific capacitance and energy and power density values.

4.3. Characterization. The optical property was characterized using a Fourier FTIR spectrophotometer, Shimadzu IRAfinity-1. The microscopic property of the synthesized material was determined by a JEOI JEM-2100 transmission electron microscope. The structural characterization was performed by a PANalytical X’pert Pro diffractometer operated at 40 kV and 40 mA. XPS measurements were performed on a VG MultiLab 2000 system with a monochromatic X-ray source.

4.4. Device Fabrication for Electrical and Electrochemical Characterization. A flexible paper substrate, supported by a glass slide to provide mechanical strength, was used for the device fabrication process. Initially, bottom electrodes (gold) were deposited on the flexible paper. A slurry of BMO was prepared using ethyl acetate. On the bottom electrodes, a thin layer of BMO was deposited in a cross-bar fashion, and finally, a sandwich-structured device (Au∥BMO∥Au) was used for the device fabrication process. Initially, bottom electrodes were deposited in a cross-bar fashion, and finally, a sandwich-structured device (Au∥BMO∥Au) was formed using HMDA-stabilized bismuth–manganese bimetallic oxide nanoparticles. The bottom electrode was connected to the high-voltage terminal, whereas the top electrode was connected to the ground terminal of Keithley 2401 for electrical characterization under the scan rate of 0.17 V s⁻¹.

Electrochemical characterization was performed with a potentiostat (Bio-Logic SP 300) connected to a data controller. The impedance property of the system under the AC potential frequency was measured using BioLogic SP-200 equipped with electrochemical impedance spectroscopy within the frequency range from 7 MHz to 10 mHz. A three-electrode system, glassy carbon electrode as the working electrode, saturated calomel as the reference electrode, and platinum as the counter electrode, was employed to extract the electrochemical properties of the material. An alkaline solution of KOH (1 mol dm⁻³) was used as the electrolyte solution. The Nafton-perfluorinated resin was used as a binder. A drop-and-dry technique was applied to deposit the synthesized material (active material) on the glassy carbon electrode.

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Notes
The authors declare no competing financial interest.

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